SAND2012-2955P

State-of-the-Art Analytical Electron Microscopy: Pushing sub-nm Quantification to 1000 ppm (0.1%) of farther

Paul G. Kotula

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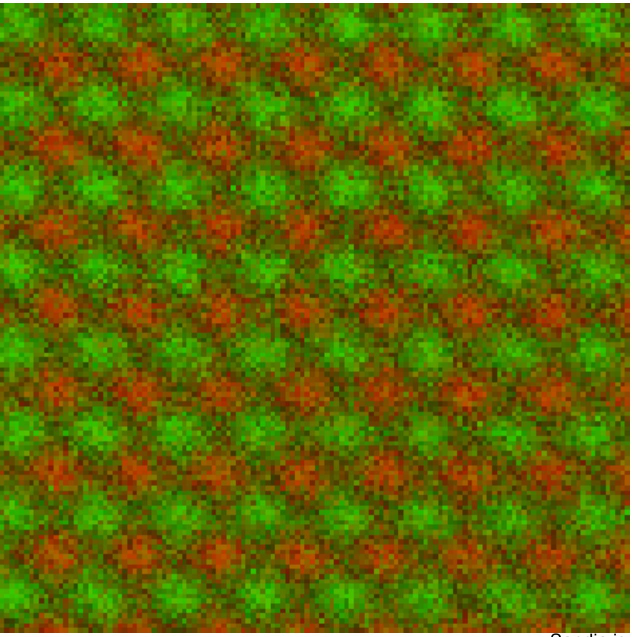
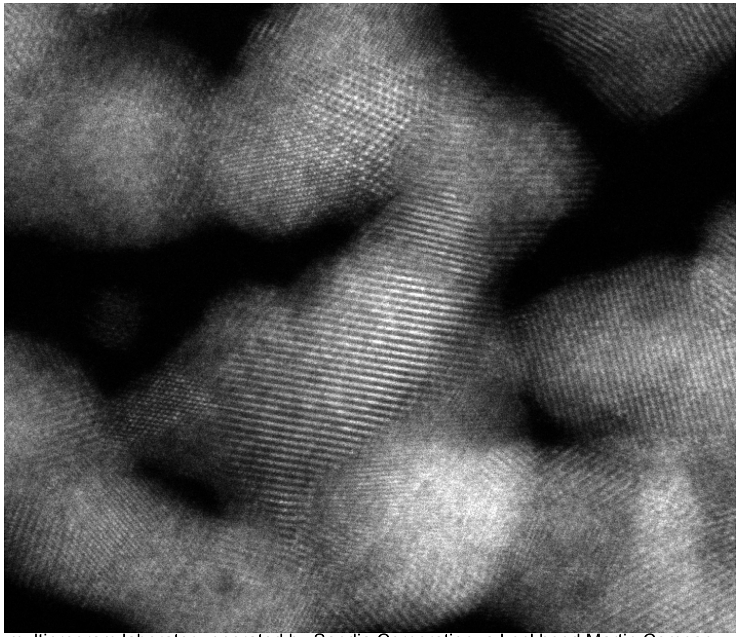
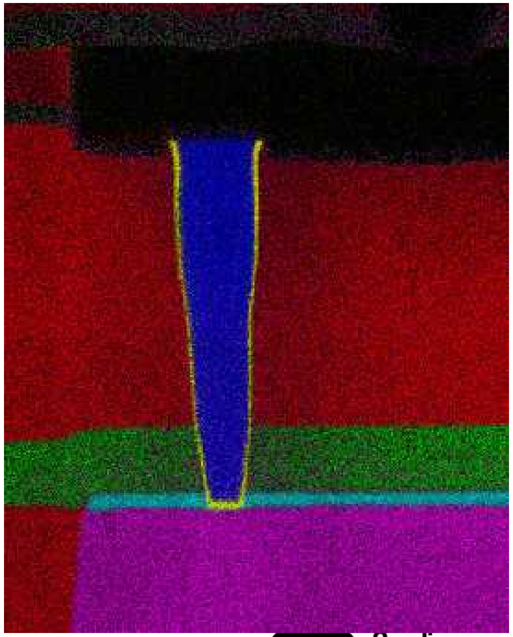
Dmitri O. Klenov and H. Sebastian von Harrach of FEI Company provided some data and collaborated on part if this presentation







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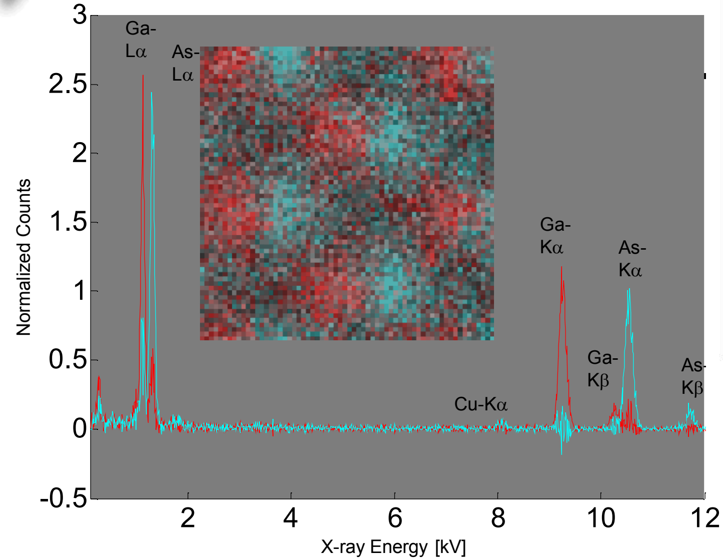
Materials Characterization Tetrahedron



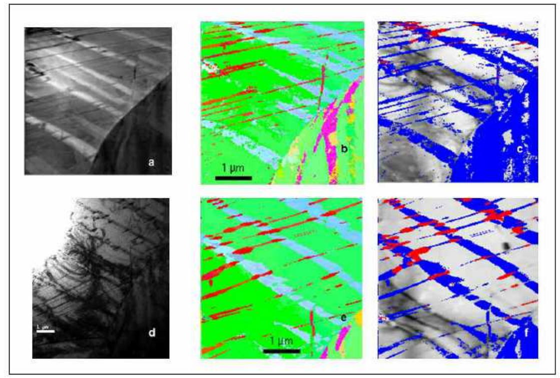
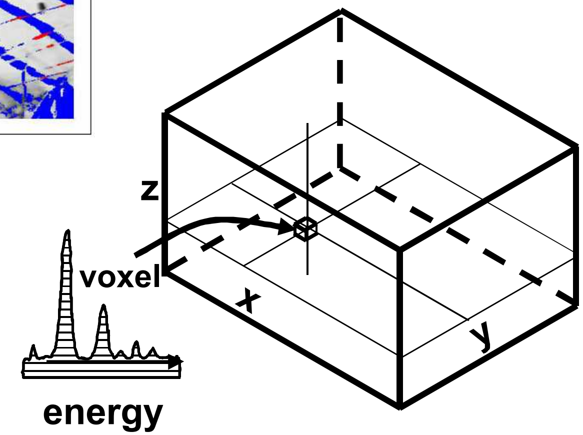
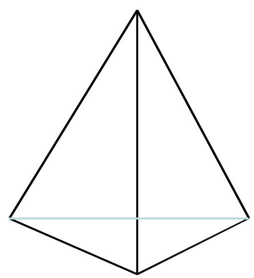
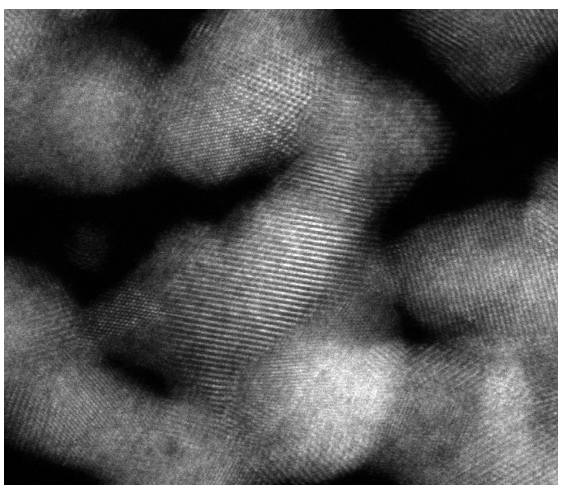
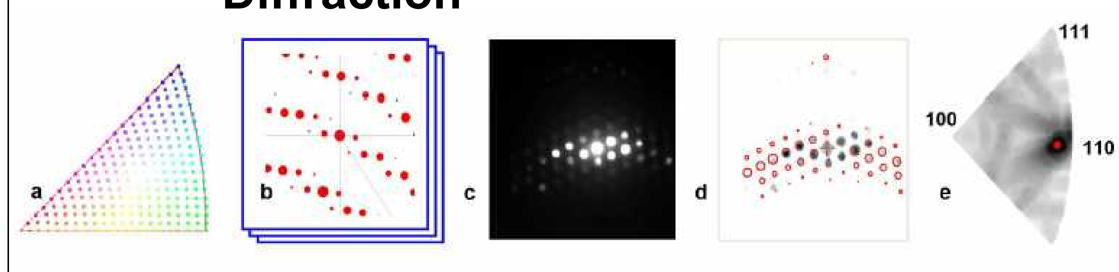


Figure 7: Austenitic stainless TRIP steel containing three distinct phases: γ fcc matrix, hcp ε bands and bcc α' martensite at bands intersections. (a) Index map coupled to (b) orientation (b) and phase (c) maps acquired without precession. (d) Brightfield image coupled to orientation (e) and phase (f) maps acquired with precession. Step size 22 nm, precession angle 0.4°, acquisition time 1 hour 9 minutes.







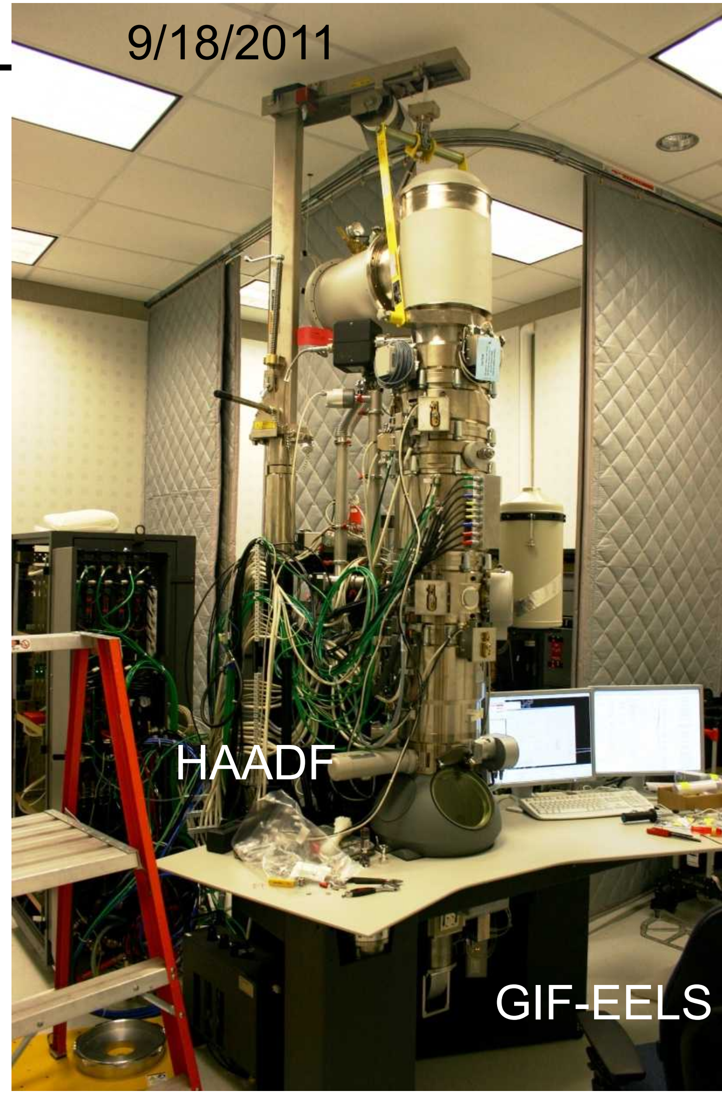


Nanomegas

STEM in materials characterization

- Microscope and stable lab space
  - Bright gun, probe corrector, efficient detectors
  - Quantification requires detector characterization
- Imaging (not really covered here extensively)
- Diffraction (search on Nanomegas)
  - OIM, EBSD for TEM/STEM
- Microanalysis (MSA data analysis methods)
  - Low end (several μm field of view, 10+ nA)
  - Medium end (nm to sub-nm, 1-2 nA)
  - High end (atomic resolution, 100 pA-500 pA)
  - Higher-dimension analyses…3D

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 from CM-30 (1987) room

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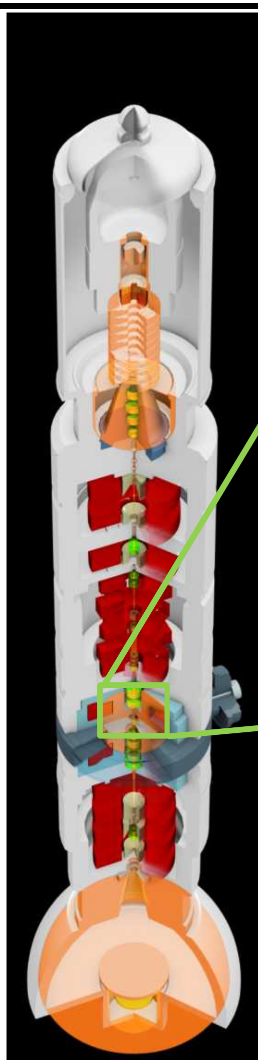
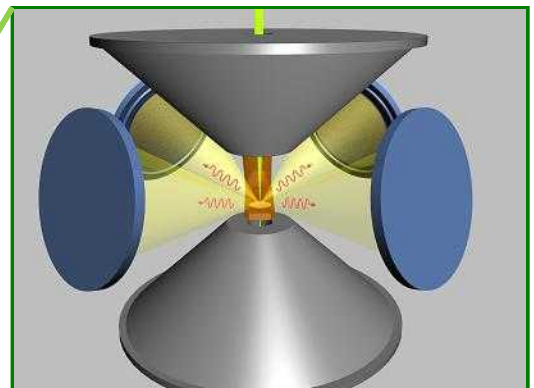
Atomic resolution x-ray microanalysis

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

All of these elements have been integrated on the FEI Titan ChemiSTEM-P (200kV)
SNL has one of the first

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

New Shottky emitter technology

- New Shottky emitter with the brightness of a cold FEG
- FEI X-FEG brightness increased to ~ 10^8 A/sr/m^2/ V
    - ~2 x 10^9 A/cm^2/sr @ 200 kV
- Probe current (w/o corrector)
    - 0.5 nA in 0.3 nm diameter
    - **Increased by 5x** relative to regular Schottky FEG
- Probe current (with DCOR probe corrector)
    - 200 kV, 1.3 nA in 0.2 nm diameter probe
    - 80 kV, 0.5 nA in 0.2 nm diameter probe
- Energy-spread = 0.9 eV

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Detector Efficiency: Arrays

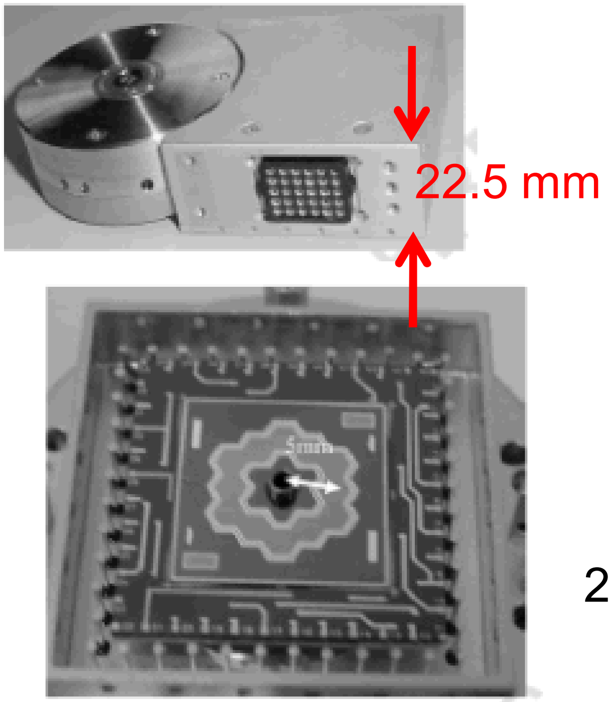
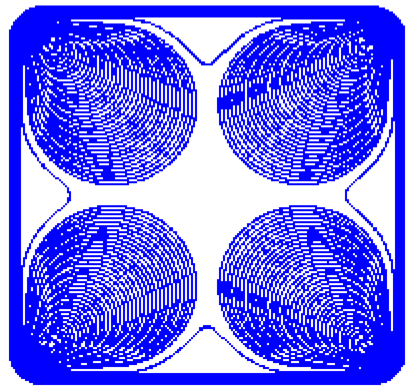
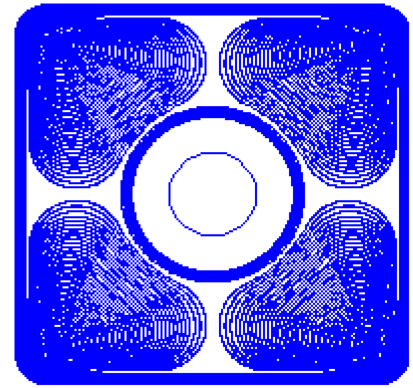


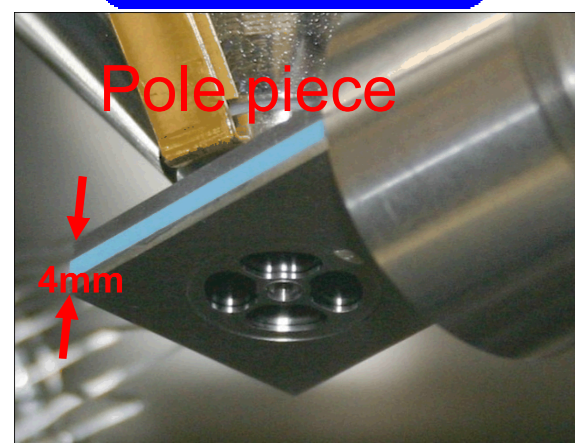
Figure 2. The Ketek 12-element annular SDD chip mounted in its package. The tantalum ion collimator that protects the SDD from scattered protons can be seen protruding through a hole in the center of the chip.

2005 Ketech/Custom imp.
2^{nd}-3^{rd} generation annular
(1.1 sr)



2005 pnSensor/Roentec
4-5^{th} generation
conventional
(40 mm^2, 0.06 sr)



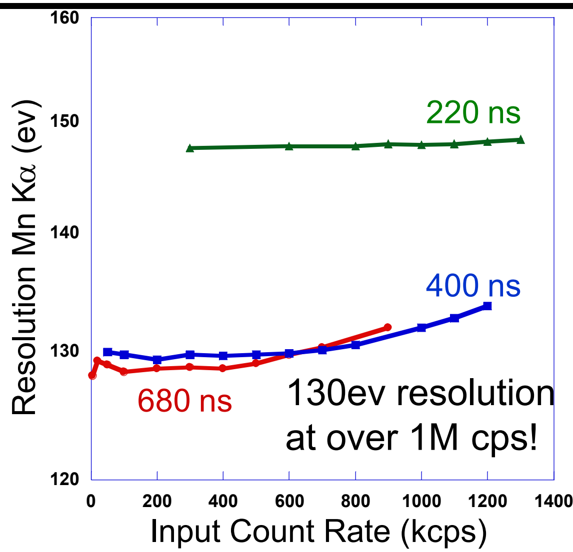


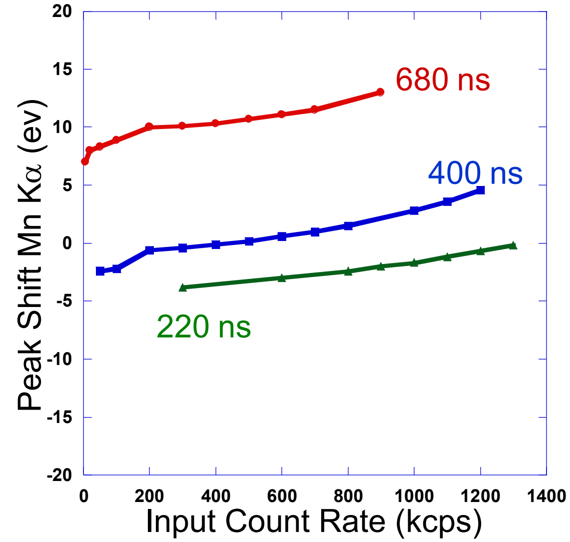
2007 pnSensor/Bruker
5^{th} generation annular at
SNL(60 mm^2, 1.1 sr)

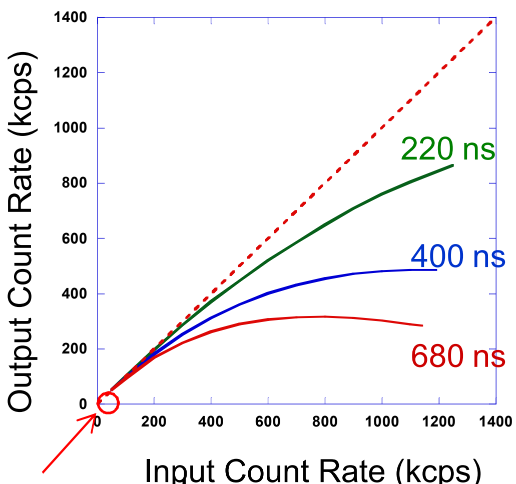
B. L. Doyle, D. S. Walsh, P. G. Kotula, P. Rossi, T. Schülein and M. Rohde, "An annular Si drift detector μPIXE system using AXSIA analysis," *X-Ray Spectrom.* (2005) 34

5th generation SDD-array performance

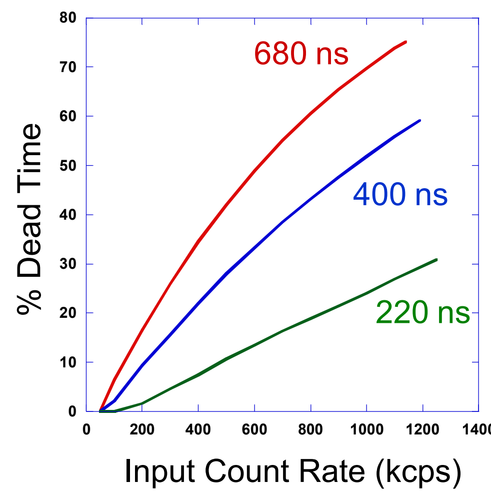
SEM data from 4-detectors summed







Si(Li) performance area at 180eV FWHM Mn-Kα



Performance superior in every way to Si(Li)

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

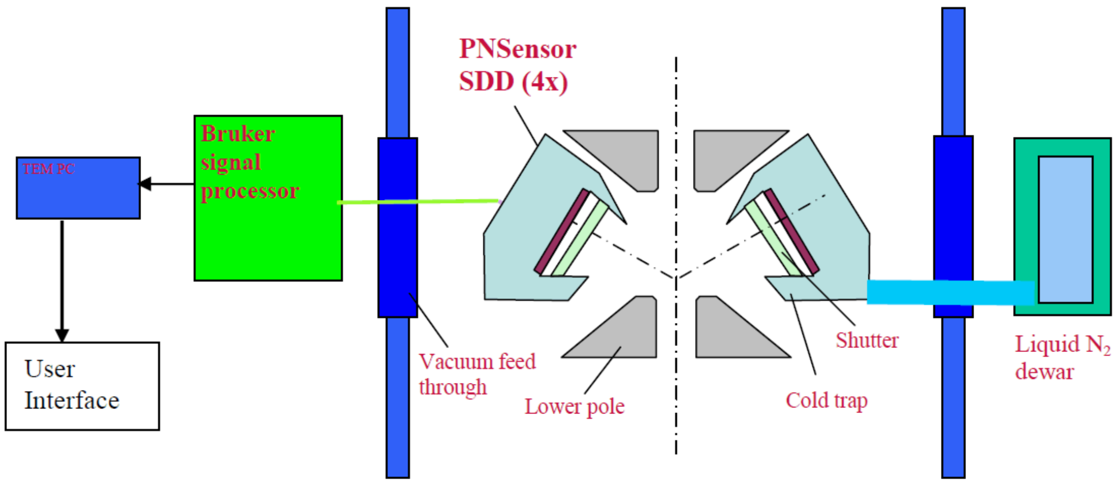
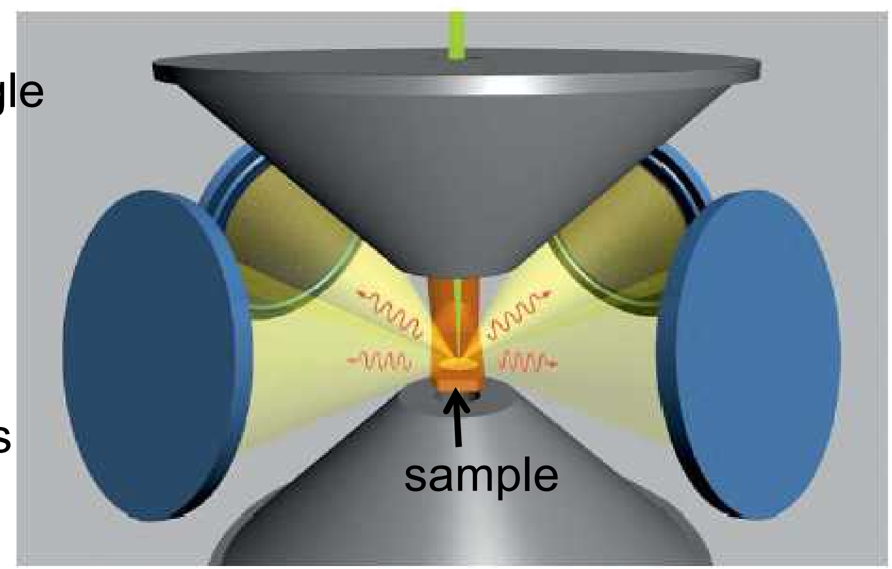


Figure 1. Schematic of Super-X detector

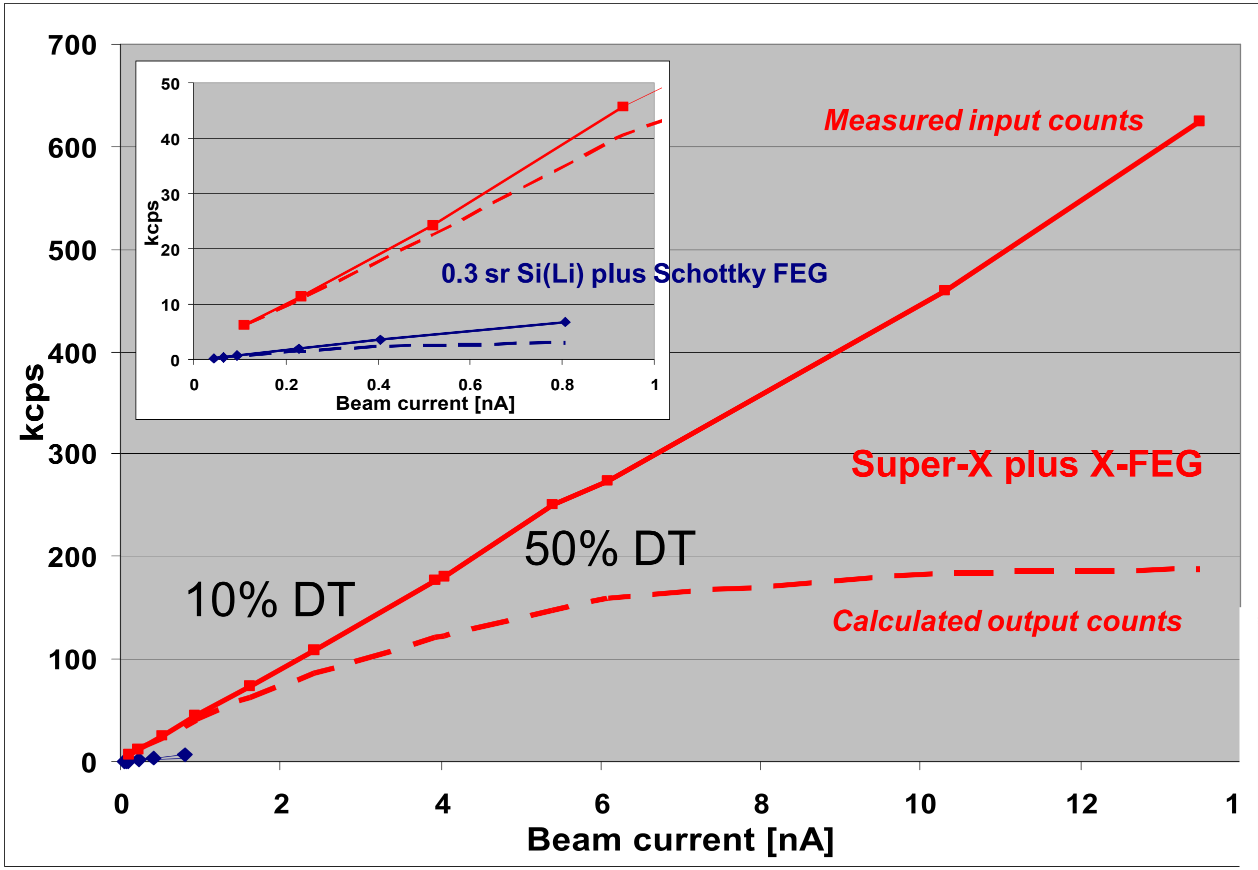
Conceived by FEI with collaboration from Bruker and pnSensor

Revolutionary change in AEM-EDS

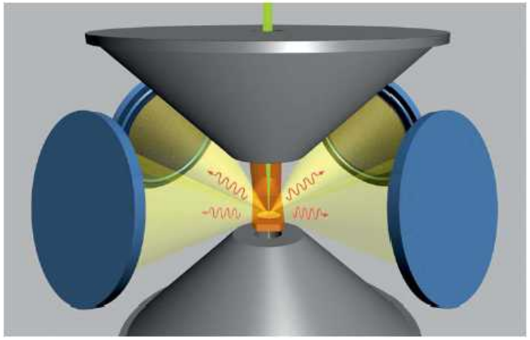
- 4-30mm^2 (120mm^2) SDDs with large solid angle
  - 0.9 sr (Osiris-uncorrected)
  - 0.7 sr (Titan-probe corrected)
  - State-of-the-art SDDs
  - Windowless & pnWindow…good light-element performance (C, N, O easily)
  - High-throughput…10 μsec instantaneous dwell times, multiple pass, drift correction



SuperX™ Detector Performance



Note: 1000 nsec shaping time
136 eV FWHM Mn-Kα



In both experiments the same FIB-cut InP sample was used with a thickness of about 200 nm.

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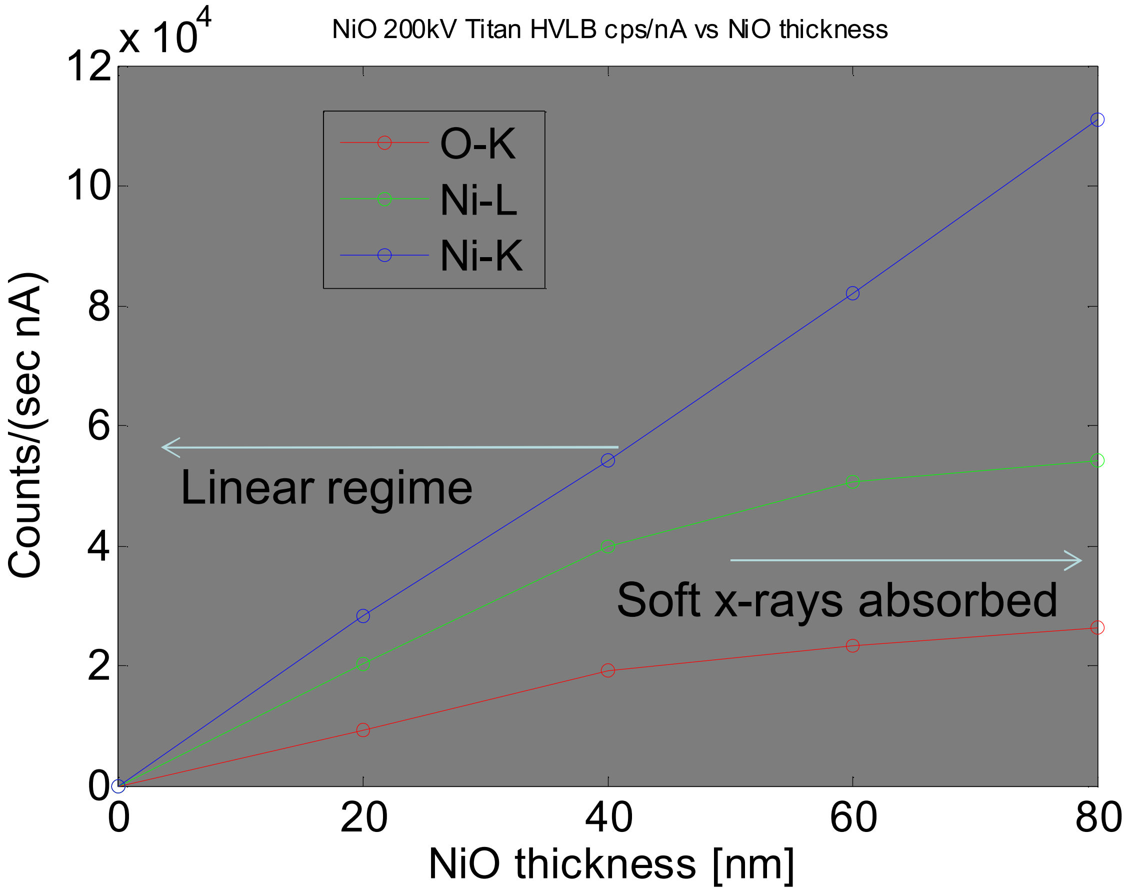
Relative x-ray detector performance with the same Fe-Ni FIB sample

Corrected for live time/probe current

Microscope	Accelerating Voltage [kV]	Figure of merit Counts/(sec*nA)	Performance relative to 200kV Tecnai Si(Li)
JEOL 2010F, 0.1 sr Si(Li)-J	200	2000	0.29
JEOL 2010F, 0.1 sr Si(Li)-G	200	2550	0.36
Tecnai F30-ST, 0.1 sr Si(Li)	300	5100	0.72
Tecnai F30-ST, 0.1 sr Si(Li)	200	7000	1.00
Titan ChemiSTEM, Gatan	200	57000	8.14
Titan ChemiSTEM, FEI High visibility holder	200	74000	10.57

If Titan w/Super X is nominally 0.7 sr then Tecnai f30-ST is really 0.066 sr and JEOL 2010F is really 0.033 sr…don't necessarily believe the solid angles!

Chemi-STEM, x-ray collection efficiency



Better way to measure relative detector efficiency is with a sample like the Egerton test sample, thin NiO. Both total and energy-dependent efficiency.

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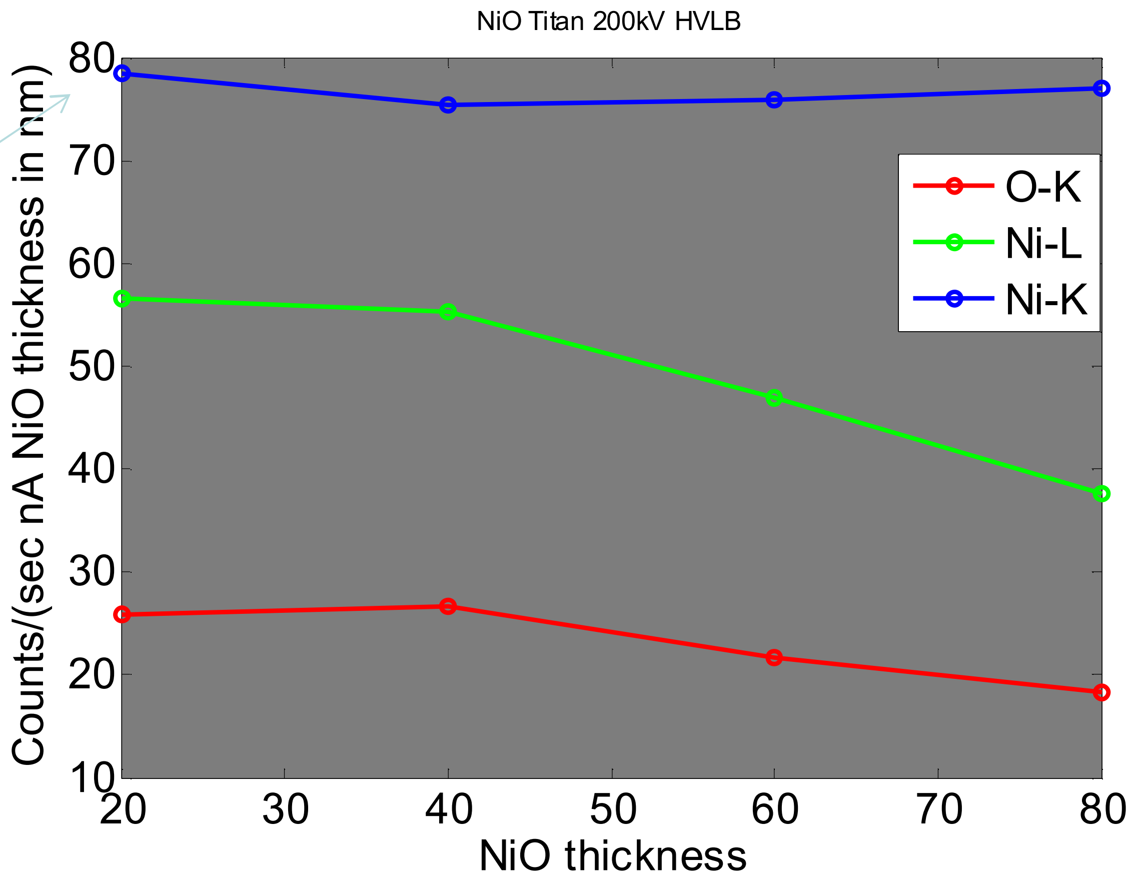
Chemi-STEM, x-ray collection efficiency
Proposed test specimen, less than 40 nm NiO

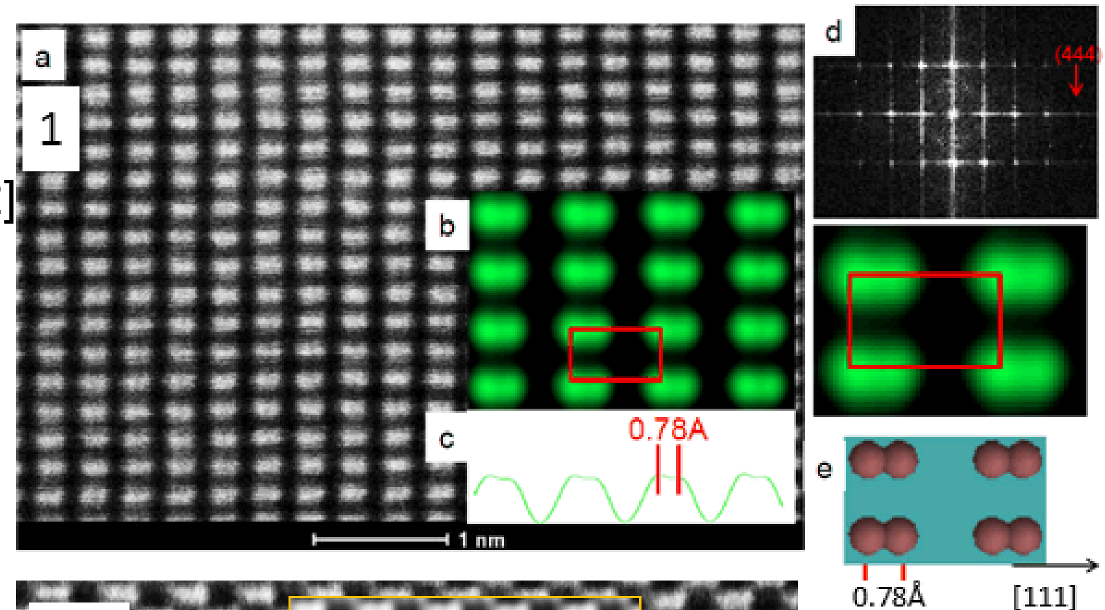
Implies that a 1 nm NiO sample would produce ~80 cps/nA Ni-K



Normalized

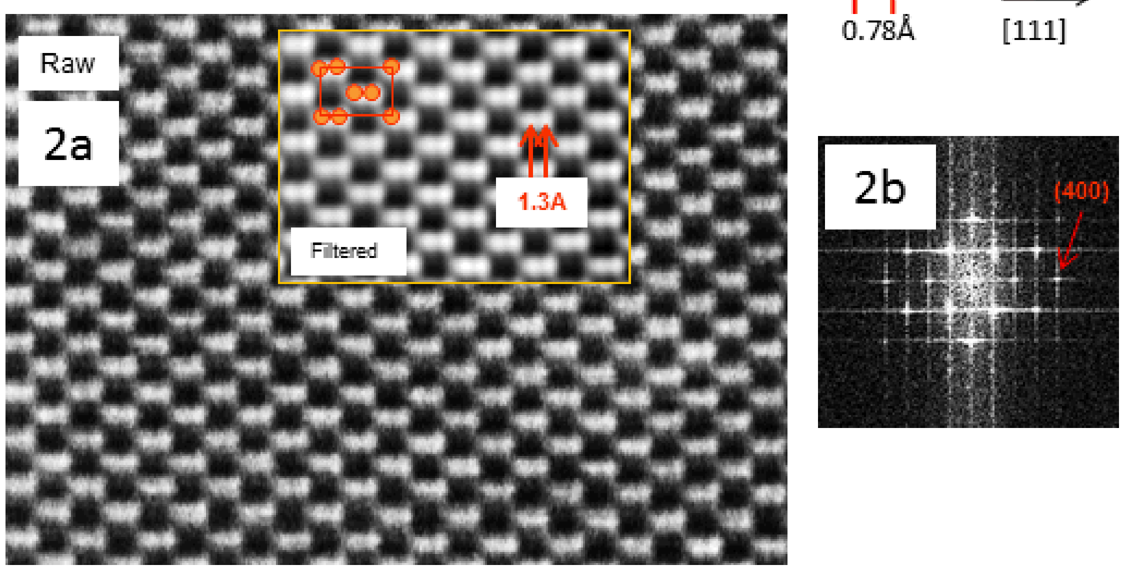
Imaging with the AC-STEM at SNL, 5 months in

200 kV Si [112]



200kV with a 5mm objective lens pole piece gap

80 kV Si [110]



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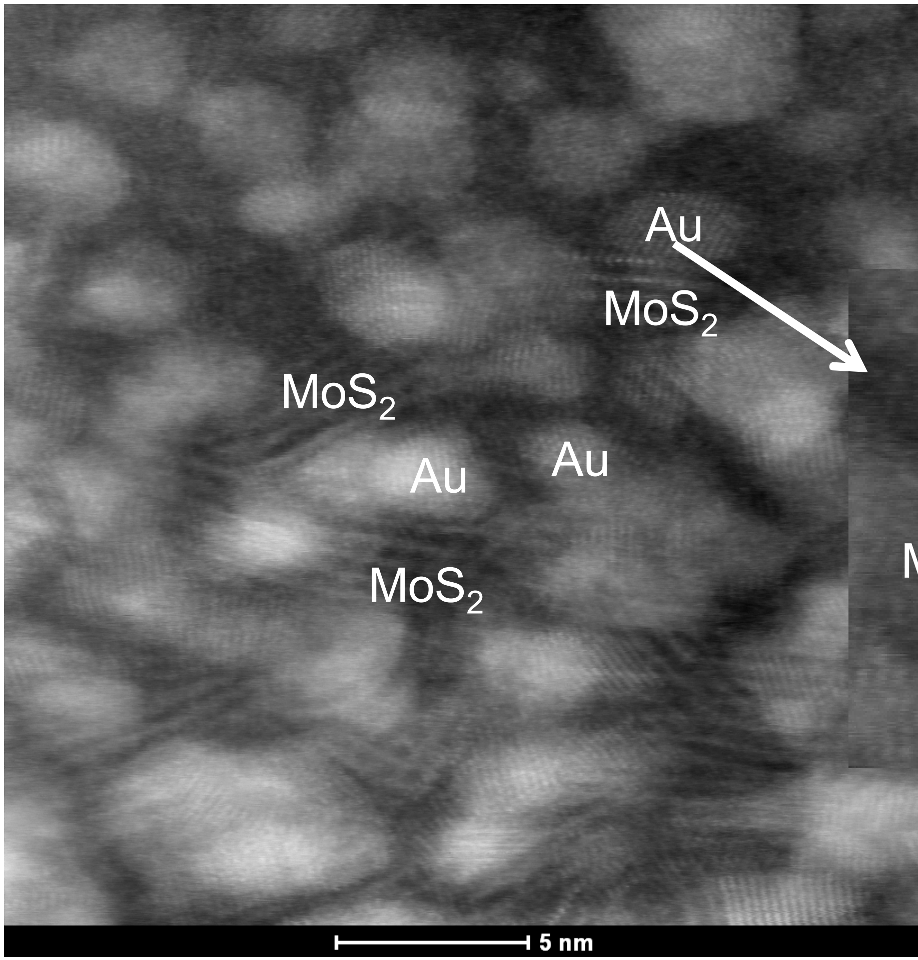
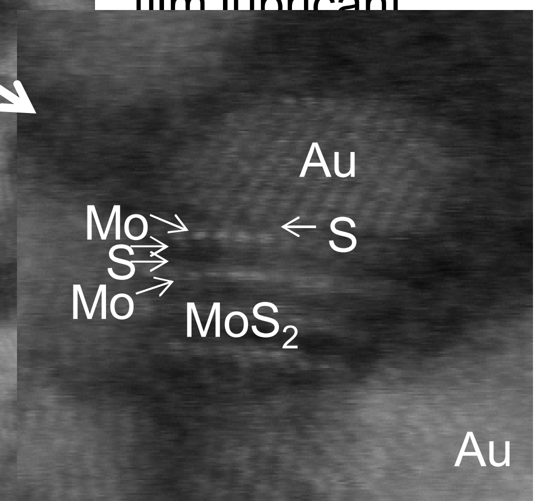
Characterization of solid-film lubricants

$Au\text{-}MoS_2$ solid-film lubricant proposed for replacement of current MoS_2 lubricant in various electromechanical devices





Atomic resolution AC-STEM image shows the morphology of the solid-film lubricant

MoS_2 terminates on a S-plane which likely bonds to Au and keeps the S from reacting with moisture

Materials from Somuri Prasad (1831) and Ron Goeke (1832)

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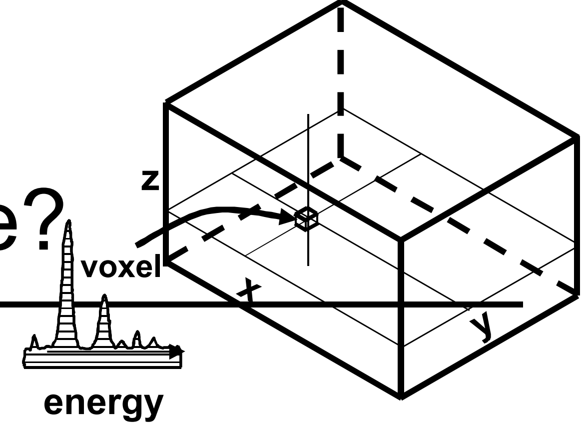
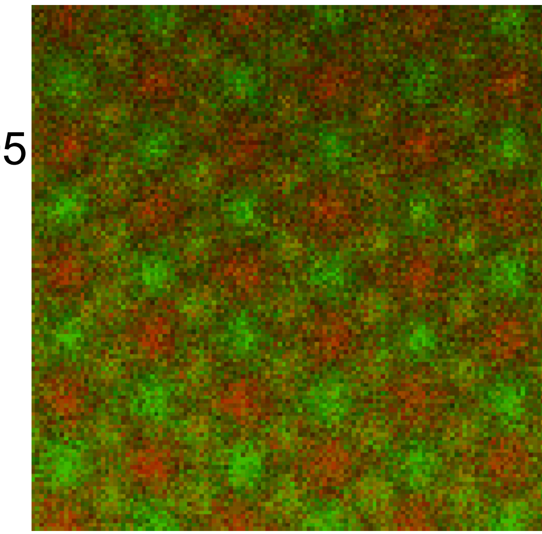
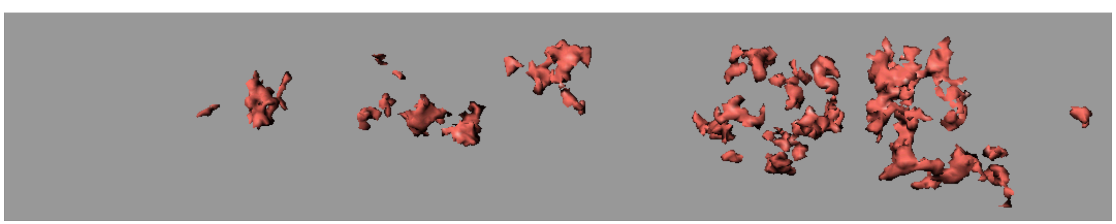
Data analysis primer
What is a spectral image?



- A series of complete spectra resolved in 2- or higher dimensions
  - Conventional spectral images-2D*
    - Demonstrated in 1979 and first product by PGT in 1995
  - Tomographic spectral images-3D**
    - Direct-FIB**, Metallography
    - Computed-Tilt series of spectral images
    - Confocal
  - Resolved in other dimensions
    - Time, process condition, projection, etc.



- As far as MSA is concerned these can all be treated the same



*e.g., P.G. Kotula et al. *Microsc. Microanal.* 9 (2003) 1-17.
**e.g., P.G. Kotula et al. *Microsc. Microanal.* 12 (2006) 36-48.

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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

*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

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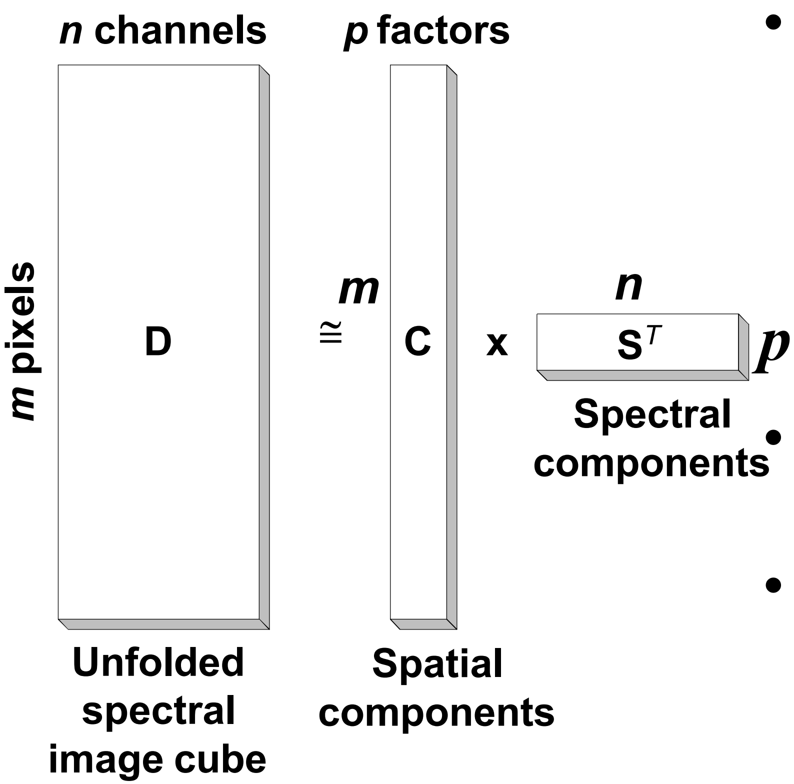
We have several options in our multivariate "Toolbox"



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 Domain Simplicity*

Often the elemental/correlated elemental viewpoint

- **$D = CS^T$ (Goal: Factor raw data into C and S…linear model)**
  - **D is an *m*-pixel × *n*-channel raw spectral-data matrix**
  - **S is an $n \times p$ matrix containing the *p* pure-component spectra shapes**
  - **C is an $m \times p$ matrix containing their spatial distributions/abundances**
- **Data is scaled to account for non-uniform (Poisson) noise****
- **Number of factors to retain is chosen (Eigenanalysis)**
- **PCA is performed on the scaled data such the spatial components are orthogonal and the spectral components are orthonormal**
- **Rotate the orthonormal spectral components to maximize their mutual simplicity with the VARIMAX procedure**
- **Apply the inverse rotation to the spatial components which relaxes orthogonally in this domain**
- **Optionally: Impose non-negativity (e.g. via MCR-ALS)*****
- **Inversely scale the components for Poisson noise**

*M.R. Keenan, *Surf. Int. Anal.* **41** (2009) 79-87.

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

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

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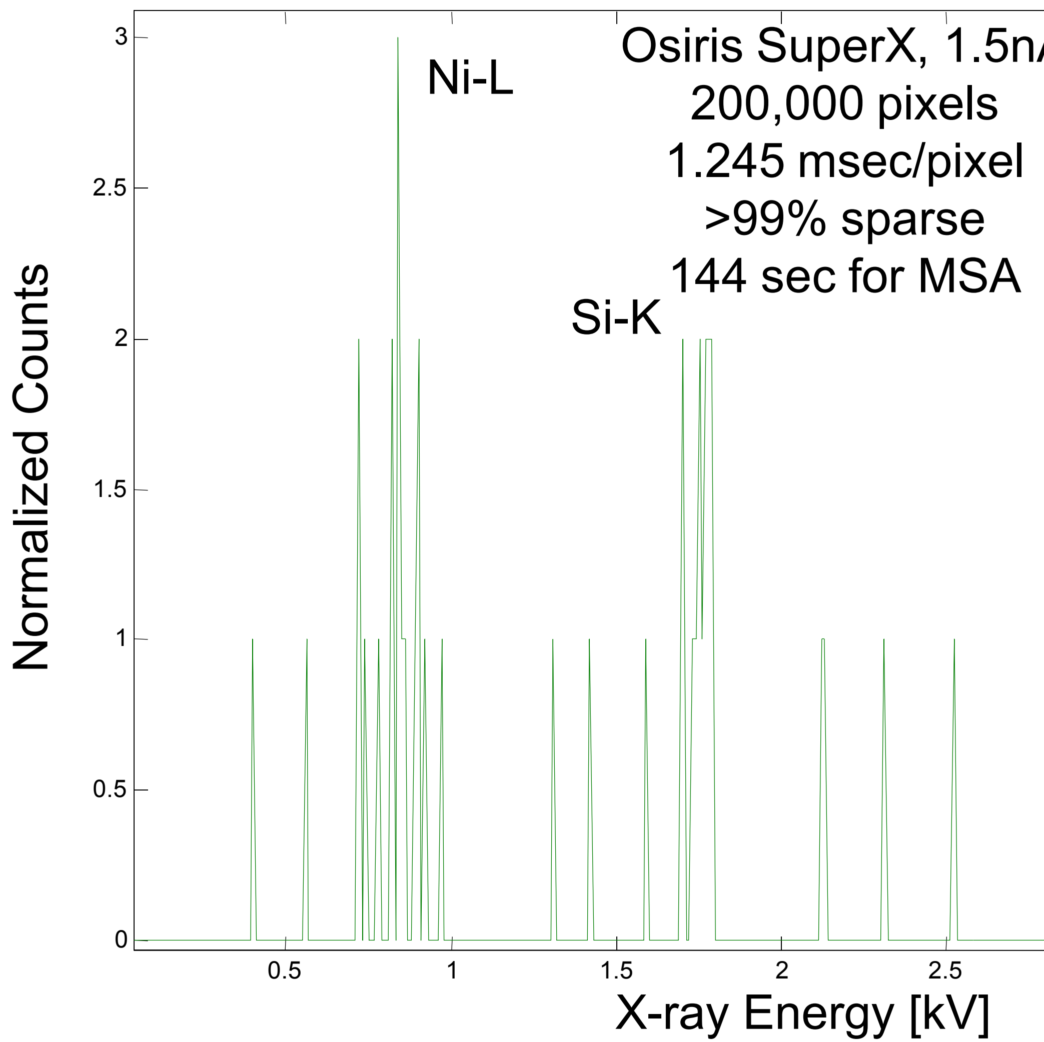
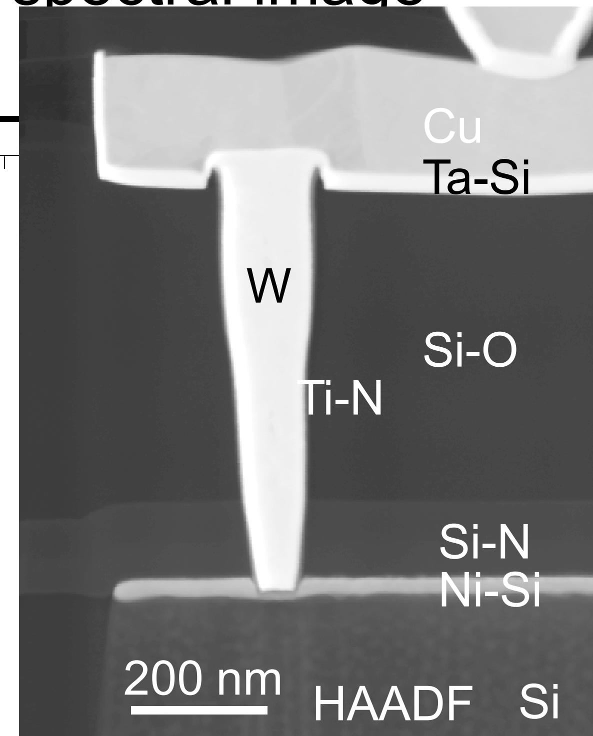
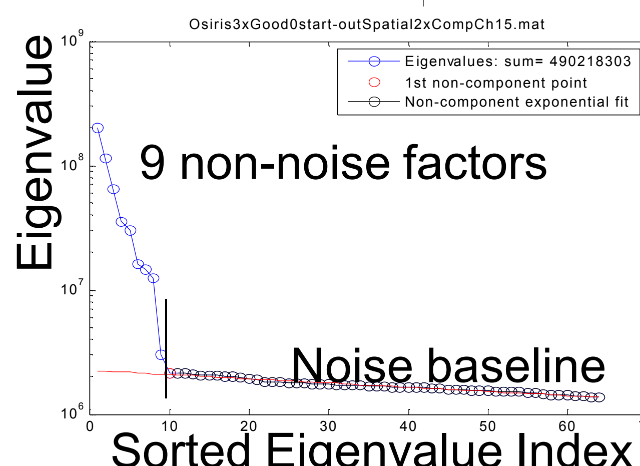
Low end spatially, high end for sensitivity
Raw spectrum from the CMOS spectral image

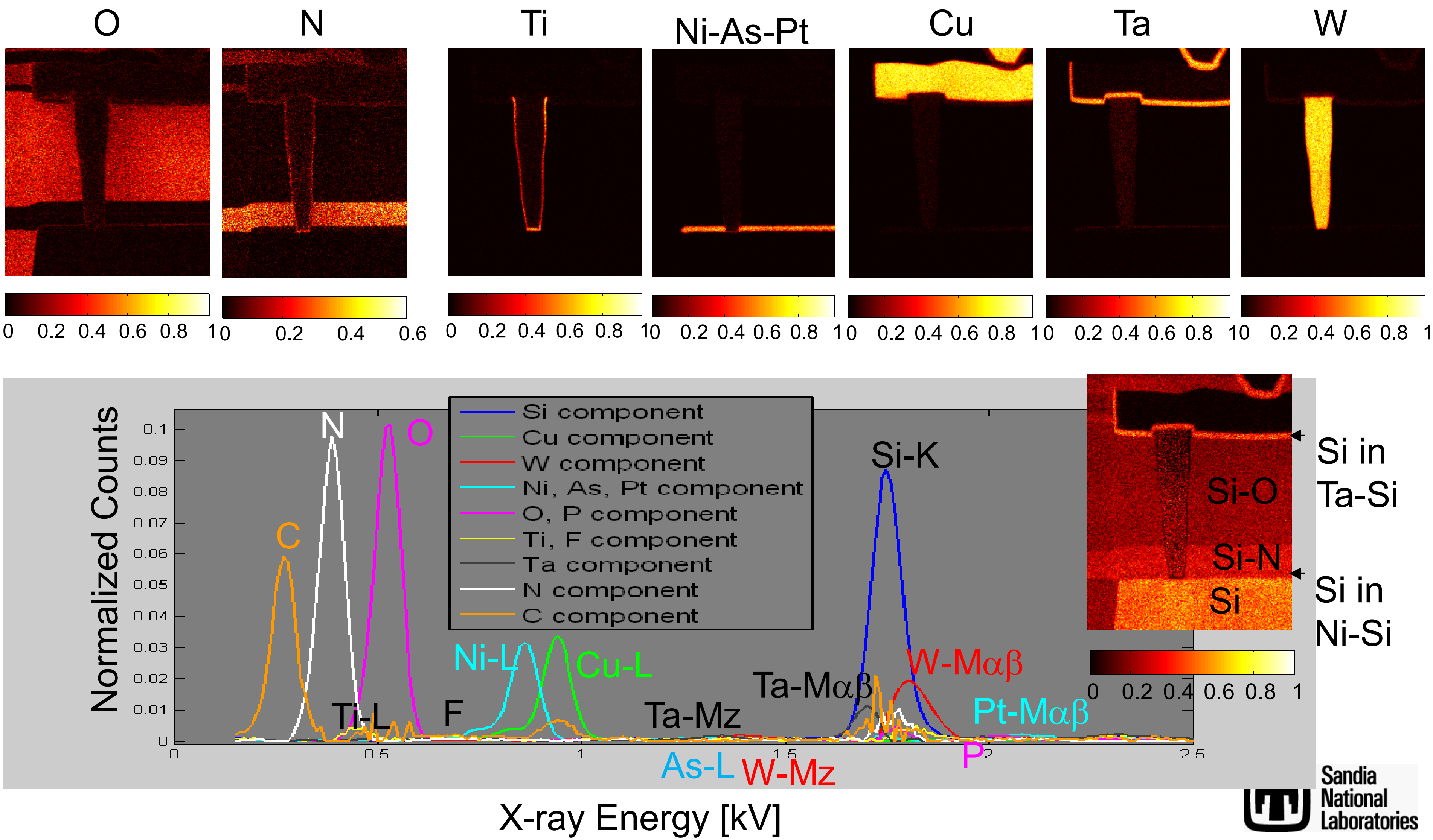




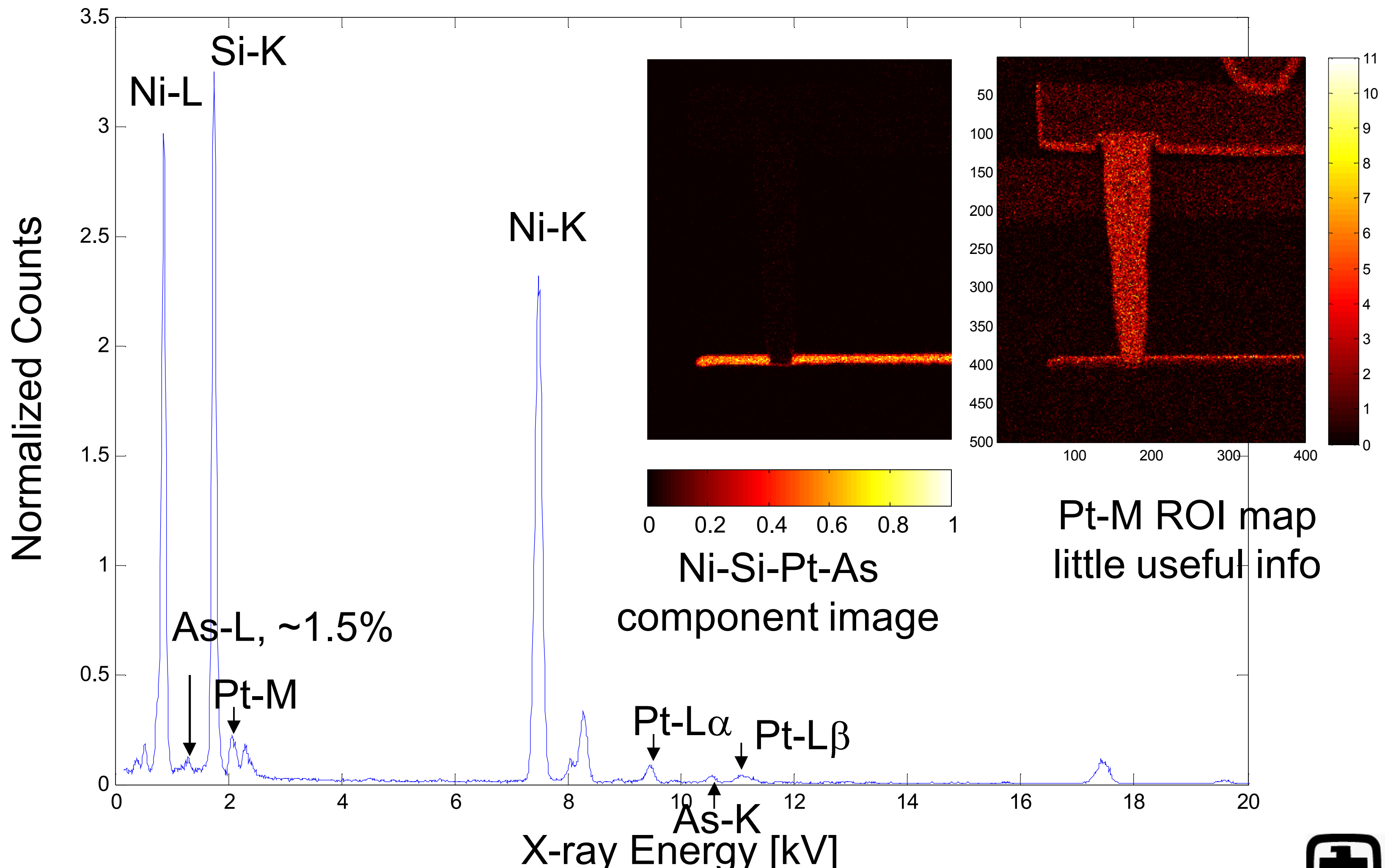


Data courtesy Dmitri Klenov, FEI on sample provide by SNL

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



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



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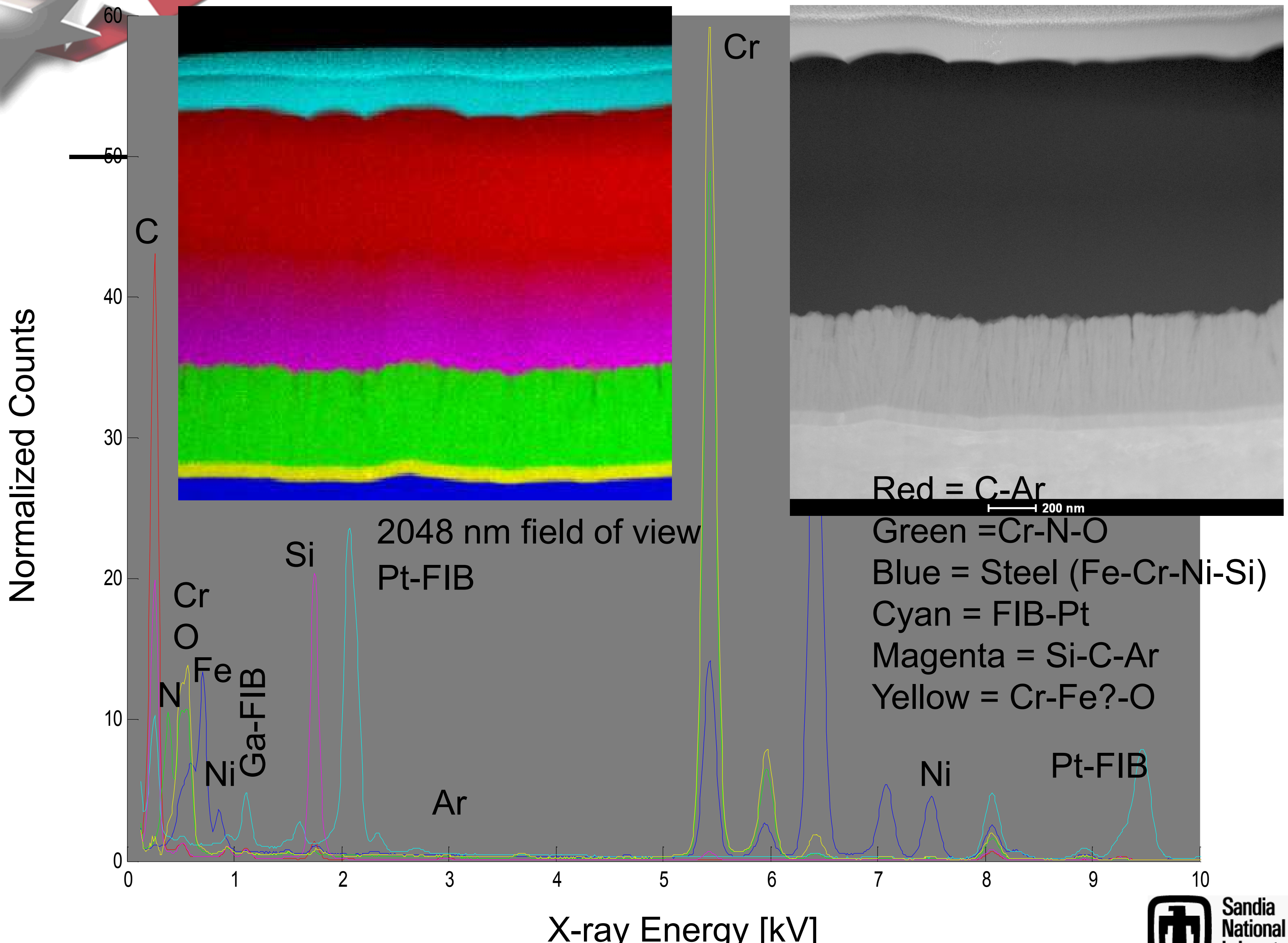
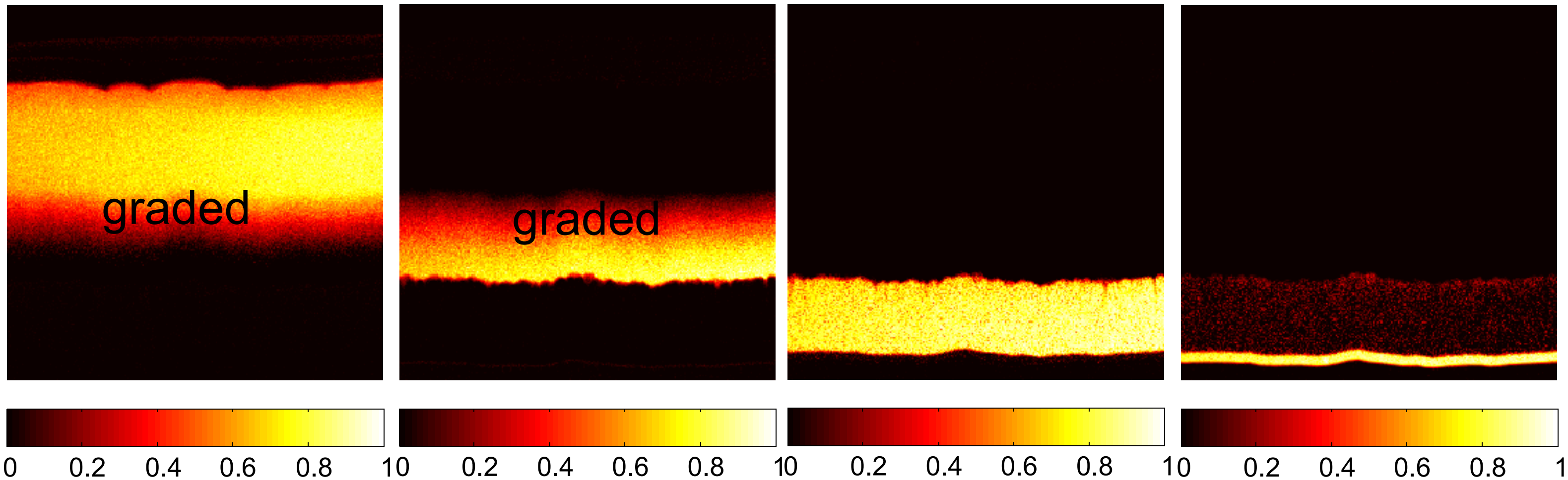
Low end…Solid-film lubricants for electromechanical devices



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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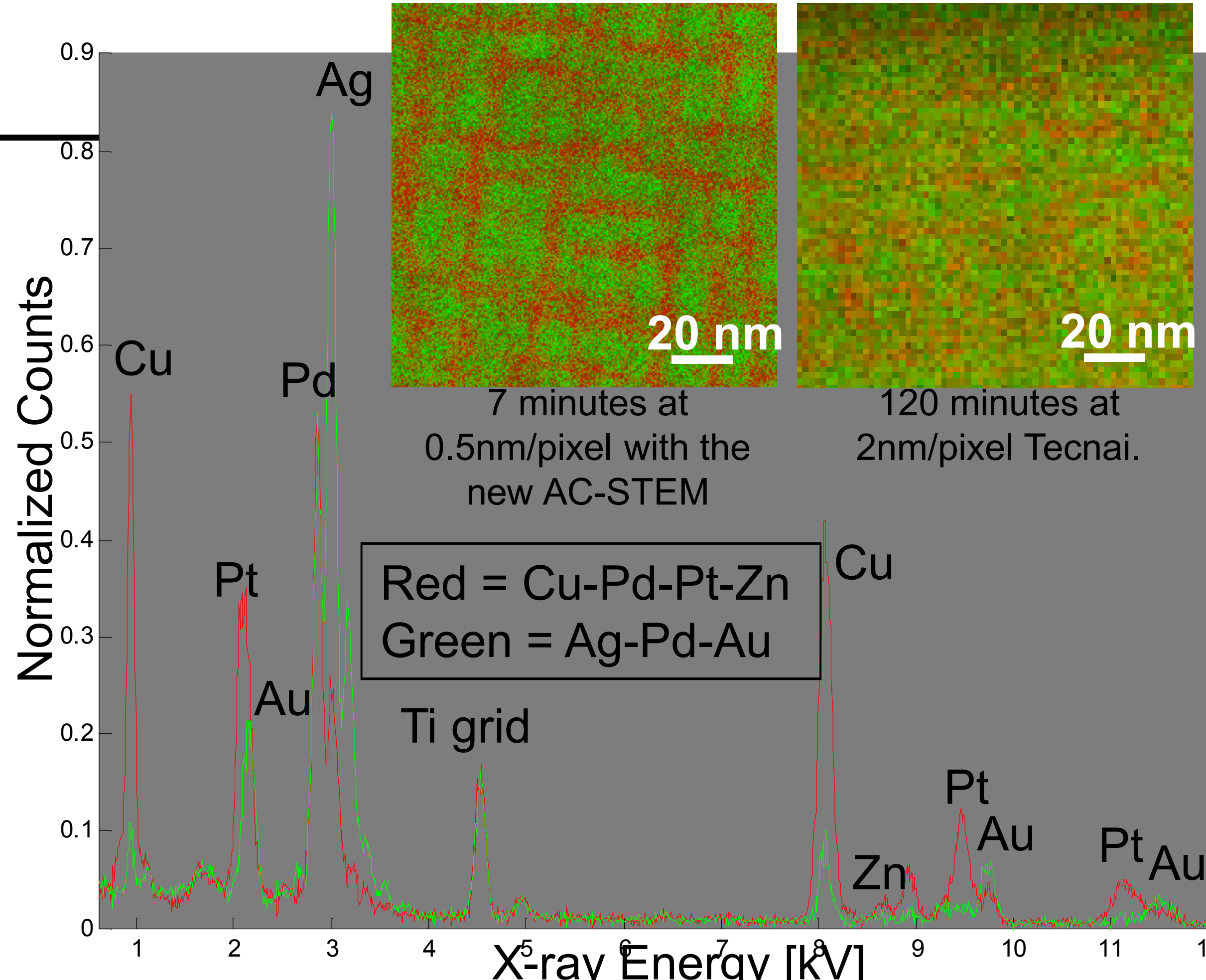
Medium end analysis
Sub-nm microanalysis of electrical contact materials

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.

Confirms predictions from the 1970s.

Materials from Don Susan (1831) and Zahra Ghanbari (1831)

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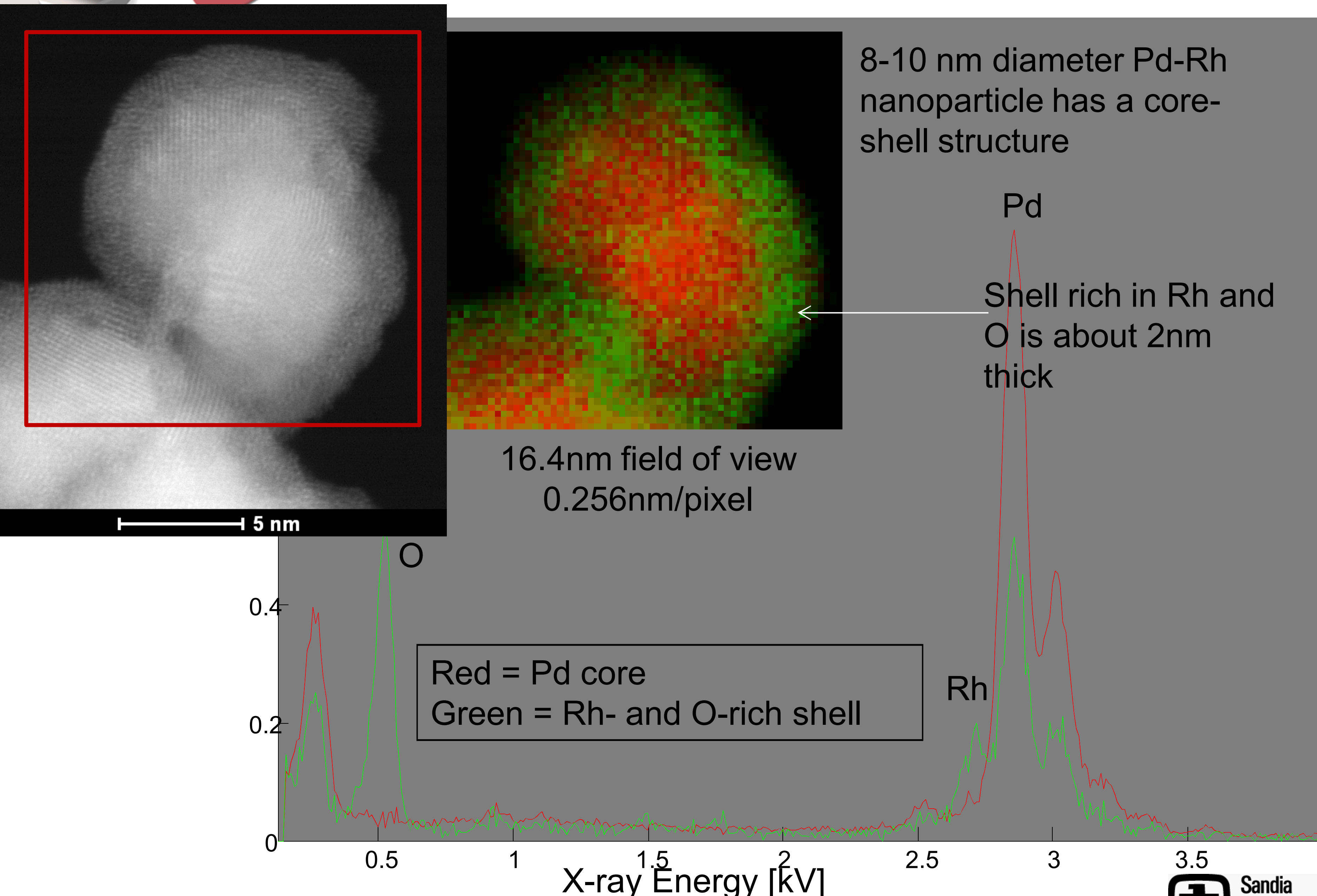
Medium end, Characterization of hydrogen isotope storage materials



Materials from David Robinson (8651) and Patrick Cappillino (8651). Collaboration with Josh Sugar (8656).

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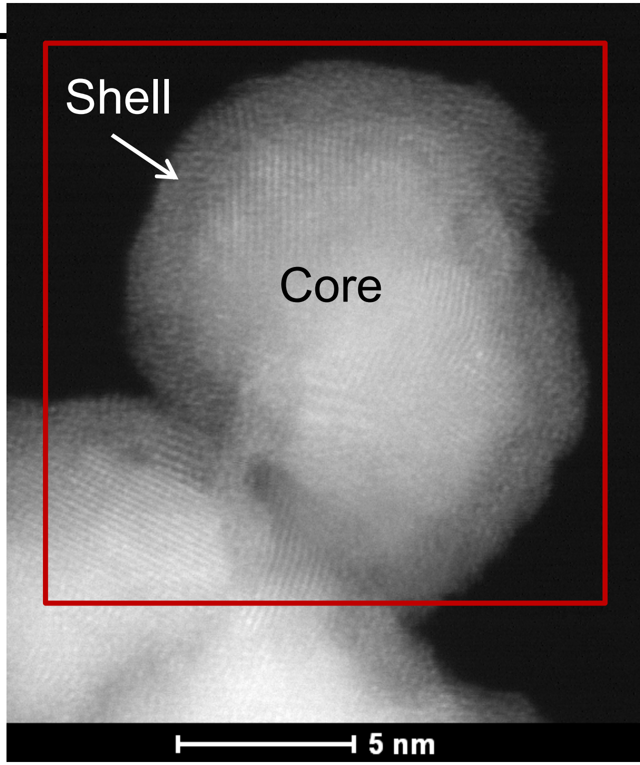
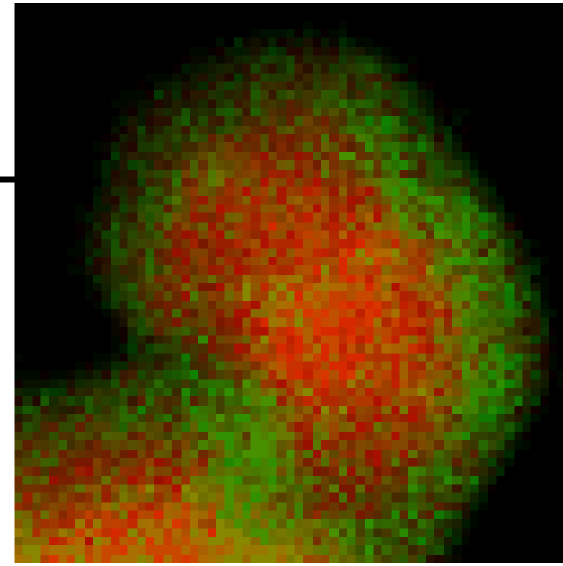
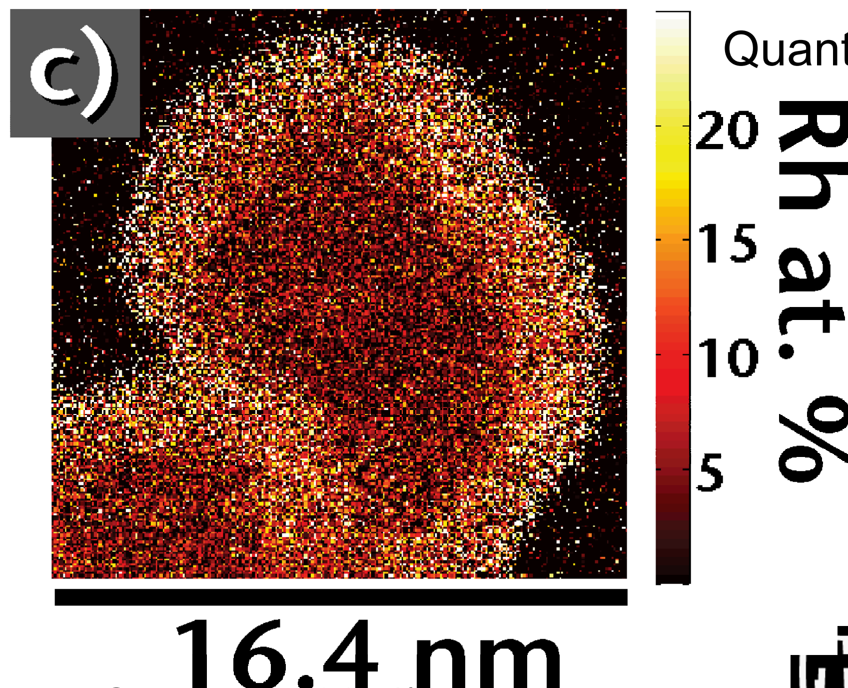
Medium end, characterization of hydrogen isotope storage materials



HAADF image



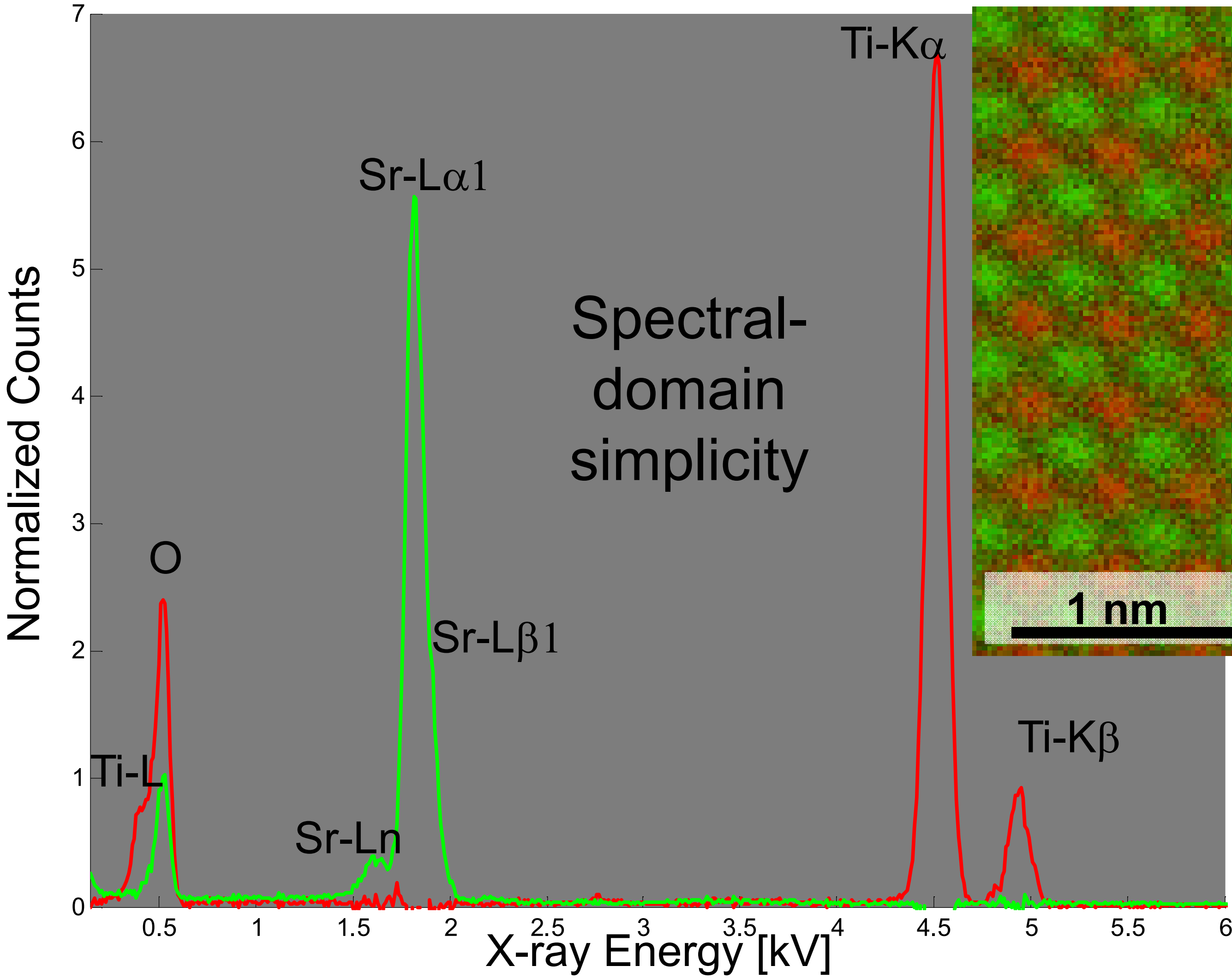
AXSIA results
Red = Pd-rich core
Green = Rh- and O-rich shell

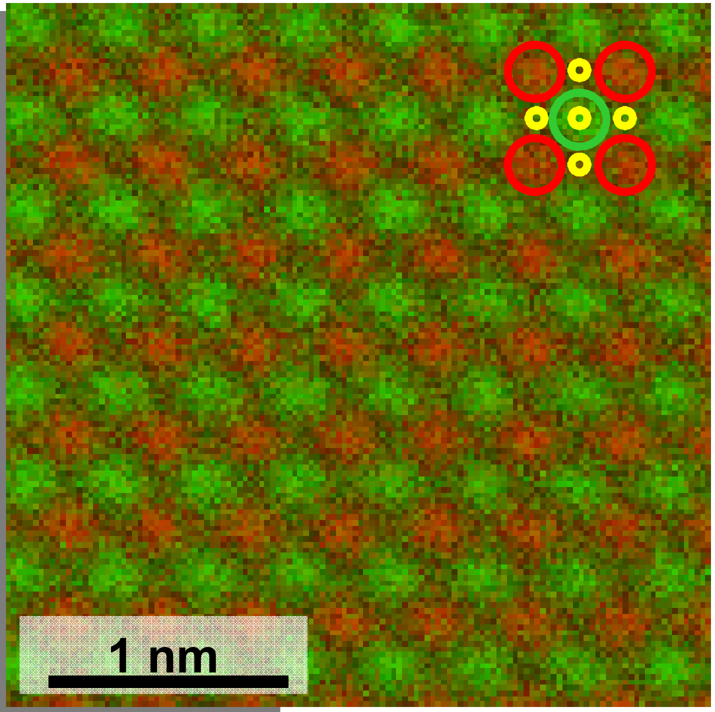


Materials from David Robinson (8651) and Patrick Cappillino (8651). Collaboration with Josh Sugar (8

High-end atomic resolution, SrTiO3 [100]

MSA-processed spectral image of $SrTiO_3$ with no *a priori* information



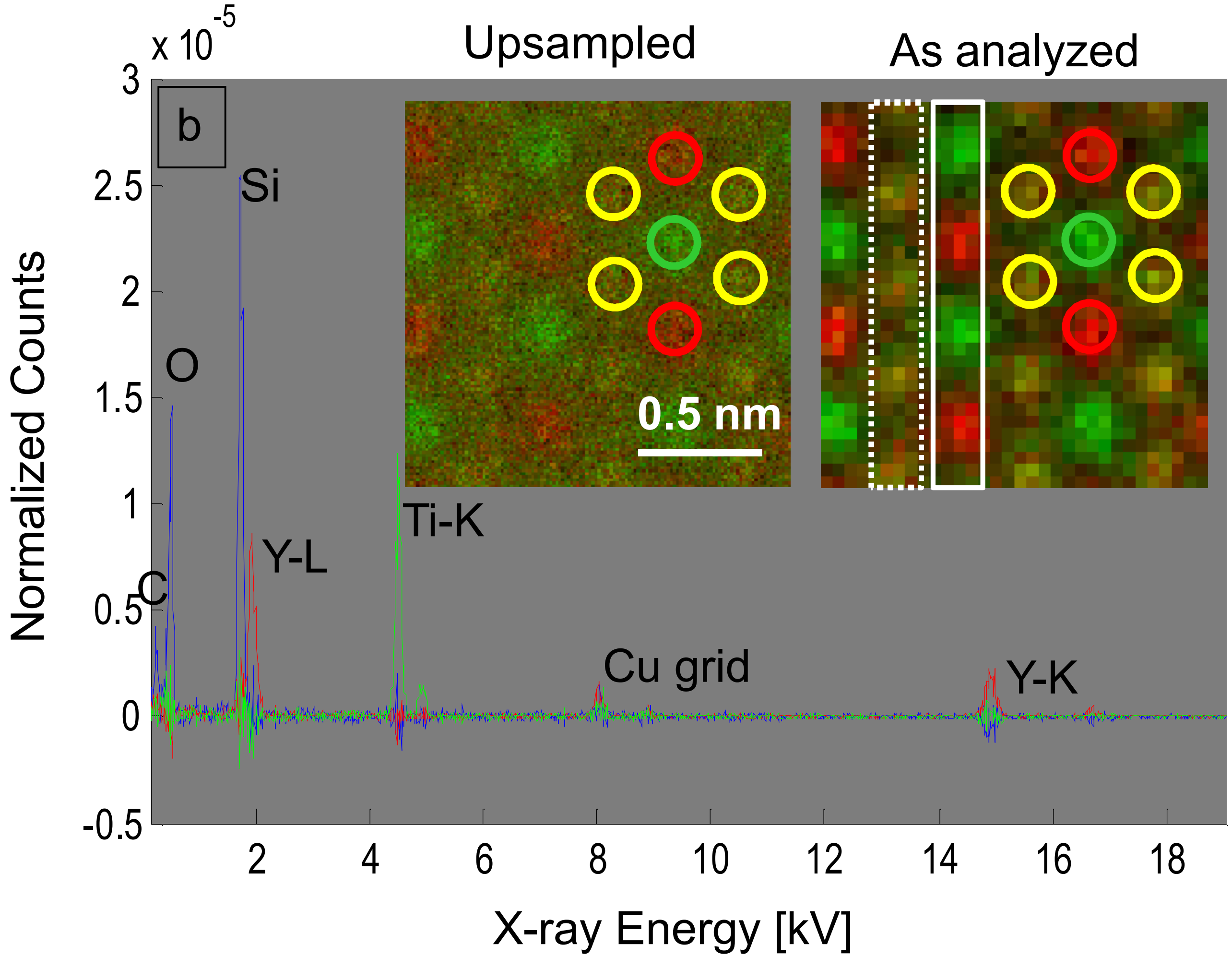


Red = Ti columns
Green = Sr columns

Sr-K lines not shown but correlate with Sr-L

$Y_2Ti_2O_7$ Pyrochlore [011]

128x128 Spectral image, 16x compression, Spectral domain simplicity



10 μsec instantaneous dwell with 272 frames plus drift correction

11,300 counts per second per nA for this specimen thickness

Convergence angle of 21.4 mrad, probe current of 40 pA, probe smaller than 0.15 nm

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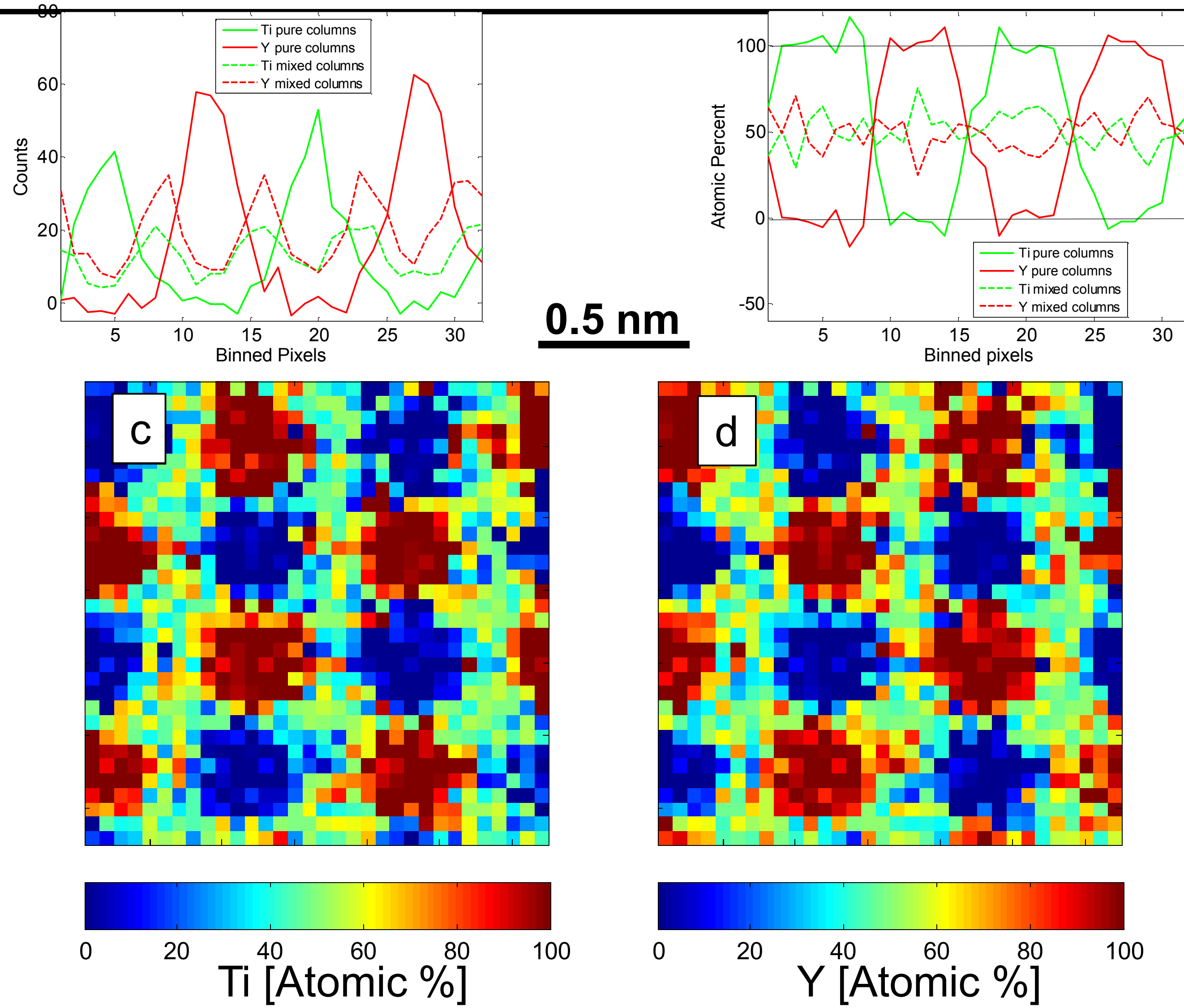
$Y_2Ti_2O_7$ Pyrochlore [011]

Progress towards atomic-resolution quantification



Pushing quantification

Data courtesy Dmitri Klenov, FEI

Fig. 1

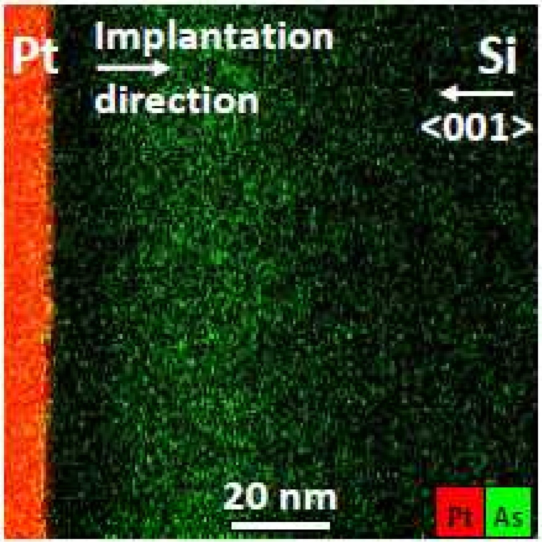


Fig. 2

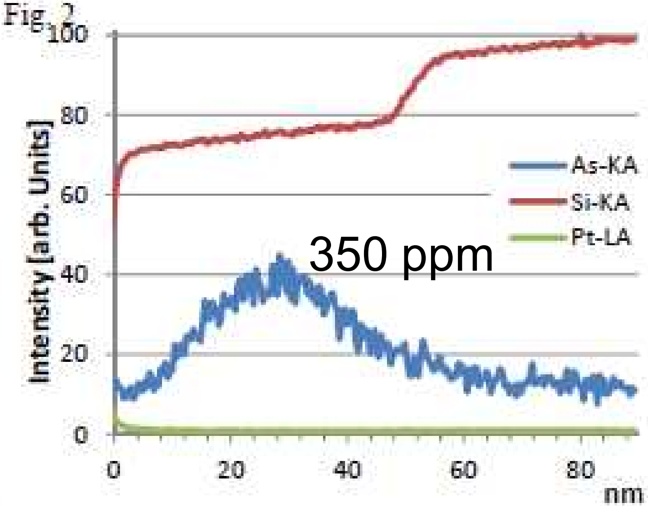


Fig. 3

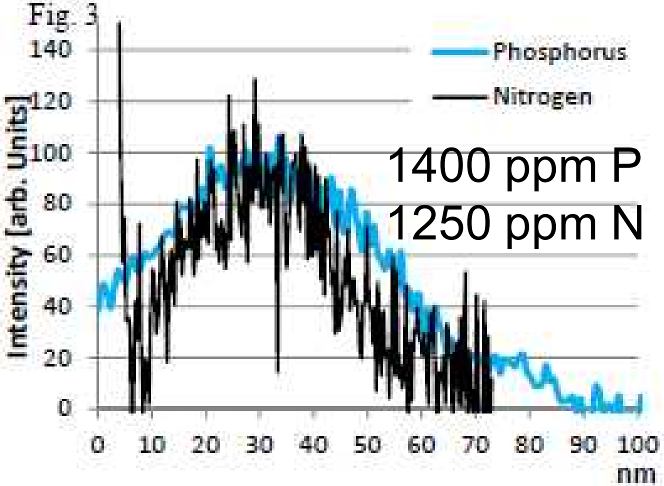


Figure 1. Example of the 256x256 map of the As distribution in Si. 5e14 at/cm2 dose of the As used. The concentration in the maxima of the distribution corresponds to 0.35 at%. The Pt is used as the protection layer during FIB sample preparation.

Figure 2. Profile of the As distribution with 5e14 at/cm2dose.

Figure 3. Normalized profiles of the P and N distribution with 2.5e15 dose. The concentration in the maxima is about 1.4 at% and 1.25at% for the P and N correspondingly. The concentration in the tails of the distribution is less than 0.3 at%.

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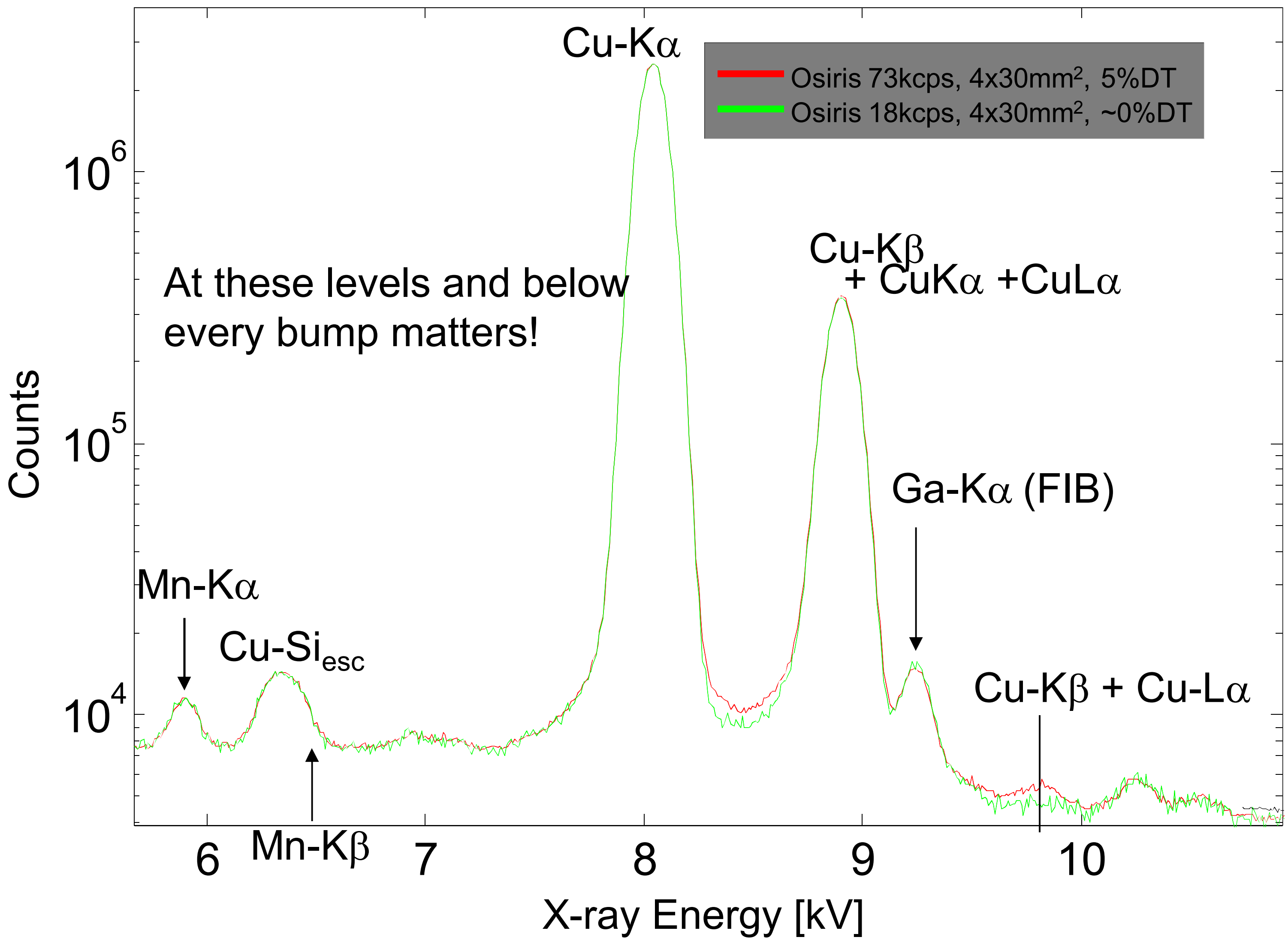
Quantitation: 0.1 wt.% Mn-Cu

1000 ppmw, in collaboration with Joe Michael at SNL



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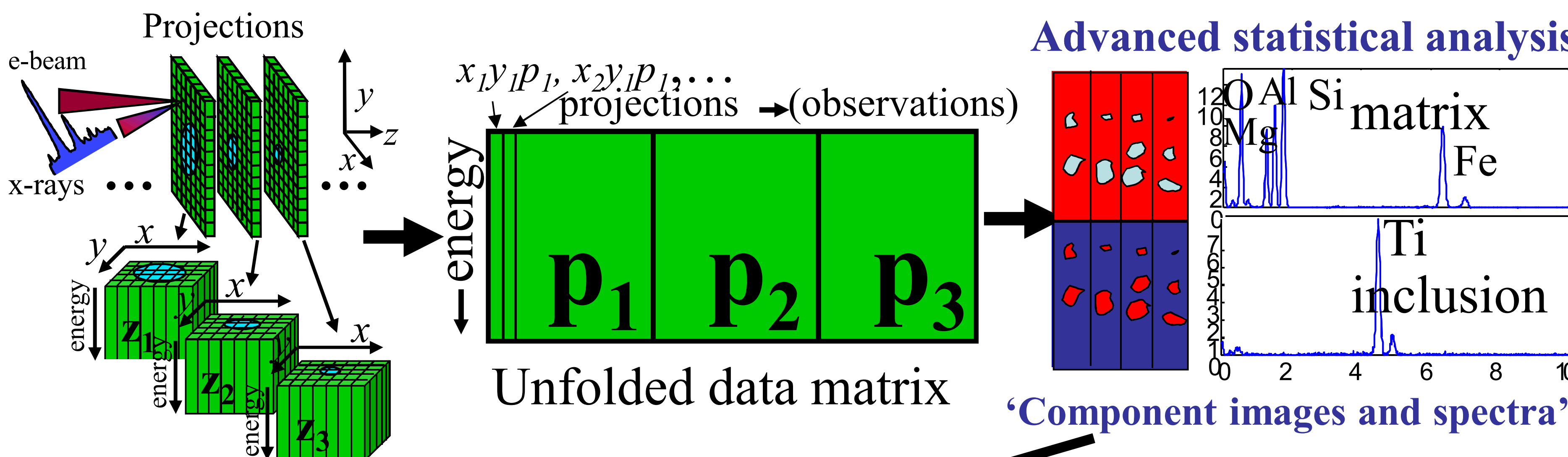
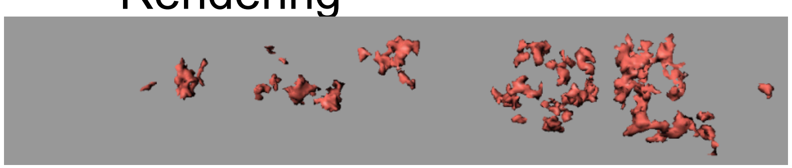
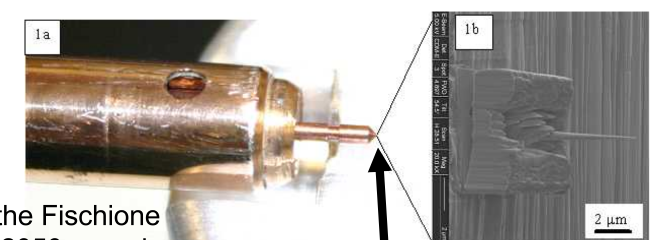
Tomographic Spectral Imaging and Multivariate Statistical Analysis



Reconstruction of component images into 3D model (Inspect 3D)

Rendering





Tip of the Fischione Model 2050 on-axis tomography holder

Atom-probe tip

SEM image of the prepared needle

P.G. Kotula, et al. Microsc. Microanal. 13 (Suppl2), 2007 1324CD-1325CD

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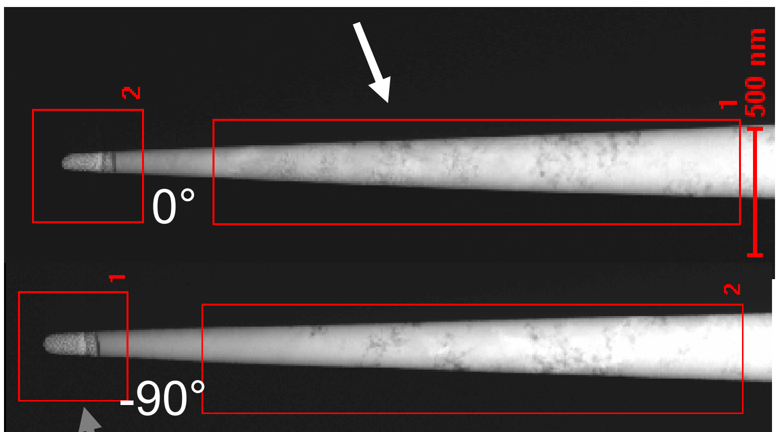
MSA of the entire projection series

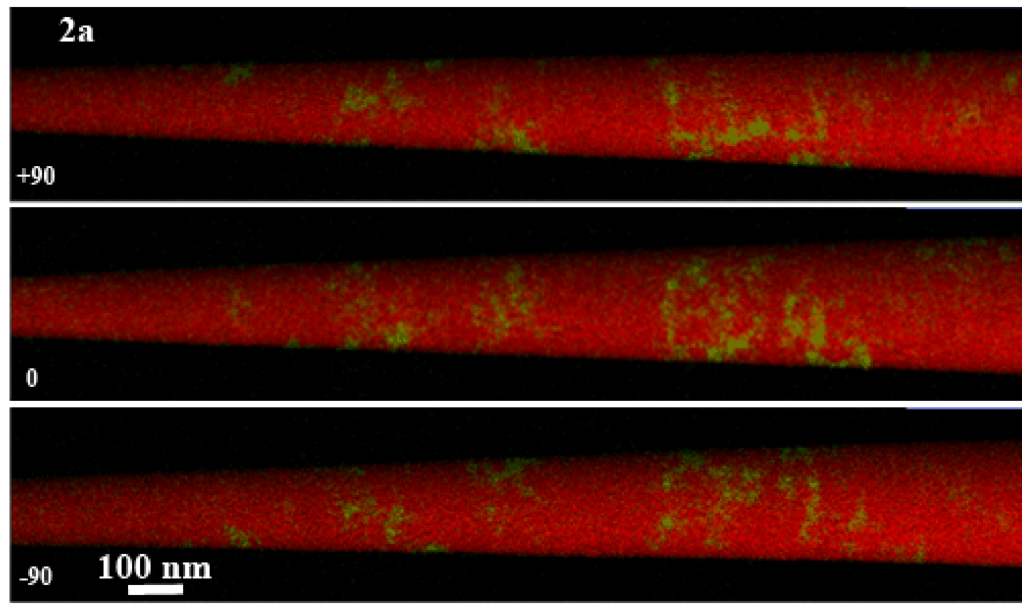
FEI Tecnai F30-ST, 0.1sr

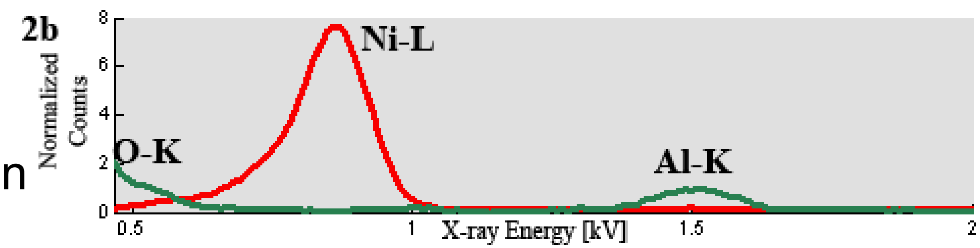
Region of spectral images 2000nm x 400nm



Drift-correction region

Color overlays of component images





19 hours (over 3 days) of data acquisition
30 min on the Titan if automated!

P.G. Kotula, et al. Microsc. Microanal. 13 (Suppl2), 2007 1324CD-1325CD

Then, reconstruct component projection images into 3D model (Inspect 3D)

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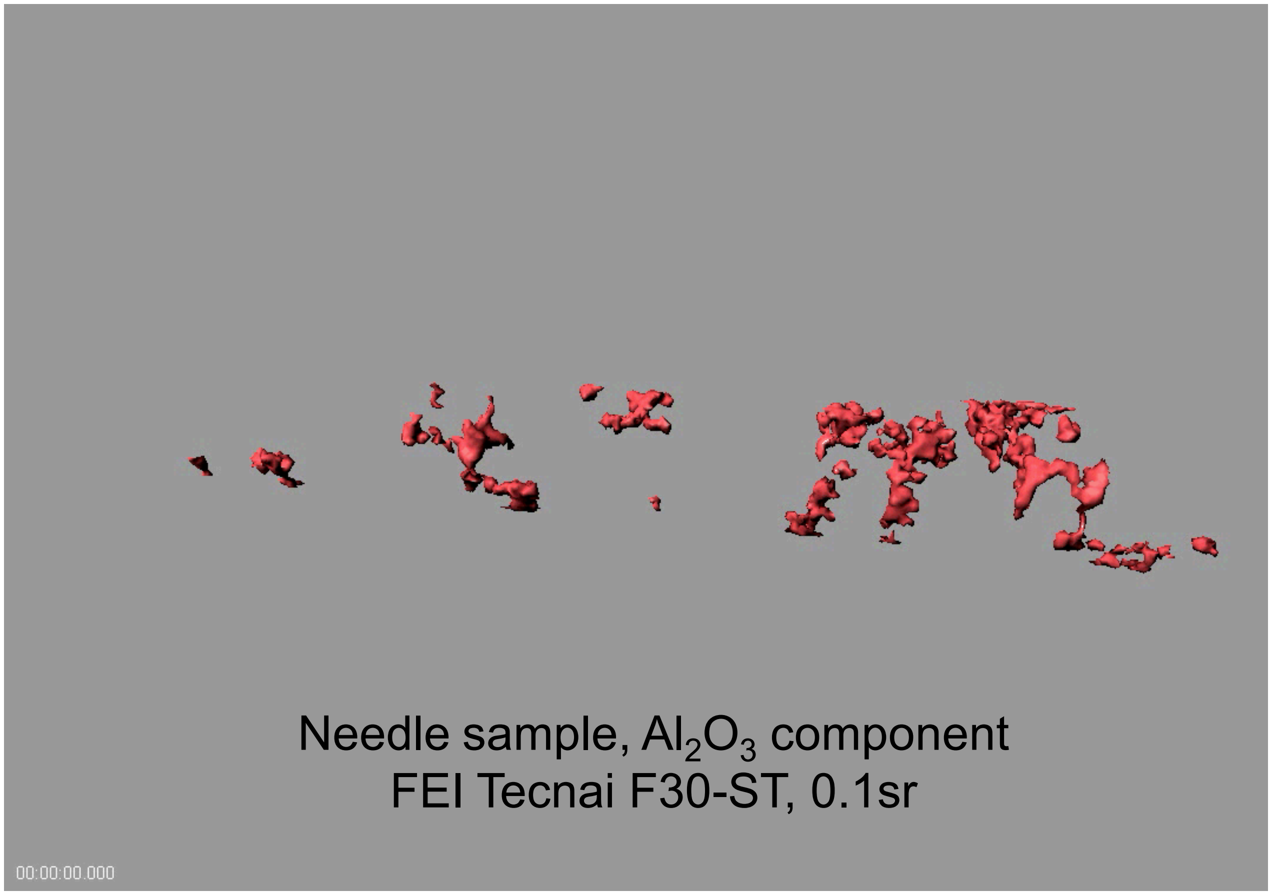
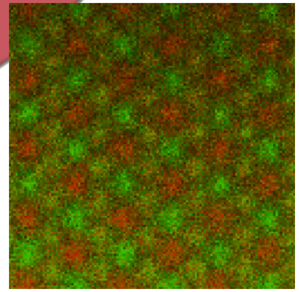
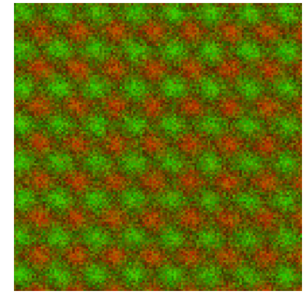
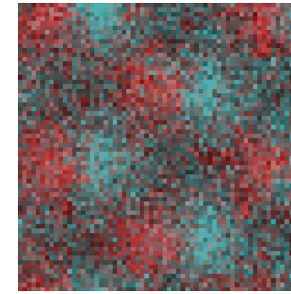
Reconstructed isosurfaces





Conclusions





- AEM is undergoing a renaissance with correctors, SDDs, novel diffraction techniques, and better sources.
- Atomic resolution EDS will become more common than EELS. Easier, more elements accessible, esp. heavy ones, more readily quantified
- 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….
- Quantitative analysis pushed to smaller volumes
  - Understanding the spectrum is critical…every bump matters!
  - Potential for 1000 ppm sensitivity at 0.2 nm?
  - 100 ppm sensitivity at 1 nm?
- Practical computed tomographic spectral imaging
- SNL has one of the first Titan ChemiSTEM-P X-FEG (200kV)

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