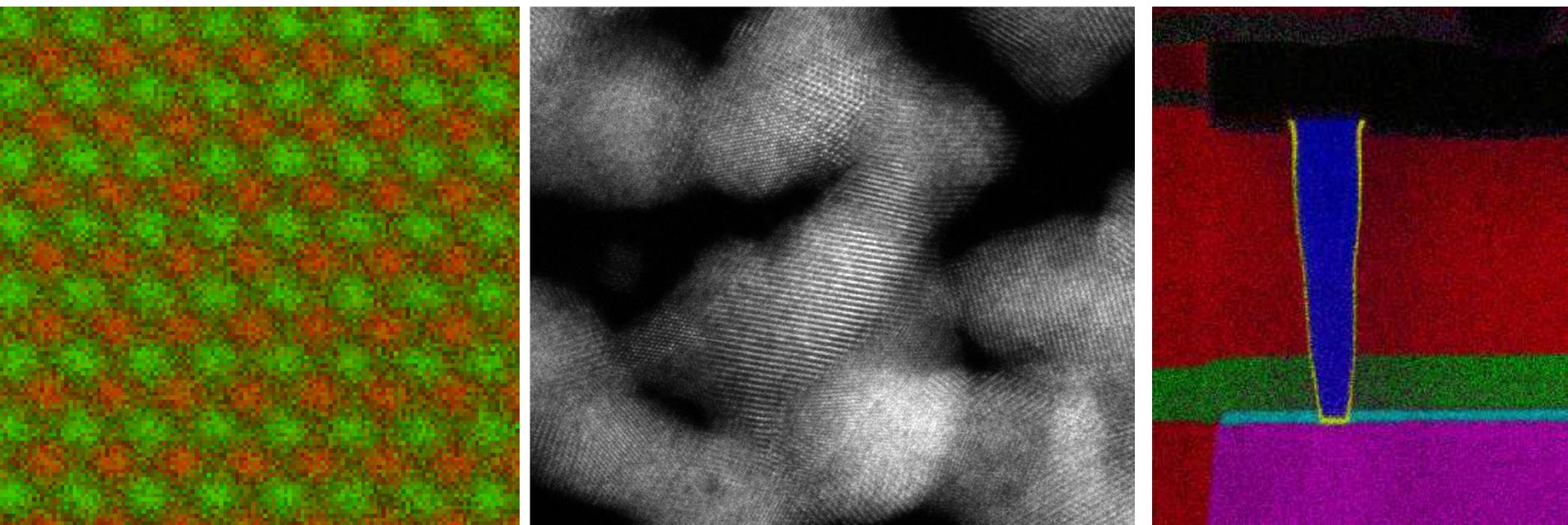


# Advances in Acquisition and Analysis of Hyperspectral Images: The basis for 2- and 3D microanalysis

*Paul G. Kotula*

*Sandia National Laboratories, Albuquerque, NM, USA*





# Outline

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- Multi vs. hyperspectral definition
  - Multi-spectral...think mapping pre-selected elements
  - Hyper-spectral is collection all the data possible
- Spectral image analysis
- Historical timeline of developments
  - Multi-to-hyperspectral happened 35 years ago
  - Commercial version less than 20 years ago
- 2D to 3D examples along the way

# Materials Characterization Tetrahedron

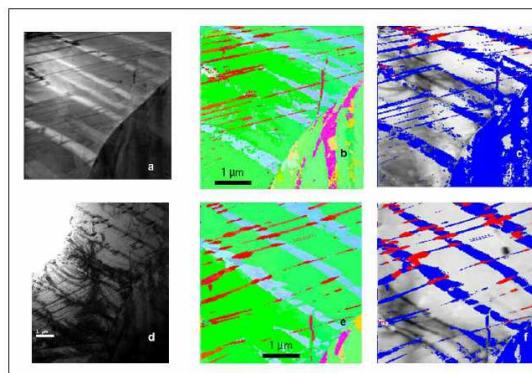
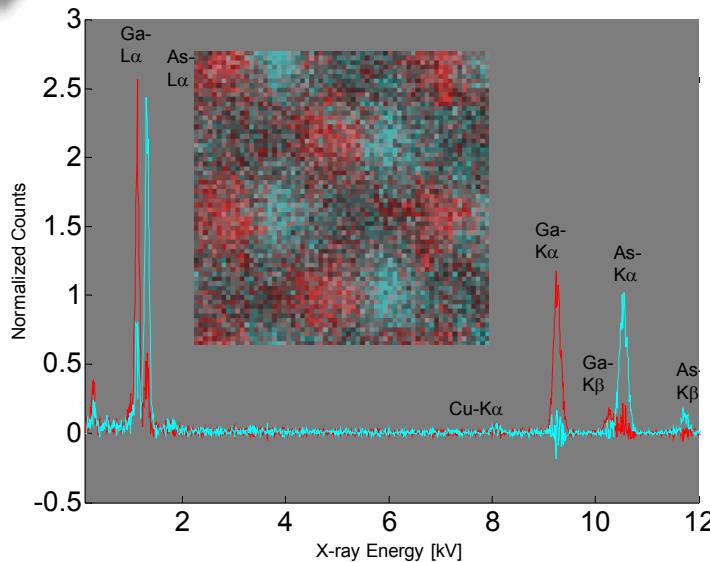
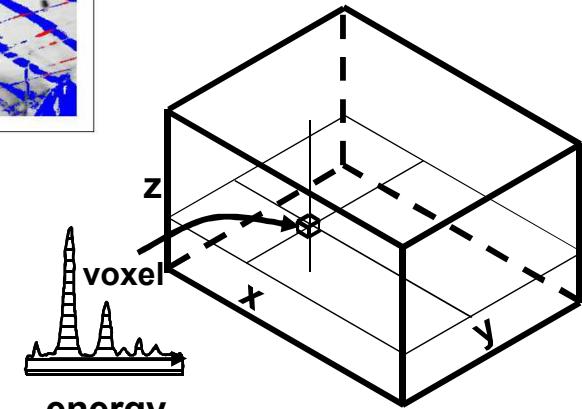
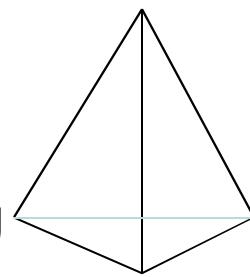


Figure 7: Austenitic stainless 309 steel containing three distinct phases:  $\gamma$  fcc matrix,  $\alpha$  fcc bands and  $\delta$   $\alpha'$  martensite at bands intersections. (a) Intensity map coupled to (b) orientation (c) and phase (d) maps acquired without precession. (e) Brightfield image coupled to orientation (a) and phase (f) maps acquired with precession. Step size 22 nm, precession angle 0.4°, acquisition time 1 hour 9 minutes.



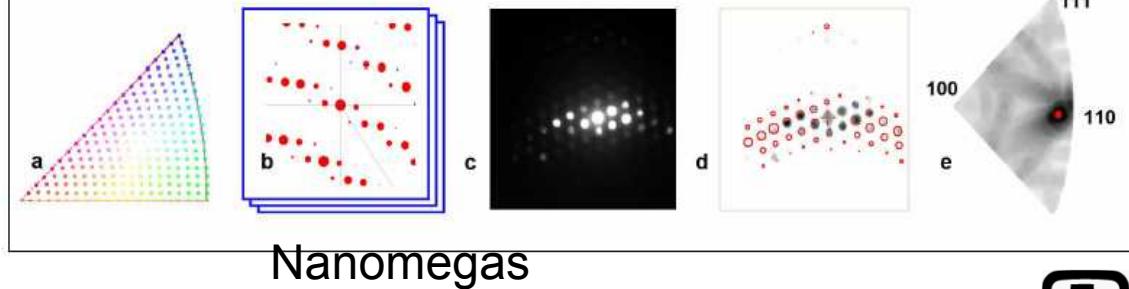
## Data Analysis

### Imaging



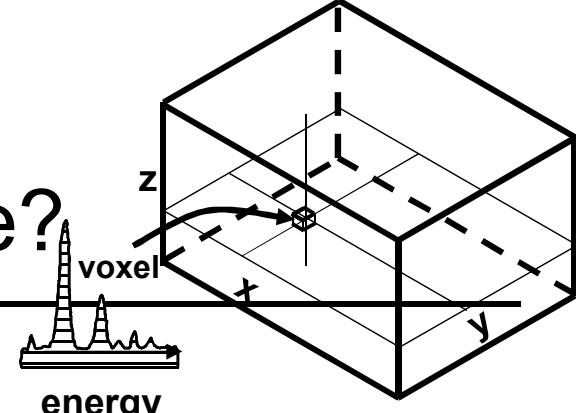
### Microanalysis

## Diffraction

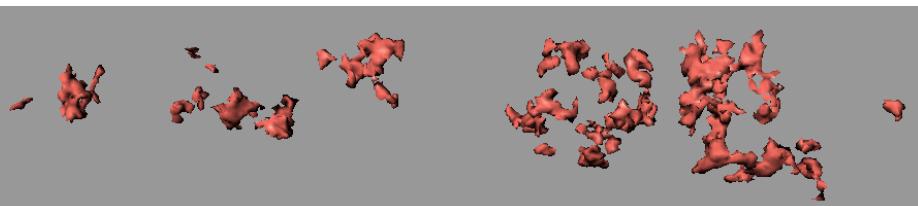
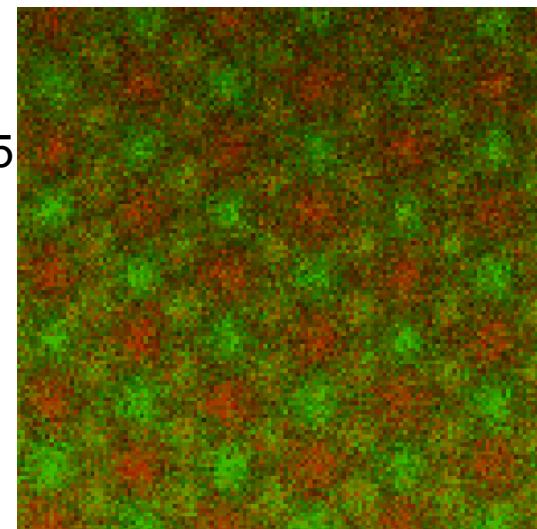


# Data analysis primer

## 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.



# What are the basic steps of MSA?

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- 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: Chichester.
- 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

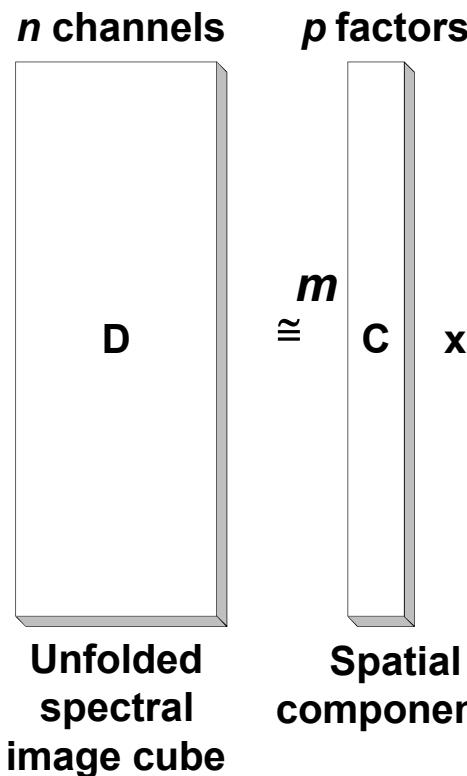
\*M.R. Keenan and P.G. Kotula, *Surf. Int. Anal.* **36** (2004) 203-212

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



# We have several options in our multivariate “Toolbox”

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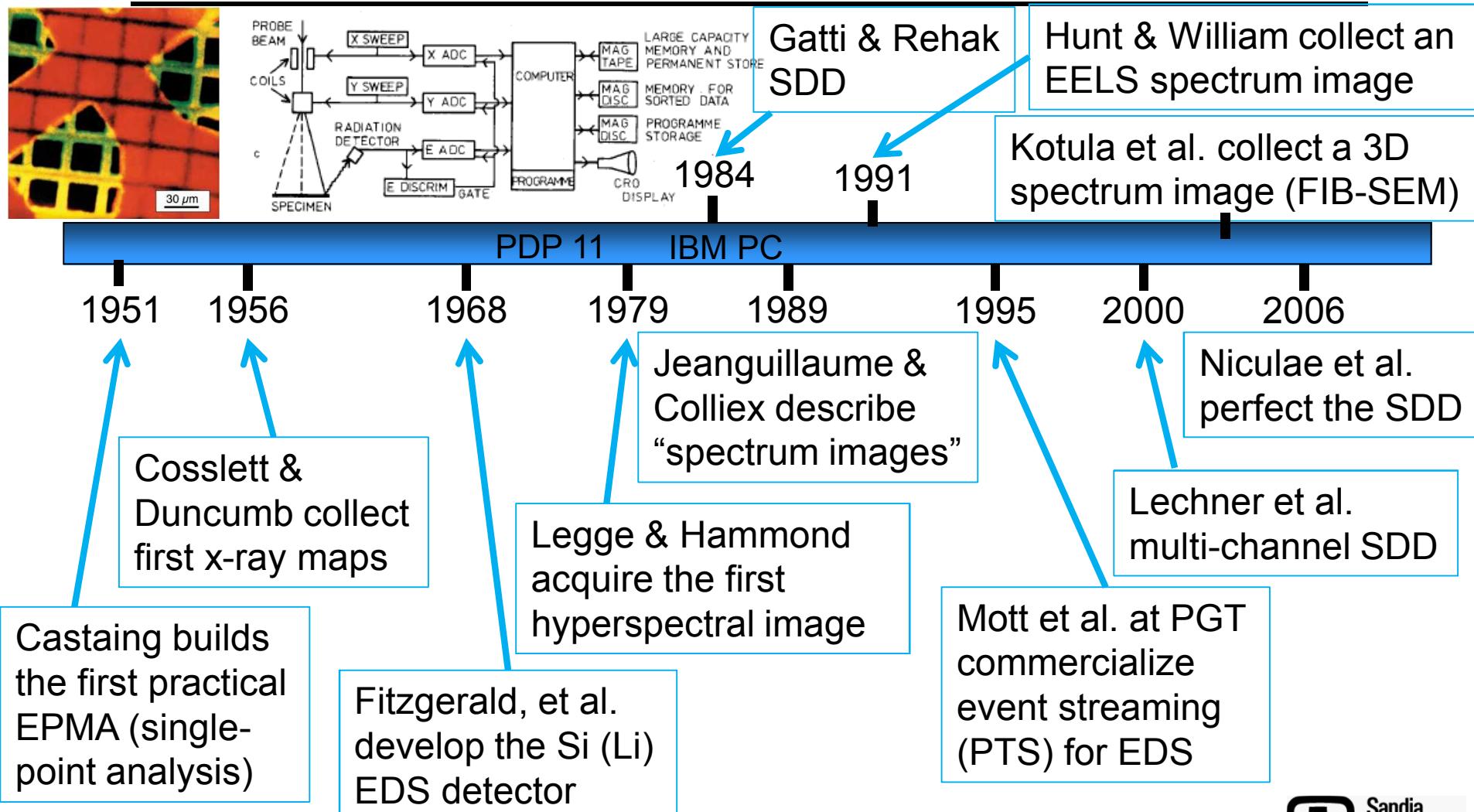
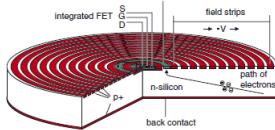


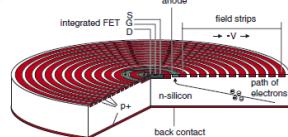
***Analysis goal: Obtain an easily interpretable representation of the data***

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

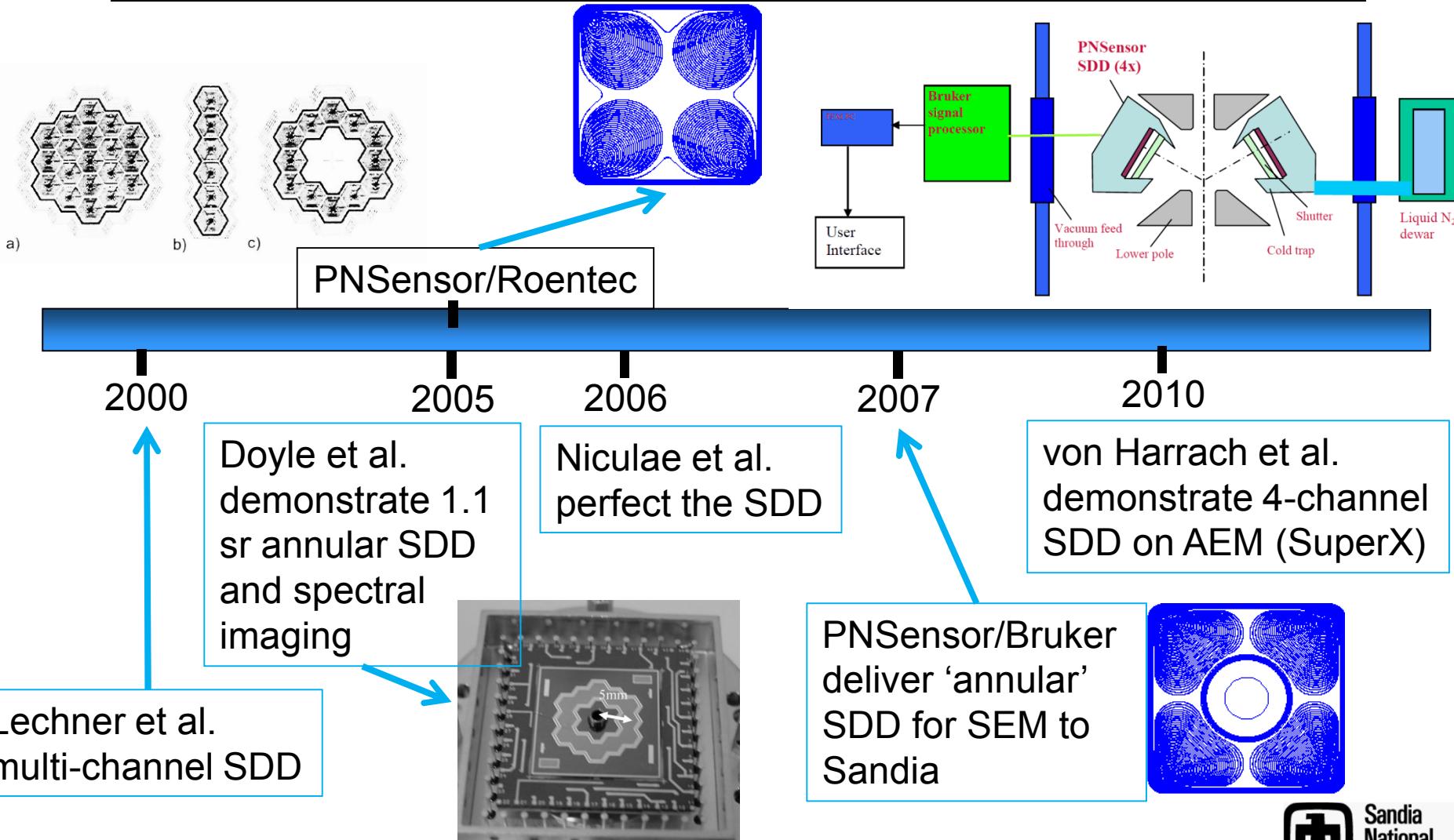
\*\*P.G. Kotula, et al. *Microsc. Microanal.* **9** (2003) 1-17.

# Historical timeline of multi- to hyperspectral imaging





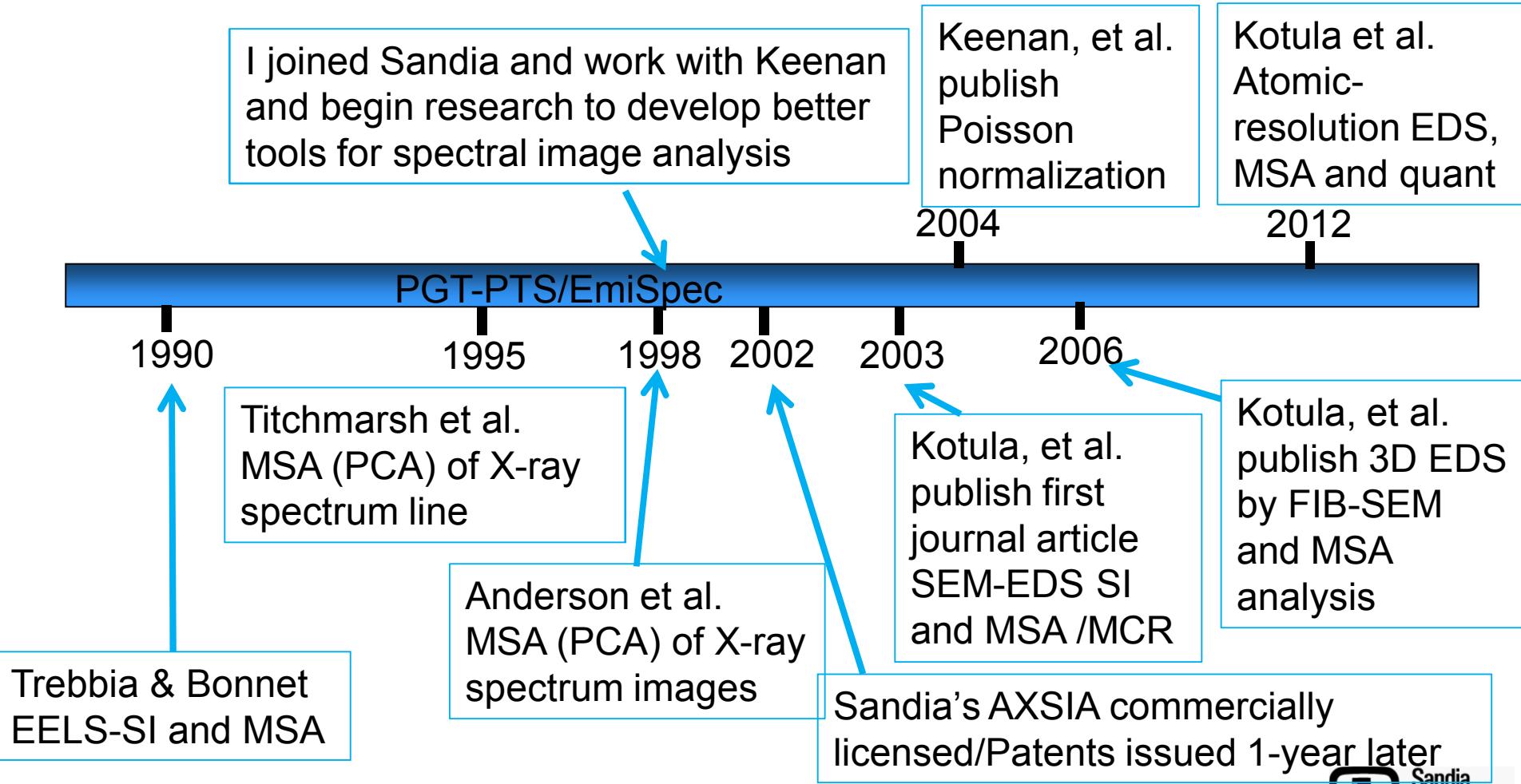
# Historical timeline of multi- to hyper-spectral imaging





# Historical timeline of hyper-spectral image analysis (partial)

(Specific influences of our early work plus some of our contributions)



# 1968, Si(Li) detector...enabling technology for spectral imaging

- Si (Li) EDS started at 600eV resolution
- Over the years improved to about 130eV FWHM at Mn-K $\alpha$
- Parallel detection
- Downsides:
  - Liquid nitrogen cooling
  - Lack of flexible geometries
  - You can get either throughput or good spectral resolution but not both

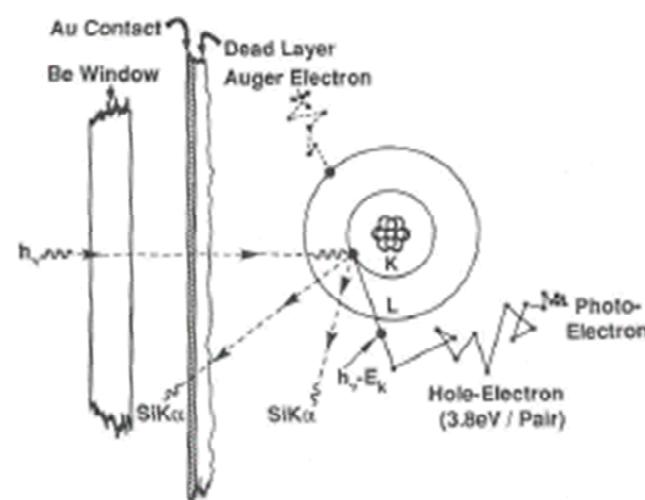
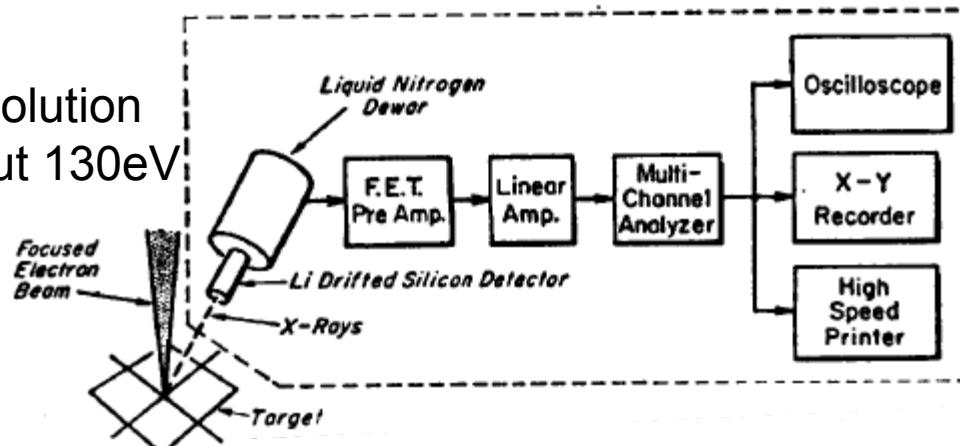


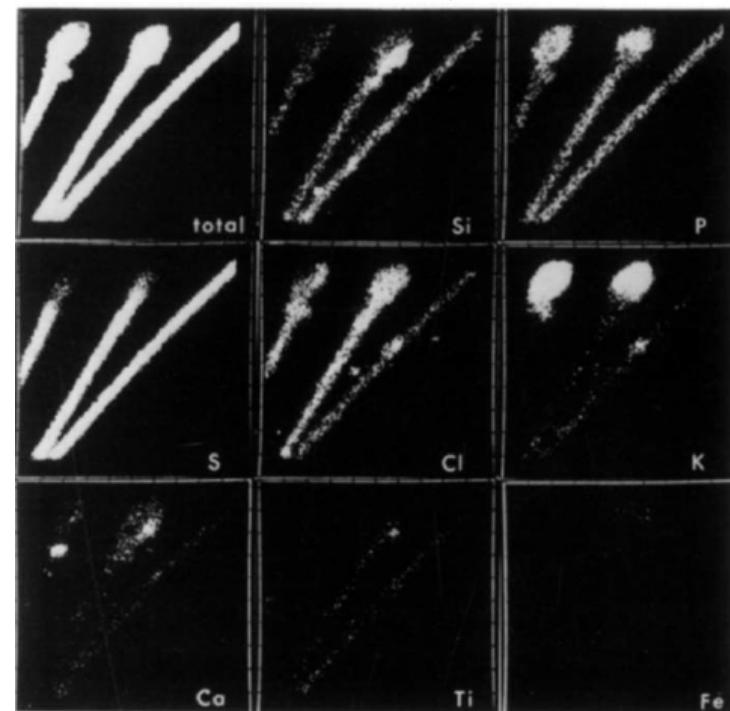
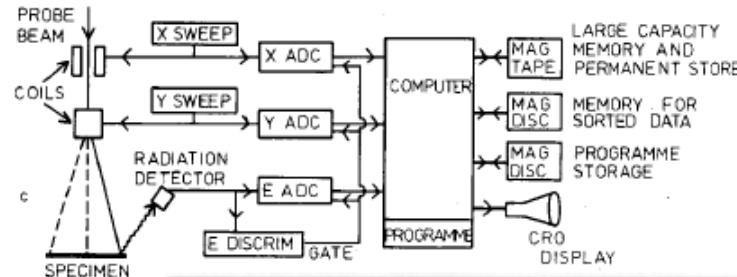
Figure 5.22. The x-ray detection process in the Si(Li) detector.

R. Fitzgerald, K. Keil, K.F.J Heinrich, *Science* (1968) 159 528-530.

# 1979, The First Hyperspectral Image

- Proton microprobe with Si(Li) EDS
- Custom-designed beam control and data acquisition
  - Events streamed to magnetic tape

Total quantitative recording of elemental maps and spectra with a scanning microprobe



by G. J. F. LEGGE and I. HAMMOND, School of Physics, University of Melbourne, Parkville, Victoria 3052, Australia

## SUMMARY

A system of data recording and analysis has been developed by means of which simultaneously all data from a scanning instrument such as a microprobe can be quantitatively recorded and permanently stored, including spectral outputs from several detectors. Only one scanning operation is required on the specimen. Analysis is then performed on the stored data, which contain quantitative information on distributions of all elements and spectra of all regions.

# 1984, SDD...eventually a game changer

## SEMICONDUCTOR DRIFT CHAMBER – AN APPLICATION OF A NOVEL CHARGE TRANSPORT SCHEME

Emilio GATTI <sup>1)</sup> and Pavel REHAK

*Brookhaven National Laboratory, Upton, New York 11973, USA*

The purpose of this paper is to describe a novel charge transport scheme in semiconductors, in which the field responsible for the charge transport is independent of the depletion field. The application of the novel charge transport scheme leads to the following new semiconductor detectors:

- 1) Semiconductor drift chamber;
- 2) Ultralow capacitance – large area semiconductor X-ray spectrometers and photodiodes;
- 3) Fully depleted thick CCD.

Special attention is paid to the concept of the semiconductor drift chamber as a position sensing detector for high energy charged particles. Position resolution limiting factors are considered and the values of the resolutions are given.

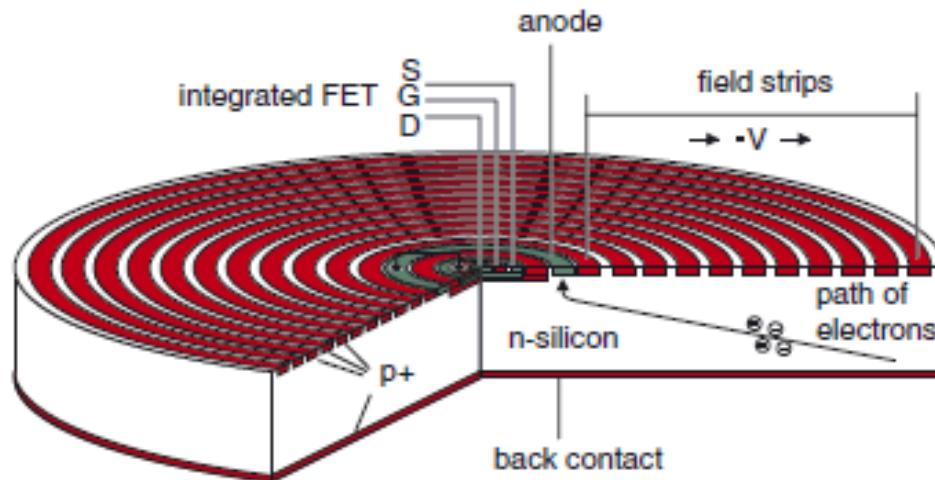
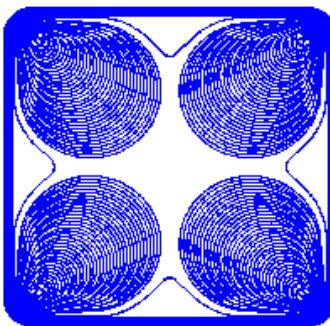
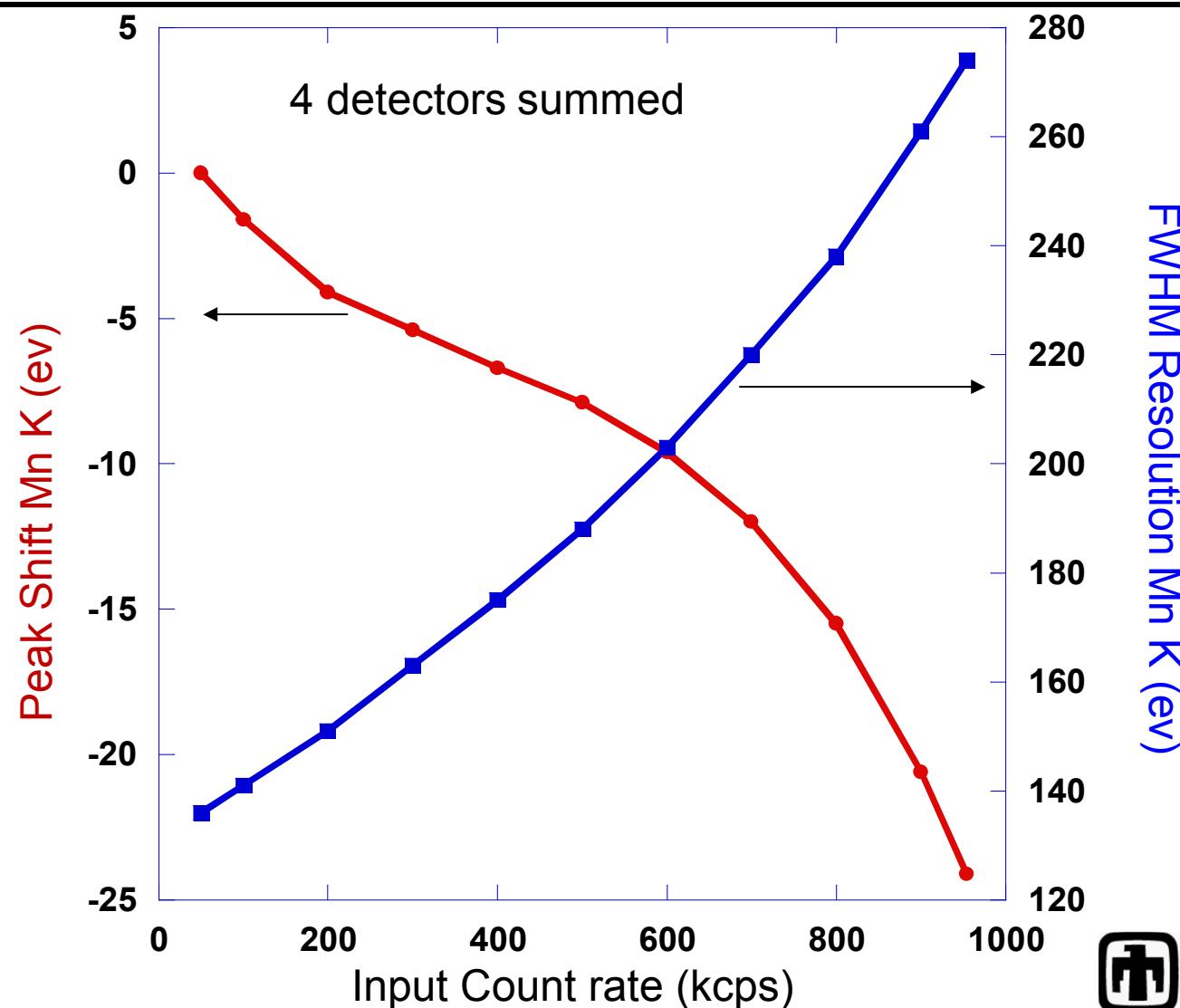


Image courtesy PNSensor

# Early SDDs had issues



Four-channel (each  $10\text{mm}^2$ ) SDD at Sandia from 2005. Peak distortion was also observed with increasing count rates.



# 2006, SDDs finally ready for prime time

- The silicon drift detector is finally better in virtually every respect than the Si(Li).
- Improved read-out scheme fixed the stability issues at higher count rates
- Thin (300  $\mu\text{m}$  to 400  $\mu\text{m}$  thick)
  - Less sensitive to high-energy photons vs. Si(Li)
- Low capacitance allows for very fast read out (short shaping times in the 100s of nsec)
- Several orders of magnitude better throughput
- Peltier cooled so flexible geometries are possible



Available online at [www.sciencedirect.com](http://www.sciencedirect.com)



Nuclear Instruments and Methods in Physics Research A 568 (2006) 336–342

NUCLEAR  
INSTRUMENTS  
& METHODS  
IN PHYSICS  
RESEARCH  
Section A

[www.elsevier.com/locate/nima](http://www.elsevier.com/locate/nima)

Optimized readout methods of silicon drift detectors for high-resolution X-ray spectroscopy

A. Niculae<sup>a,\*</sup>, P. Lechner<sup>a,b</sup>, H. Soltau<sup>a,b</sup>, G. Lutz<sup>c,b</sup>, L. Strüder<sup>d,b</sup>, C. Fiorini<sup>e</sup>, A. Longoni<sup>e</sup>

<sup>a</sup>PNSensor GmbH, Römerstraße 28, 80803 Munich, Germany

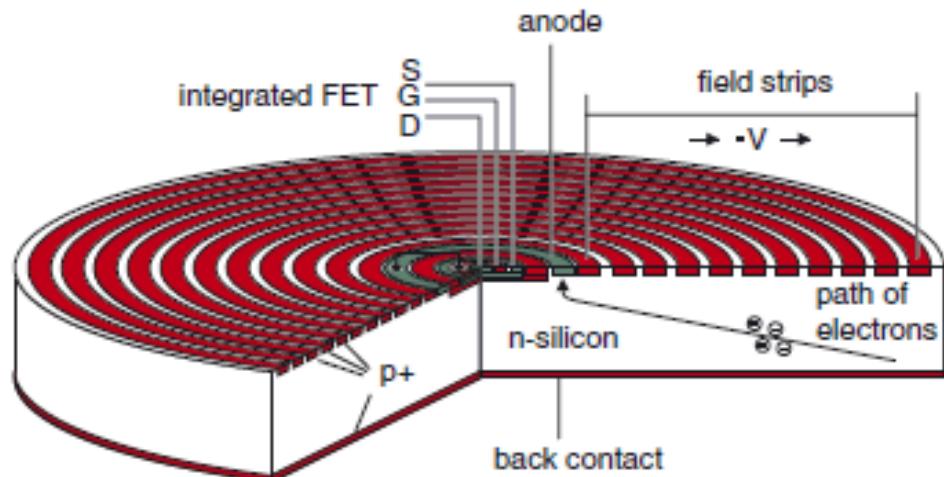
<sup>b</sup>MPI Halbleiterlabor, Otto-Hahn-Ring 6, 81739 Munich, Germany

<sup>c</sup>Max-Planck-Institut für Physik, 80805 Munich, Germany

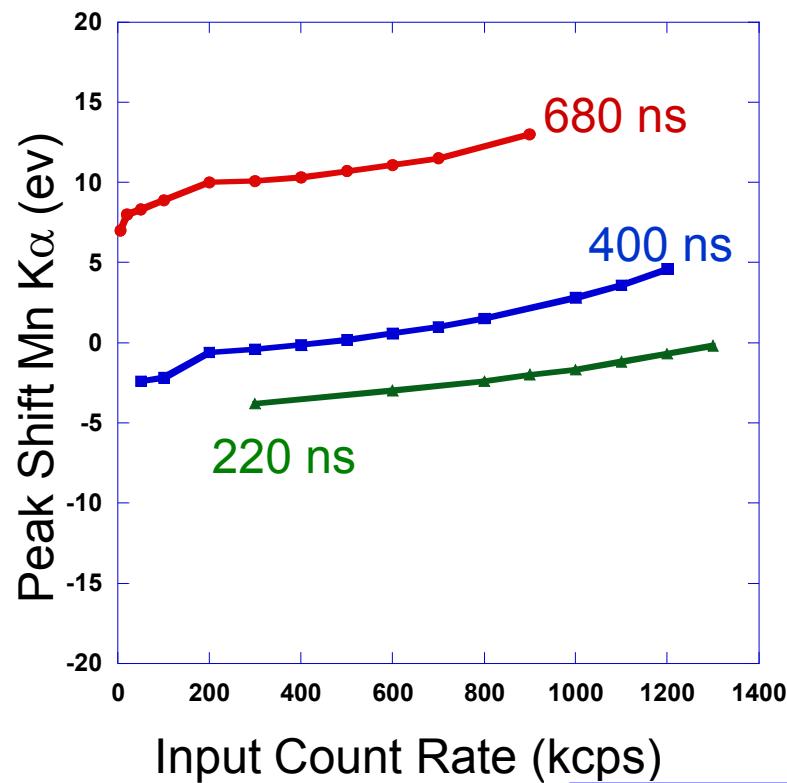
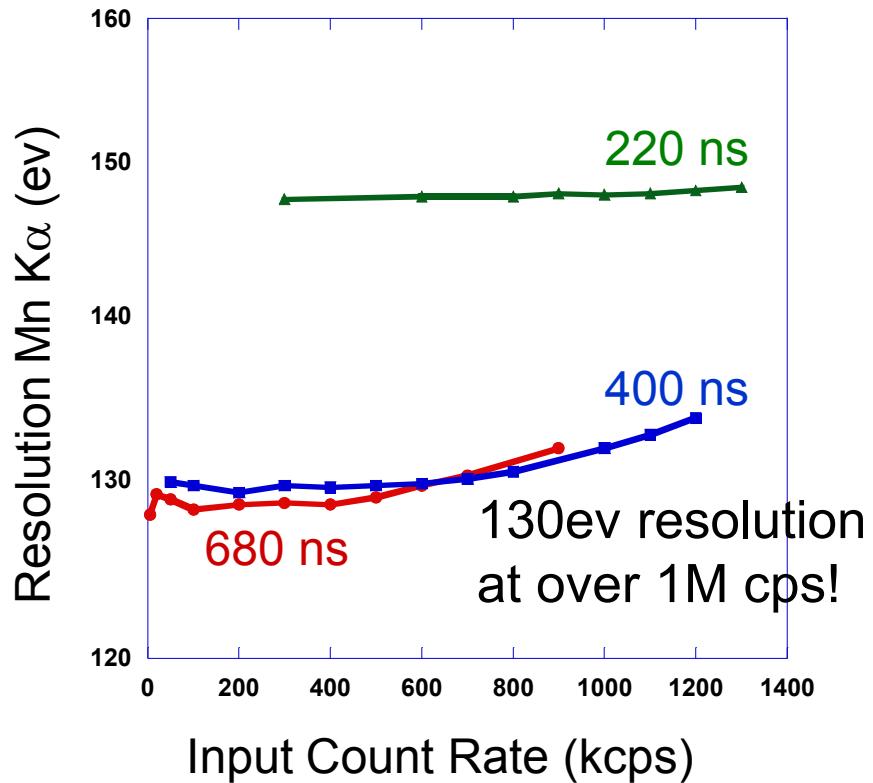
<sup>d</sup>Max-Planck-Institut für extraterrestrische Physik, 85748 Garching, Germany

<sup>e</sup>Politecnico di Milano, Dipartimento di Elettronica e Informazione, Via Golgi 40, 20133 Milano, Italy

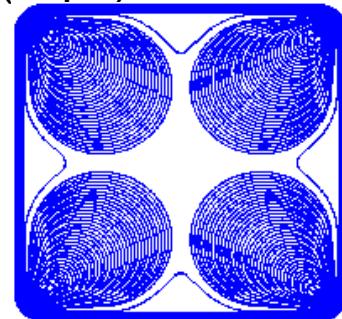
Available online 7 July 2006



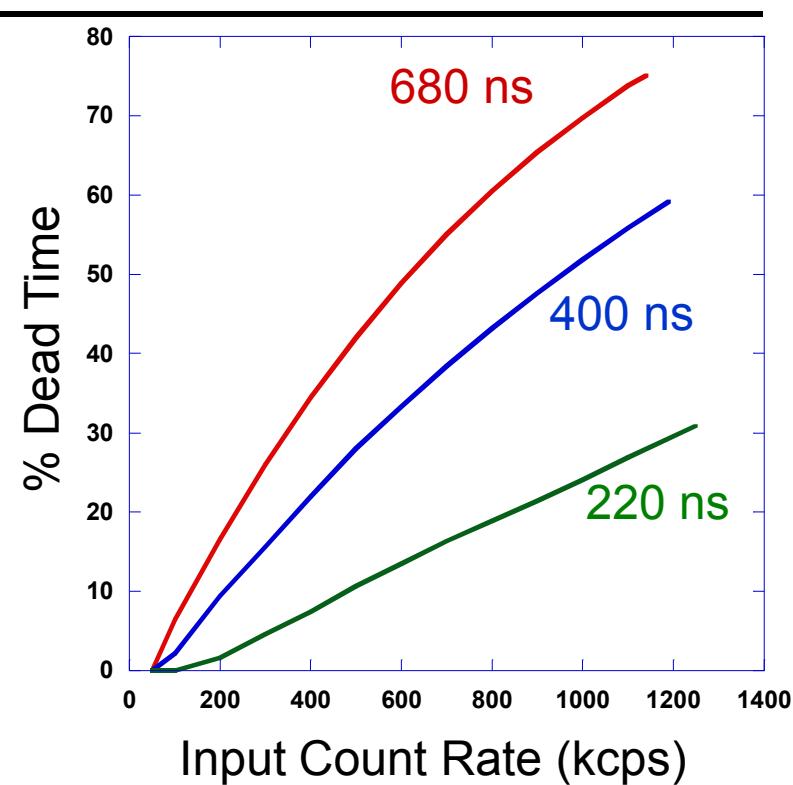
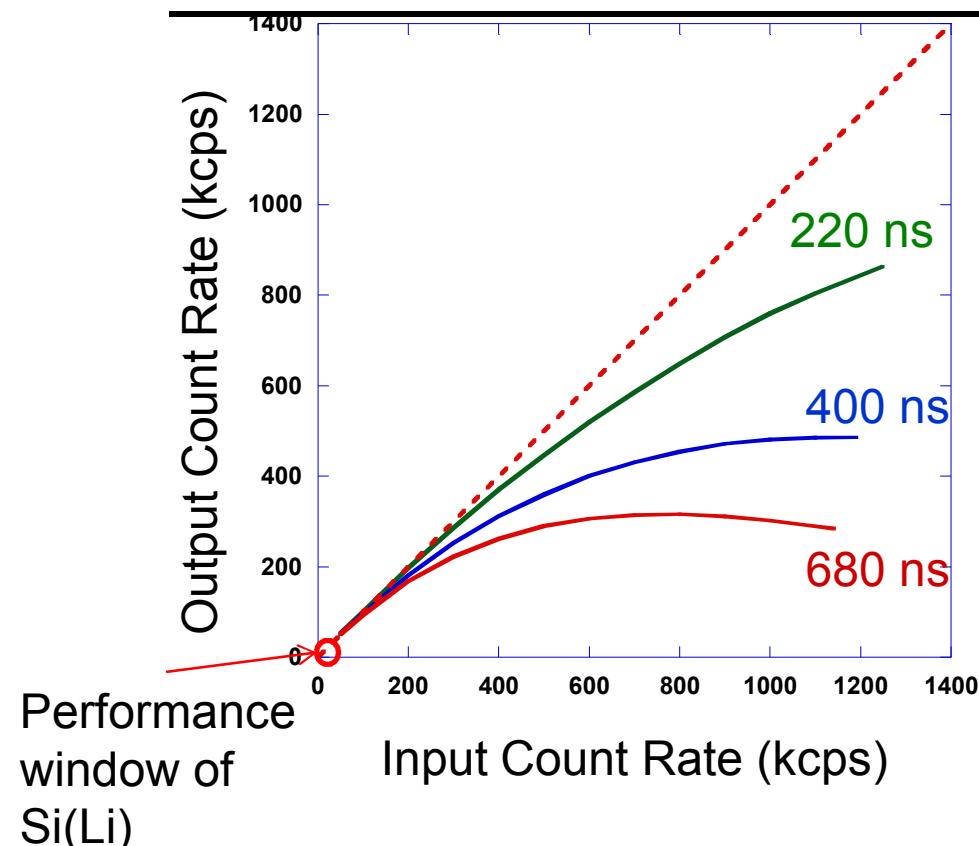
# 2006, SDDs now excellent performers



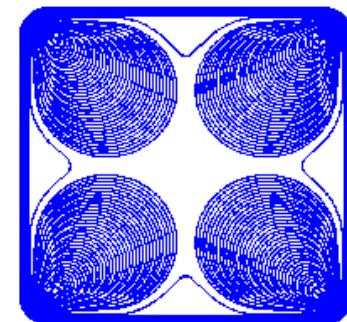
Four-channel (4 by 10mm<sup>2</sup>) SDD at Sandia from 2006. Peak position and spectrometer resolution very stable with count rate



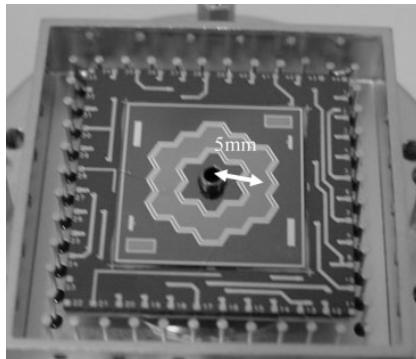
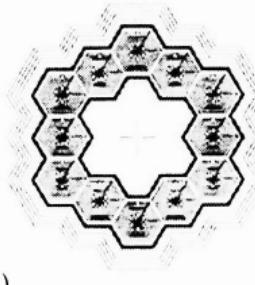
# 2006, SDDs now excellent performers



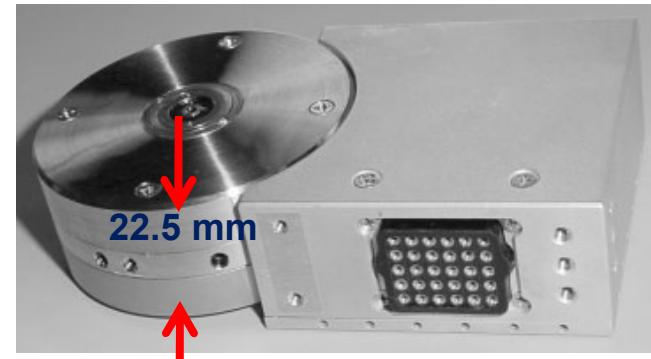
Four-channel SDD at Sandia from 2006. Peak position and spectrometer resolution very stable with count rate



# 2005, Multi-element SDD and Spectral Imaging

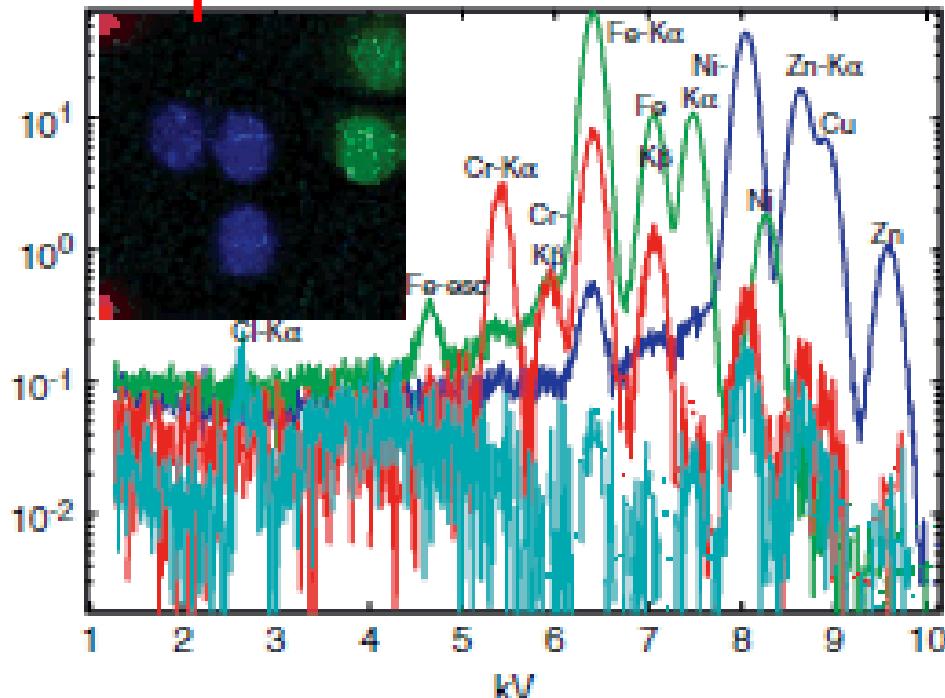


c)

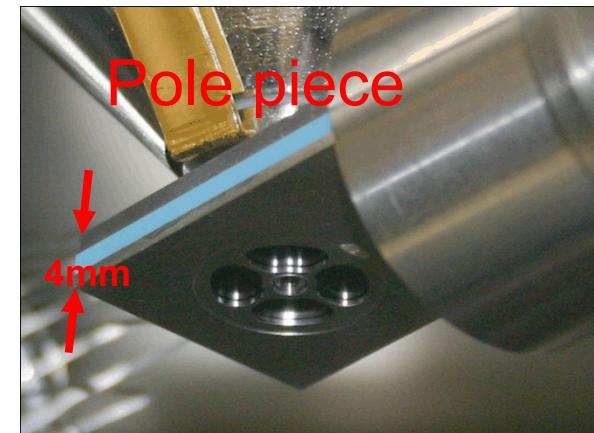
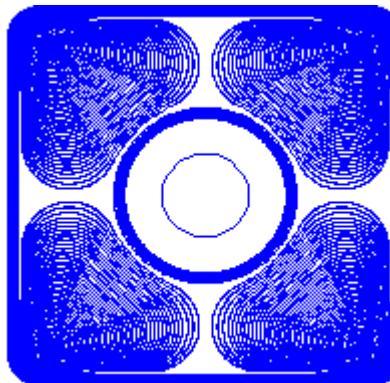
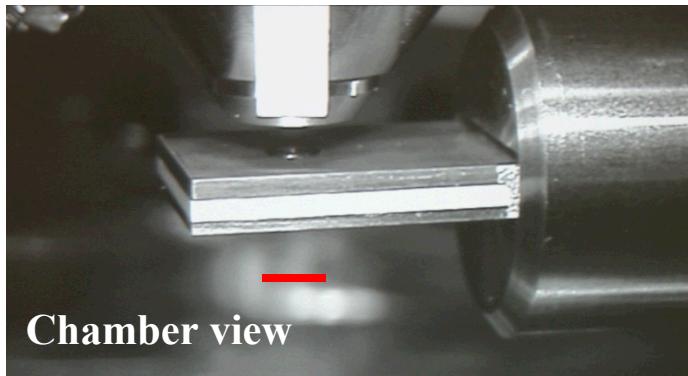


- Sandia/Rontec collaboration
- PIXE microprobe, 1.1 sr SDD array
- 3 MeV Carbon excitation.
- Ionization energies all shift.
- Spectral image acquired with custom-designed system.
- MSA data analysis
  - No *a priori* information such as peak position needed.
  - In fact peak positions were unknown for these conditions prior to this work

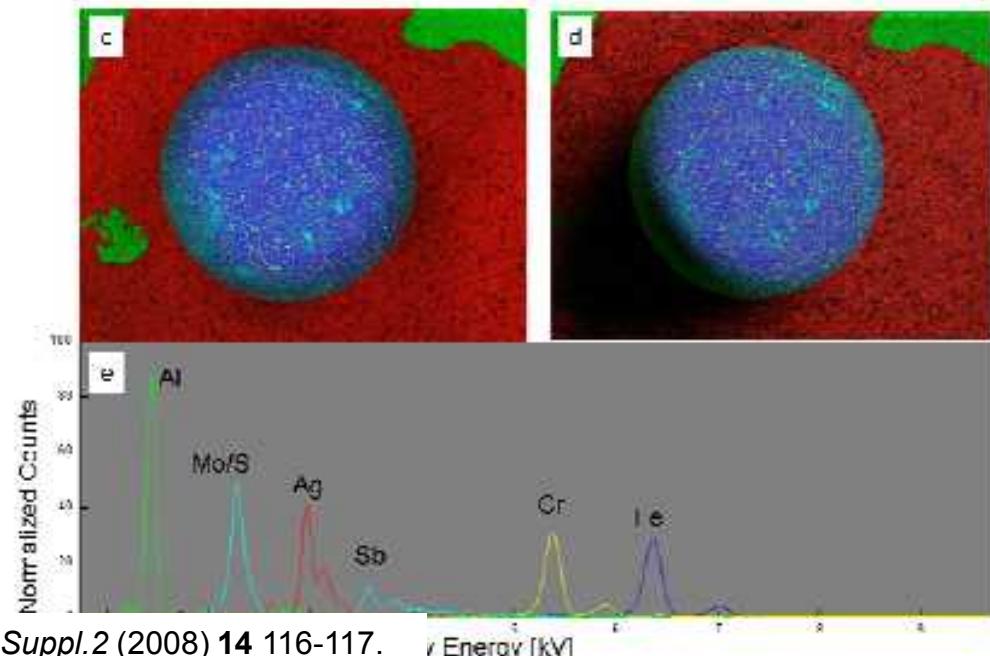
Intensity (counts) normalized to most intense pixel



# 2007, Multi-element SDD and Spectral Imaging



- Collaboration between PNSensor, Bruker and Sandia
- Funding from DHS in relation to Sandia's work for the FBI's Amerithrax investigation
- Design existed, Sandia ordered the first for SEM implementation
- $4 \times 15 \text{ mm}^2$  sensors with a hole combined solid angle of 1.1sr
- Spectral image of a  $750 \mu\text{m}$  diameter ball bearing. MSA analysis.



# Anatomy of a *Bacillus anthracis* spore



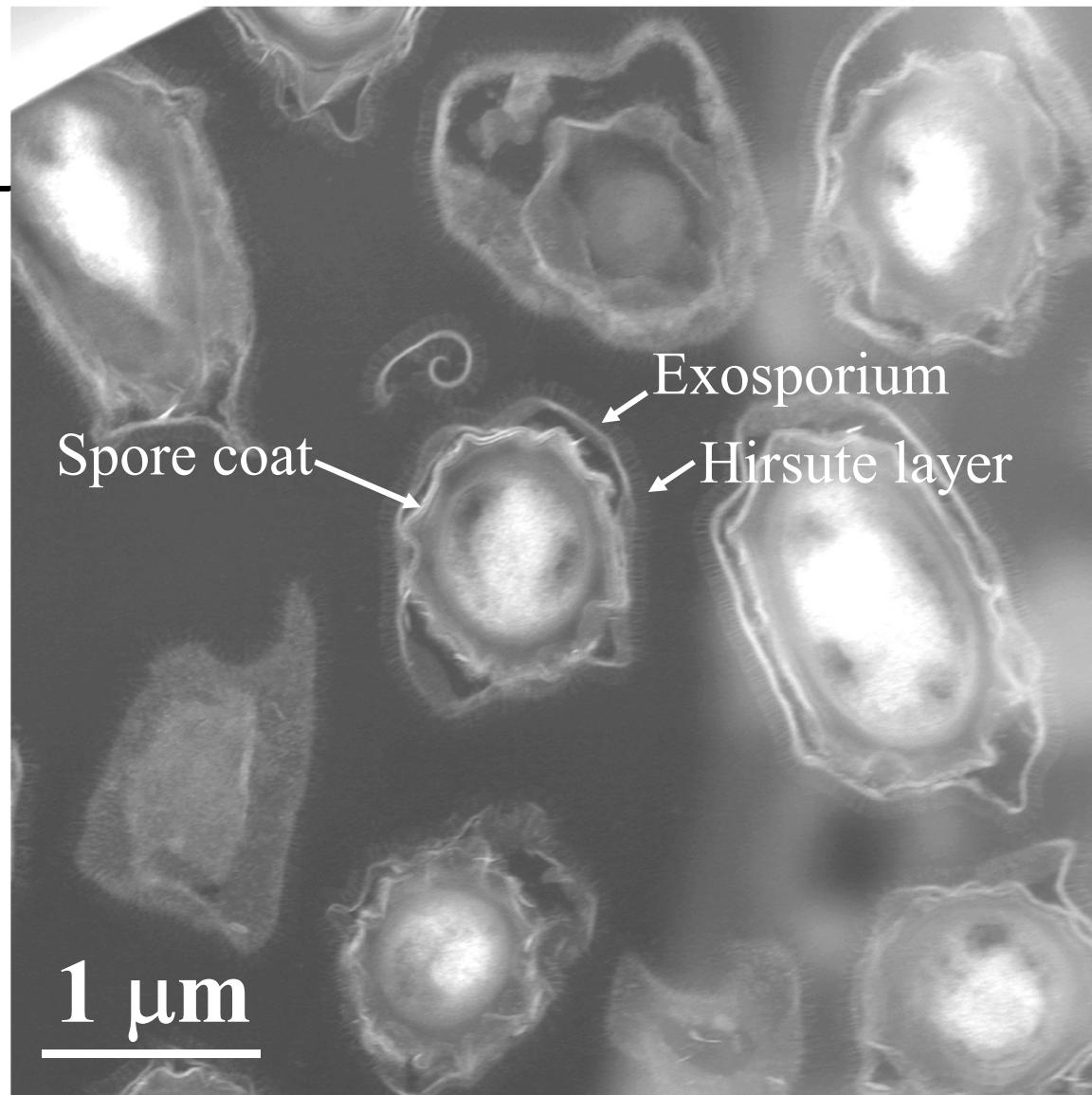
Layers present –  
Outside to inside

Hirsute Layer

Exosporium

Spore coat

Cortex

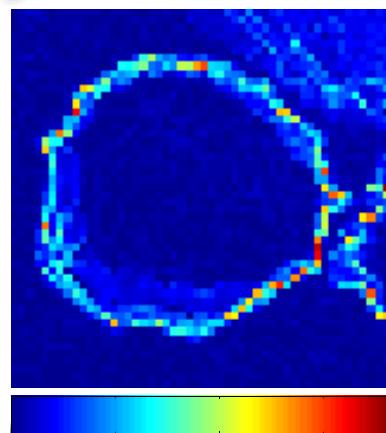


Scanning transmission electron annular dark-field image

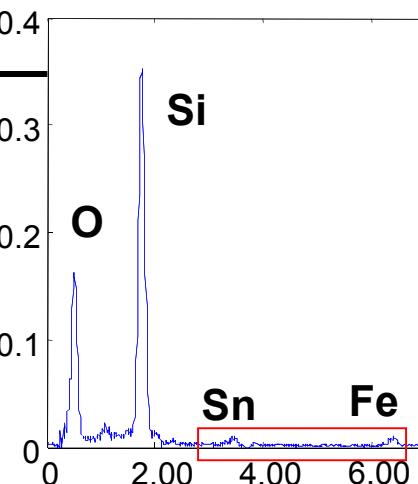
Work for the FBI's Amerithrax investigation with Joe Michael at Sandia.

# *Bacillus Anthracis* chemical signatures from 300kV AEM

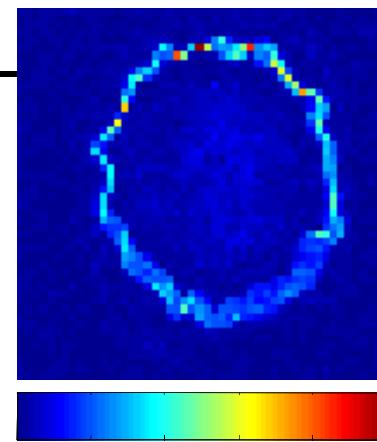
Leahy Material



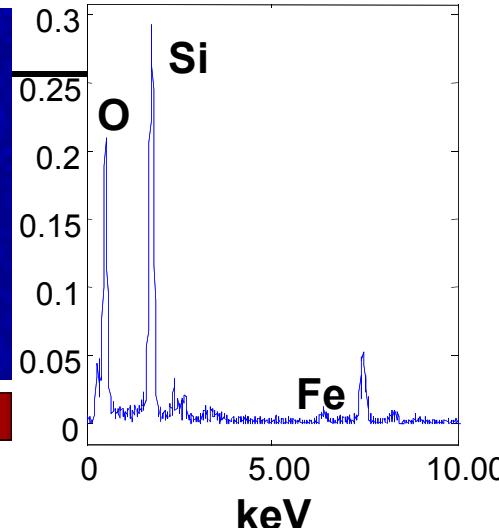
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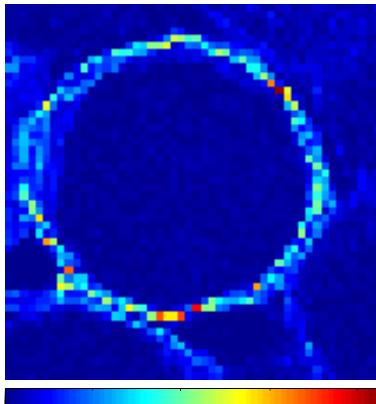
Daschle Material



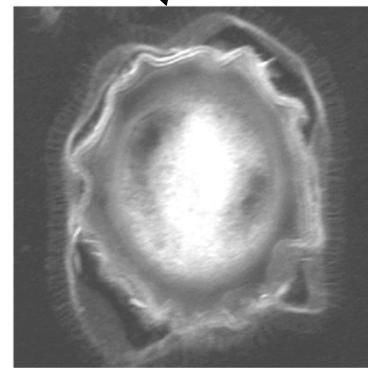
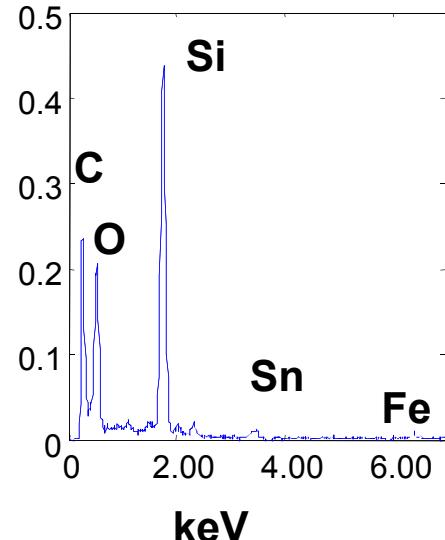
0 20 40 60 80



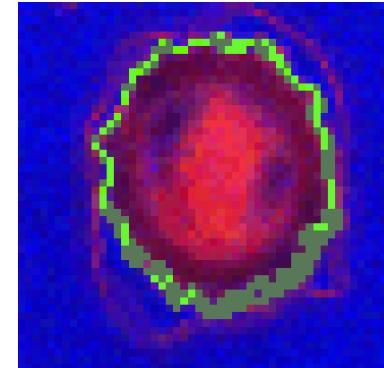
New York Post Material



20 40 60 80



STEM ADF



MSA results  
(overlay)

Red = Cortex/stain

Green = Spore coat/Si-O-Sn-Fe

Blue = Plastic

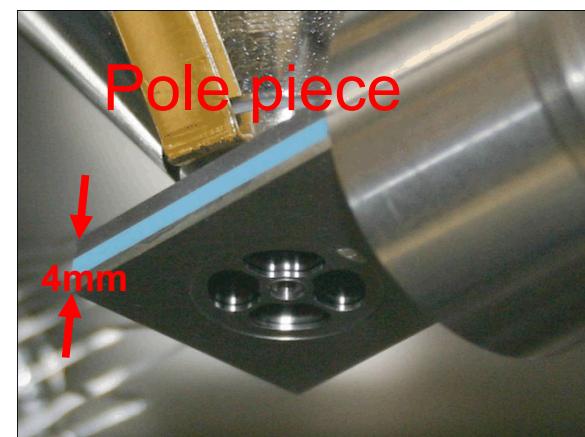
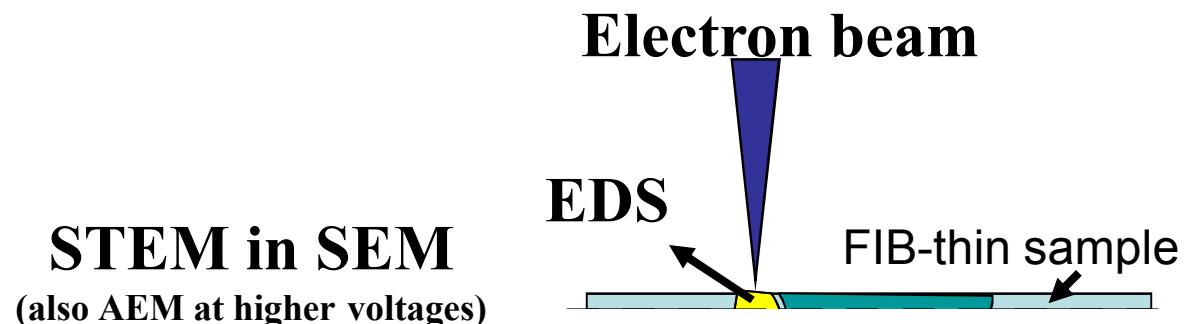
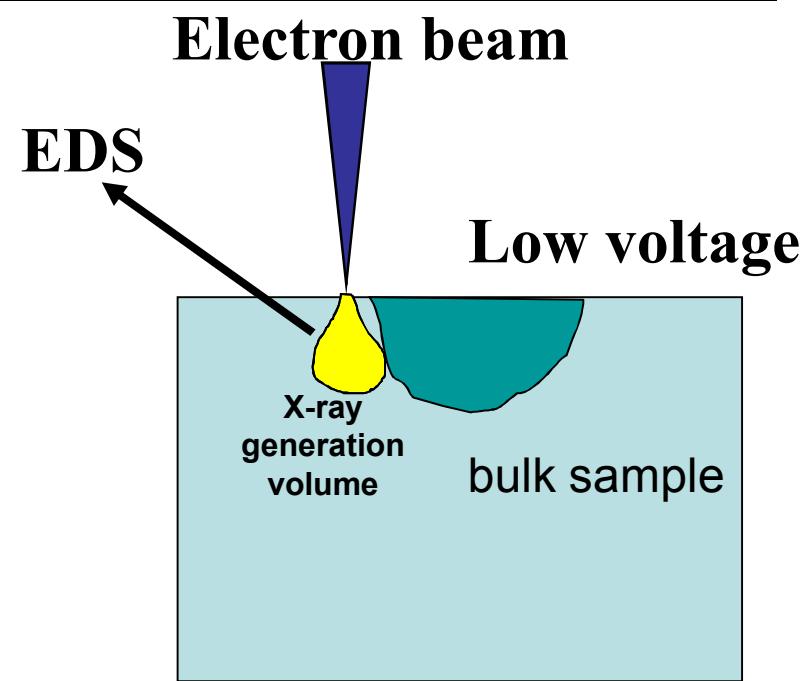
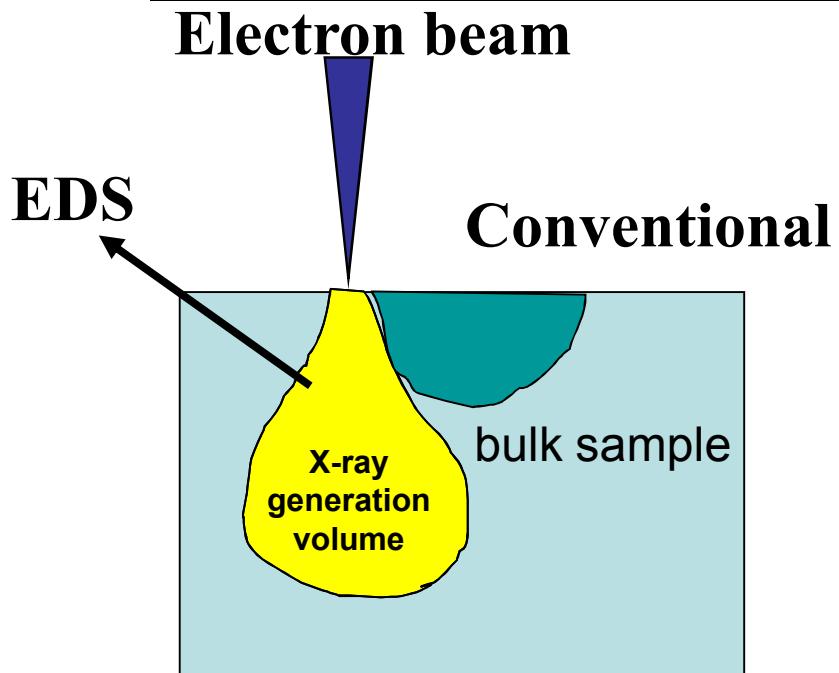


# Solving the sample throughput problem

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- Not every spore had the Si-O-Sn-Fe signature so we needed to analyze a larger population of spores...in the tens of thousands
- AEM fields of view are small...8-10 $\mu\text{m}$  while in SEM it can be millimeters
- Features of interest are 10-20 nm requiring thin samples (STEM in SEM).
- STEM in SEM would be good but typical solid angles for EDS are 60 msrad so count rates are very low for thin samples.
- One solution is a multi-sensor annular SDD

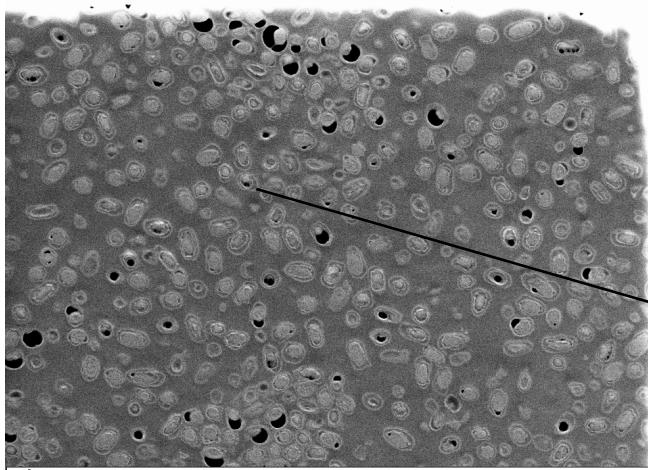
# Improved resolution- LV vs. STEM in SEM



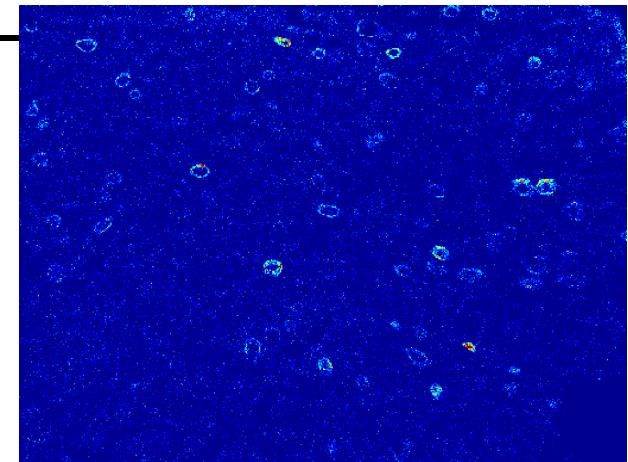


# STEM in SEM of unstained, microtomed section

(Samples from Bruce Ivans' lab at USAMRIID)

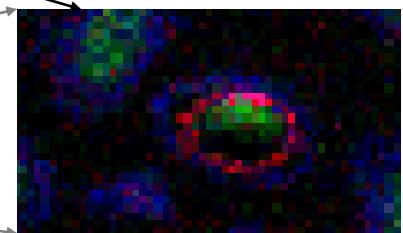
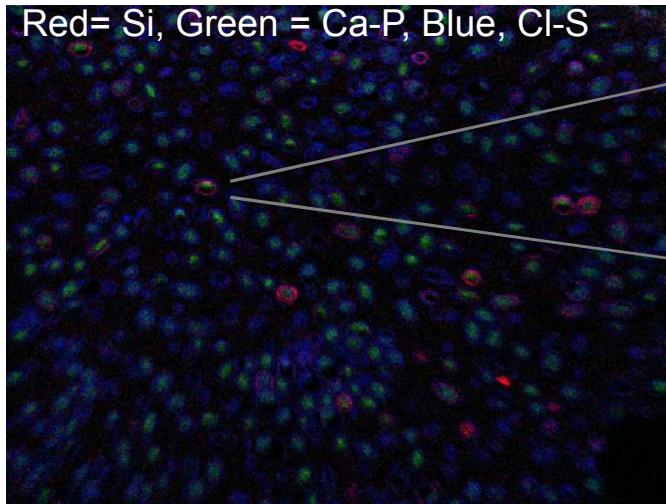


MSA identifies three chemical signatures



Si-containing spore coat

SEM defines field of view for spectral image acquisition



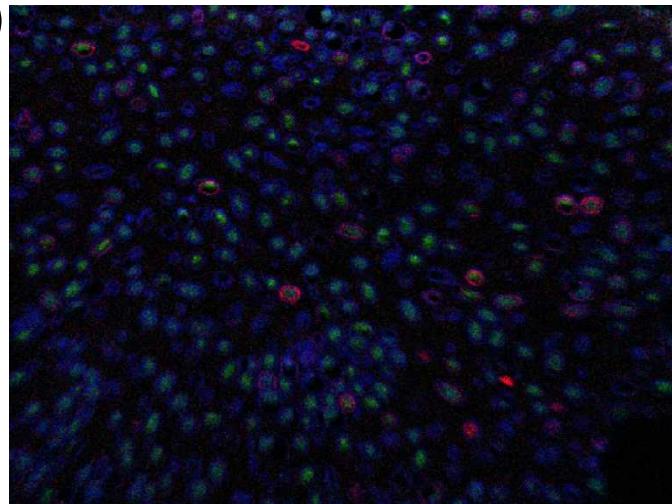
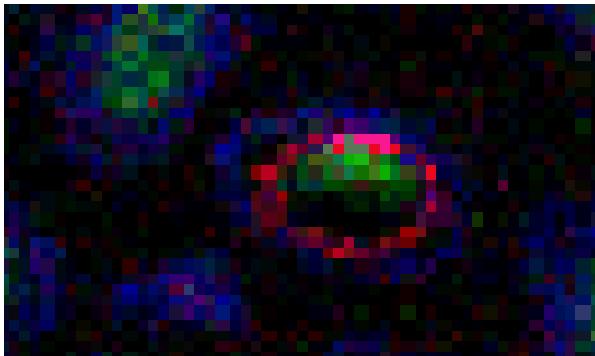
From this it is possible to count  $x$  and  $n$



# The true test of the annular detector: 13 samples from the investigation

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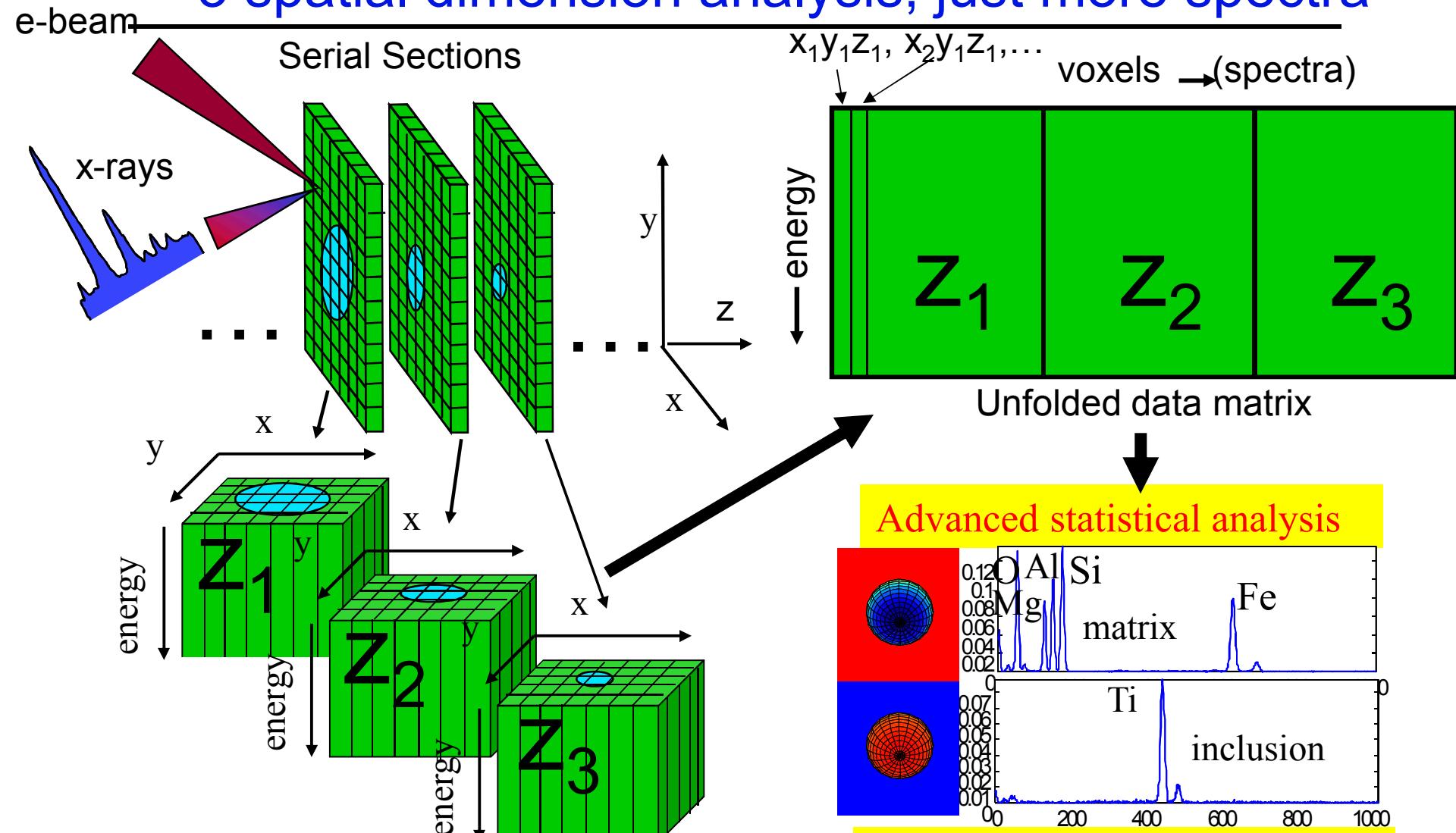
- In April of 2008 we were provided 13 samples for analysis
- Over 40 STEM in SEM x-ray spectral images were acquired by a Technologist with the new annular x-ray detector
  - Over 13,000 spores imaged in 3 work-days (24 hours)
  - MSA and counting populations took 7 work-days (56 hours)
  - 10 days (80h) total for over 13,000 spores
  - 0.04 seconds per spore for identification (compare with 2 minute per spore for STEM)



Thanks to Bonnie McKenzie at  
Sandia for data acquisition.

# 2006, 3D spectral imaging via FIB-SEM/EDS

## 3 spatial dimension analysis, just more spectra

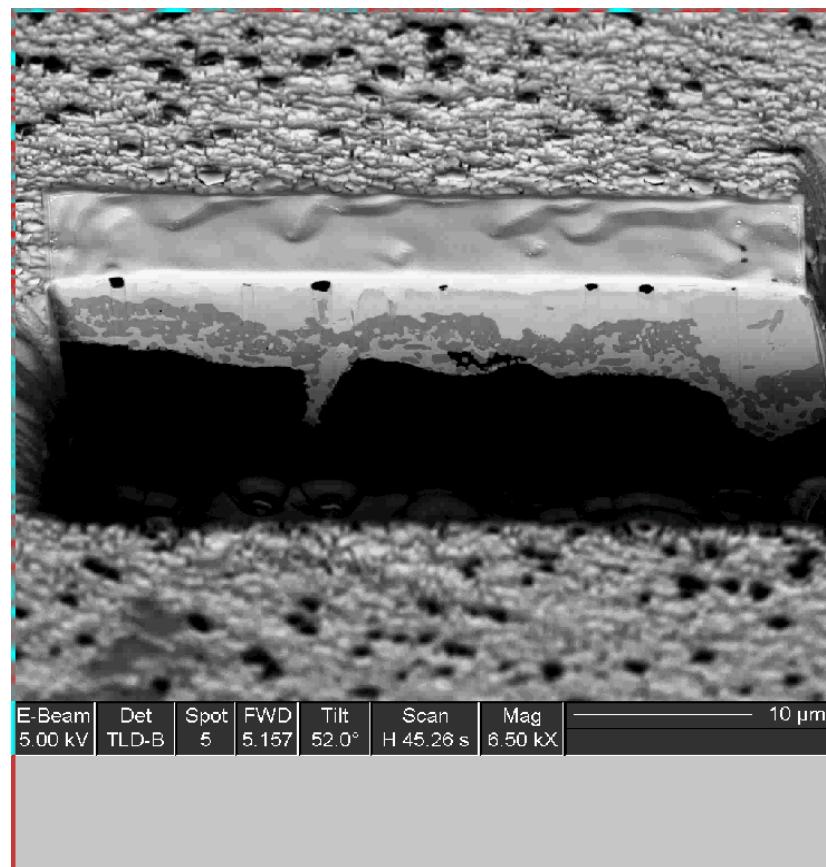




# 3D EDS spectral imaging Analysis of Ag-2Zr/Alumina Braze

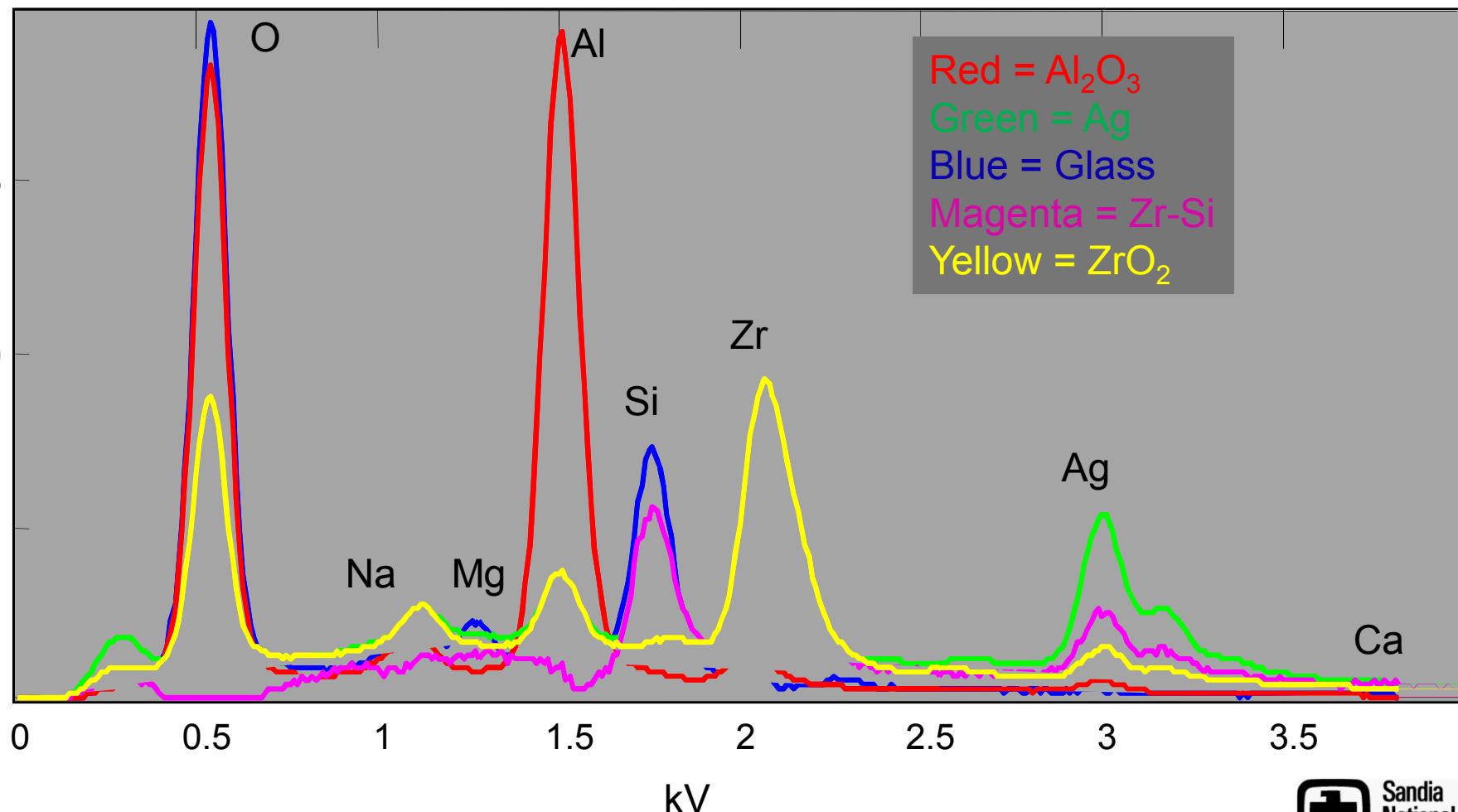
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Movie of  
electron images



# MSA Analysis of SI of Ag-2Zr/Alumina Braze (5kV)

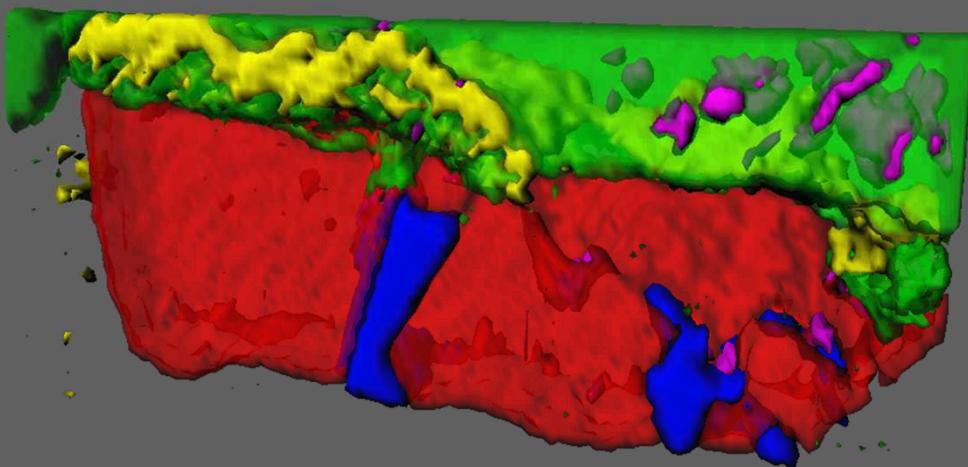
## Spectral shapes





# Analysis of Ag-2Zr/Alumina Braze: 3D Component Images

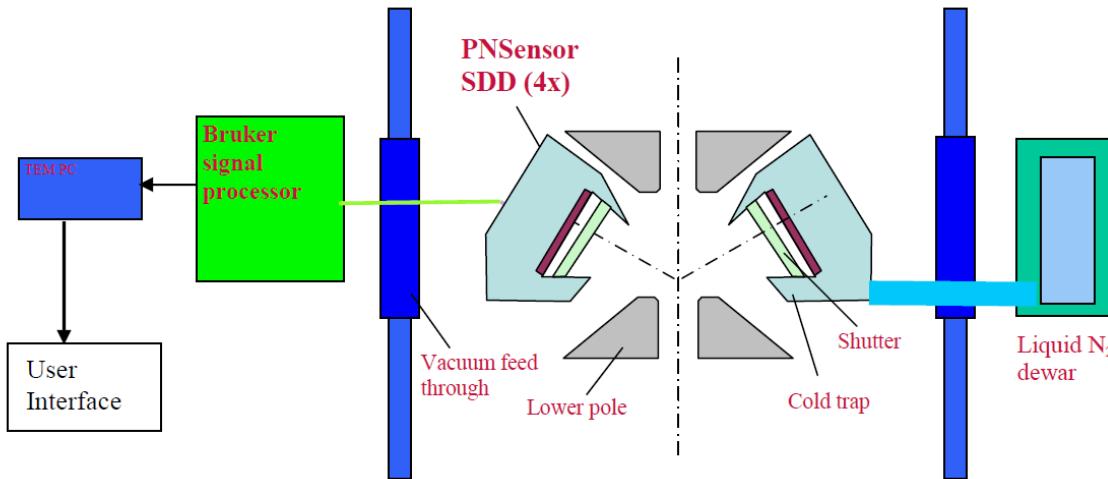
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Red =  $\text{Al}_2\text{O}_3$   
Green = Ag  
Blue = Glass  
Magenta = Zr-Si  
Yellow =  $\text{ZrO}_2$



# 2010, SuperX™: Large solid angle silicon drift detector array provides more flexible AEM

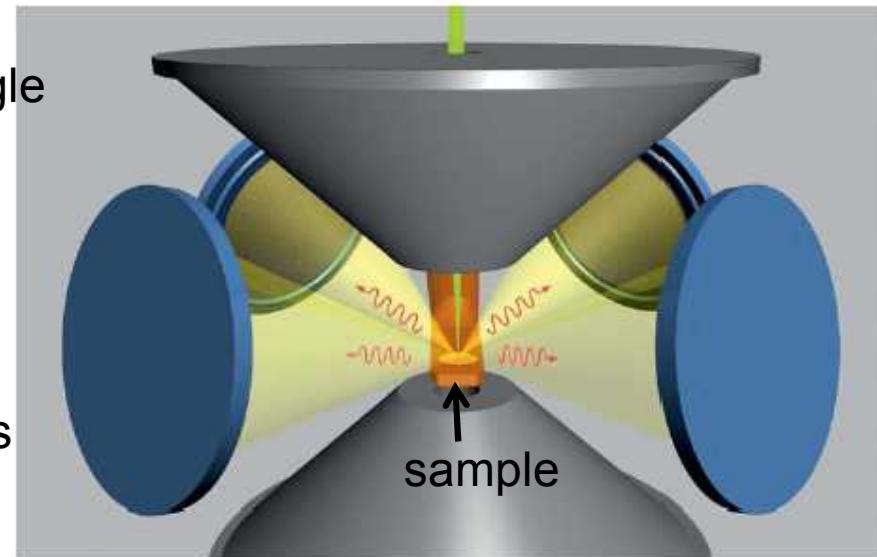


Conceived by FEI with collaboration from Bruker and PNSensor

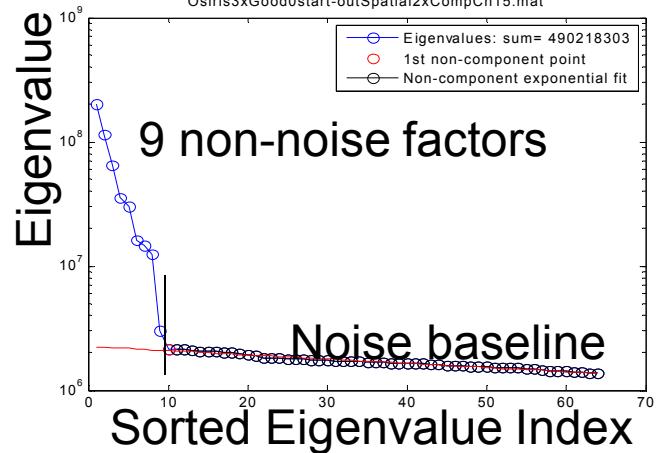
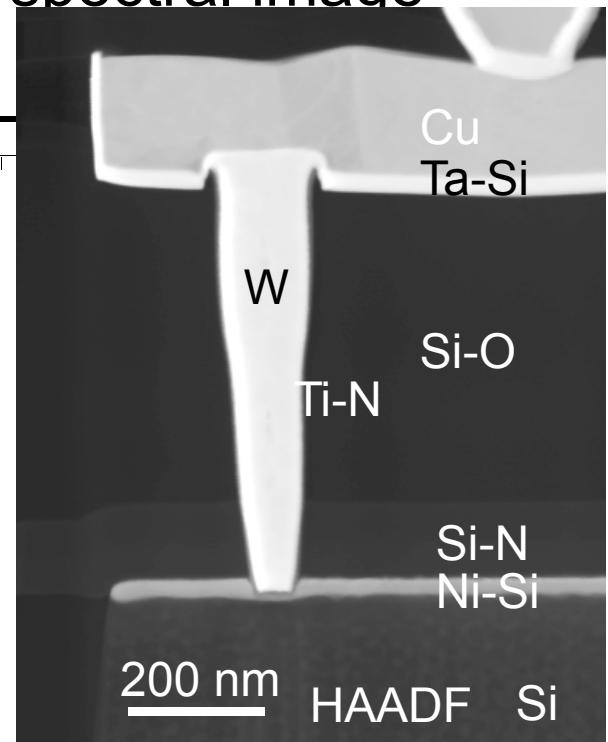
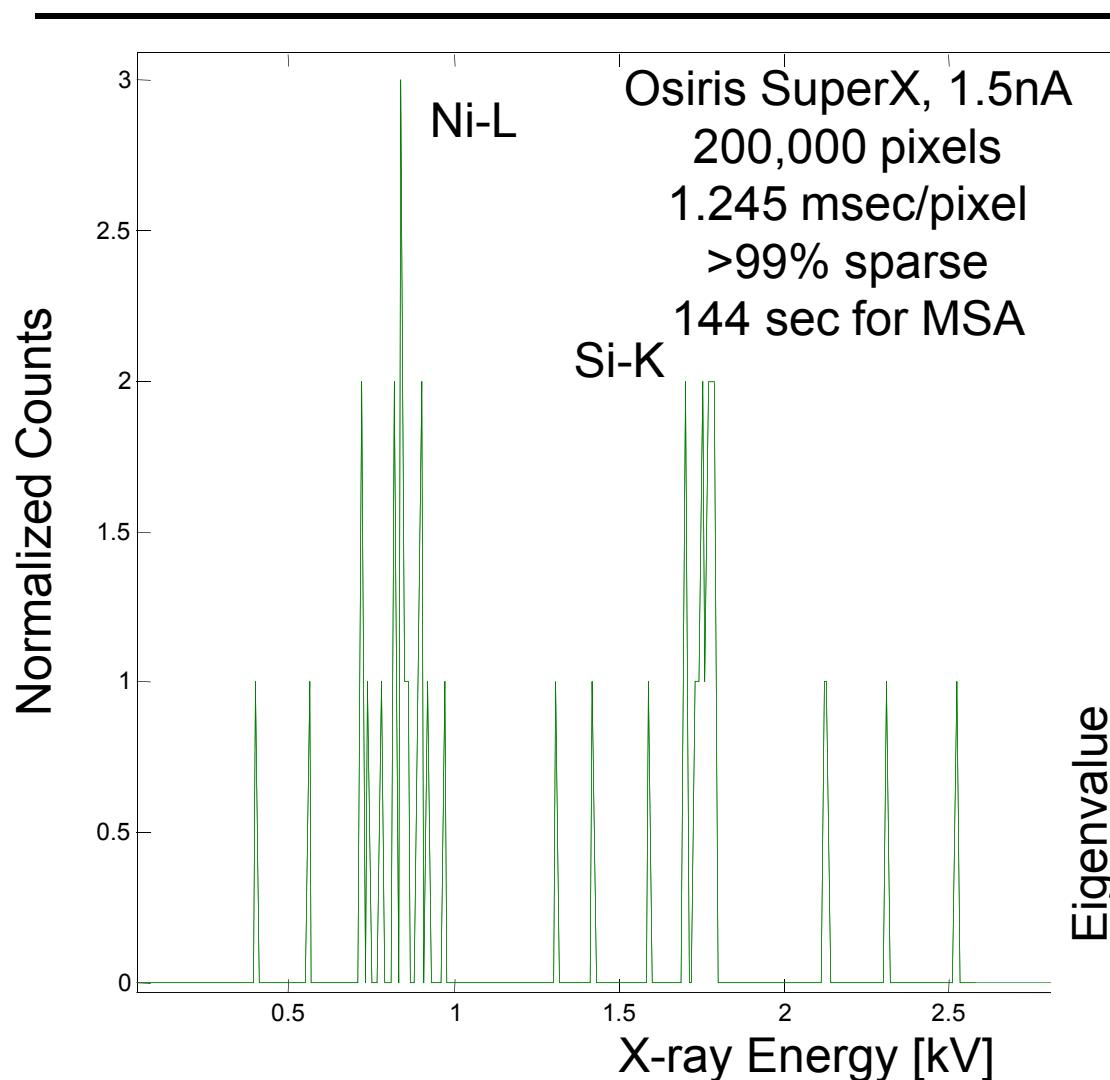
**Revolutionary change in AEM-EDS**

Figure 1. Schematic of Super-X detector

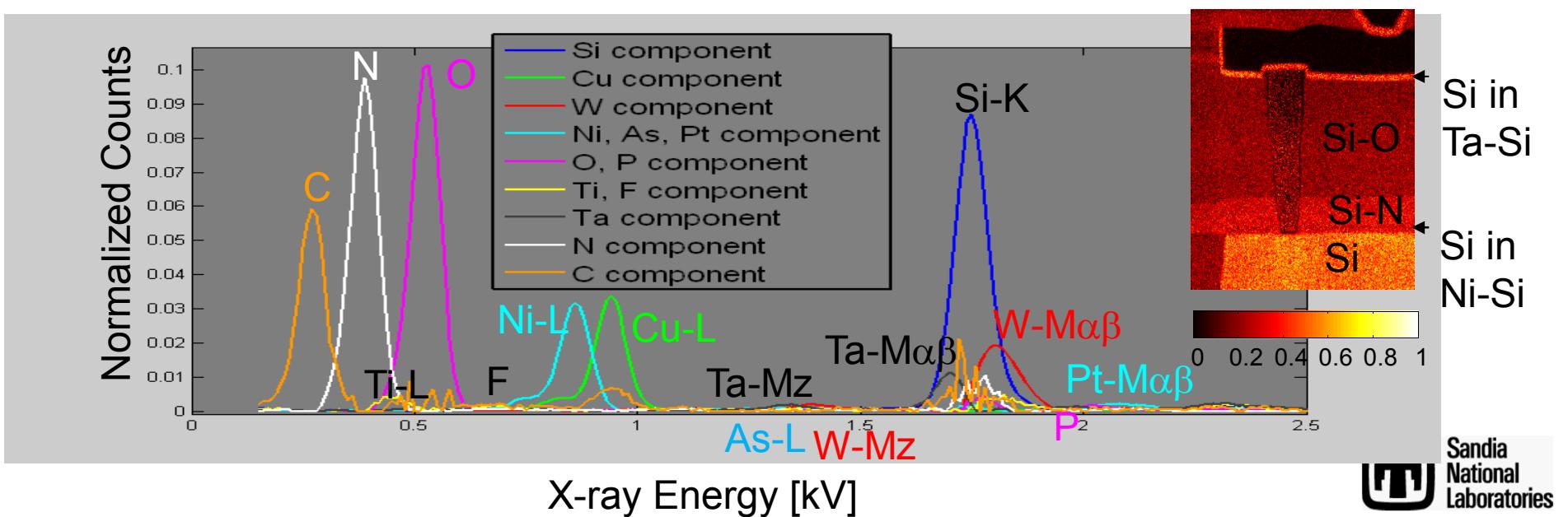
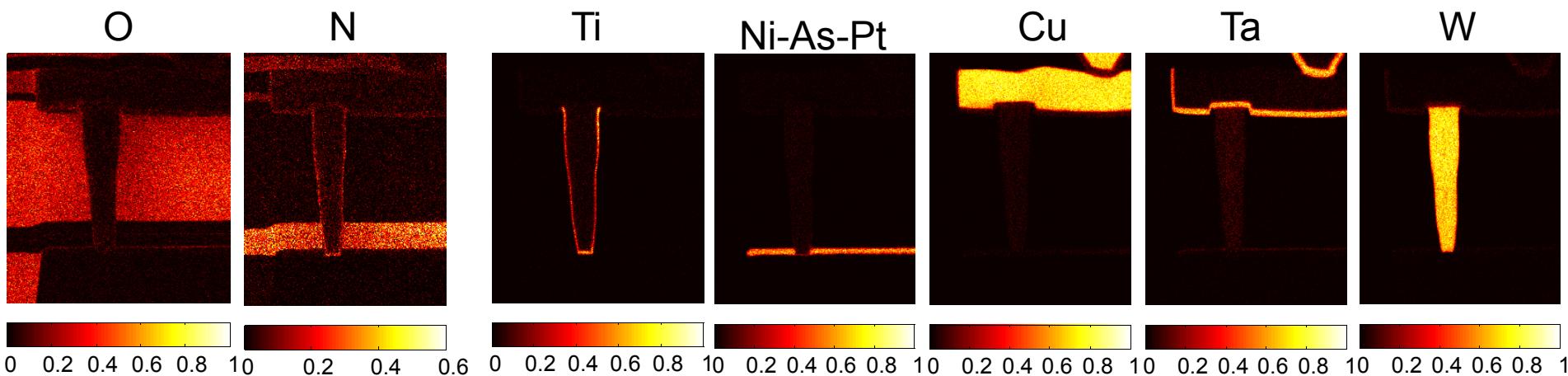
- 4-30mm<sup>2</sup> (120mm<sup>2</sup>) SDDs with large solid angle
  - 0.9 sr (Osiris-uncorrected)
  - 0.7 sr (Titan-probe corrected)
  - State-of-the-art SDDs
  - Windowless & PNWindow...good light-element performance (C, N, O easily)
  - High-throughput...10  $\mu$ sec instantaneous dwell times, multiple pass, drift correction



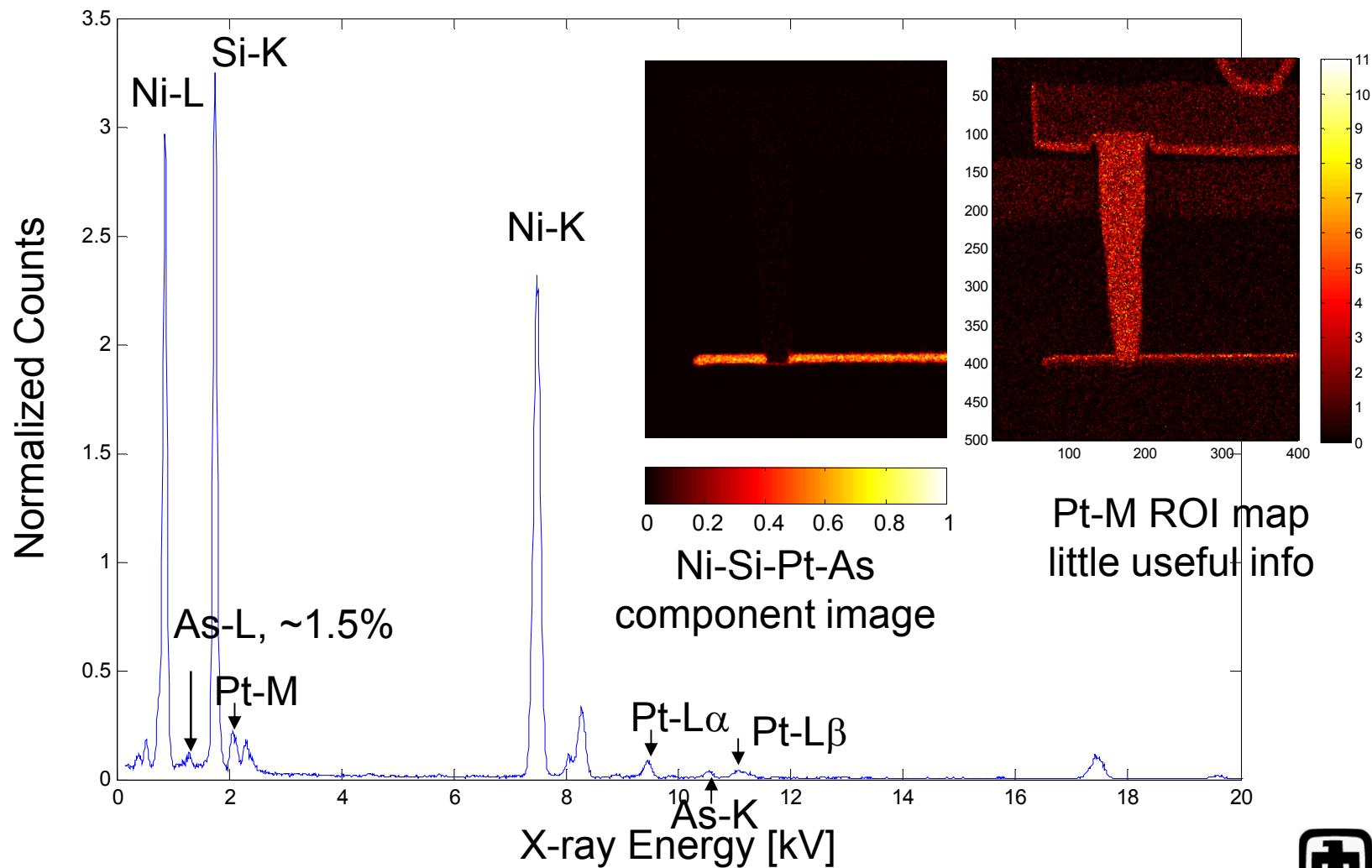
# Low end spatially, high end for sensitivity Raw spectrum from the CMOS spectral image



# Low end, Spectral-Domain Simplicity Best Spectral or Elemental 'Contrast'



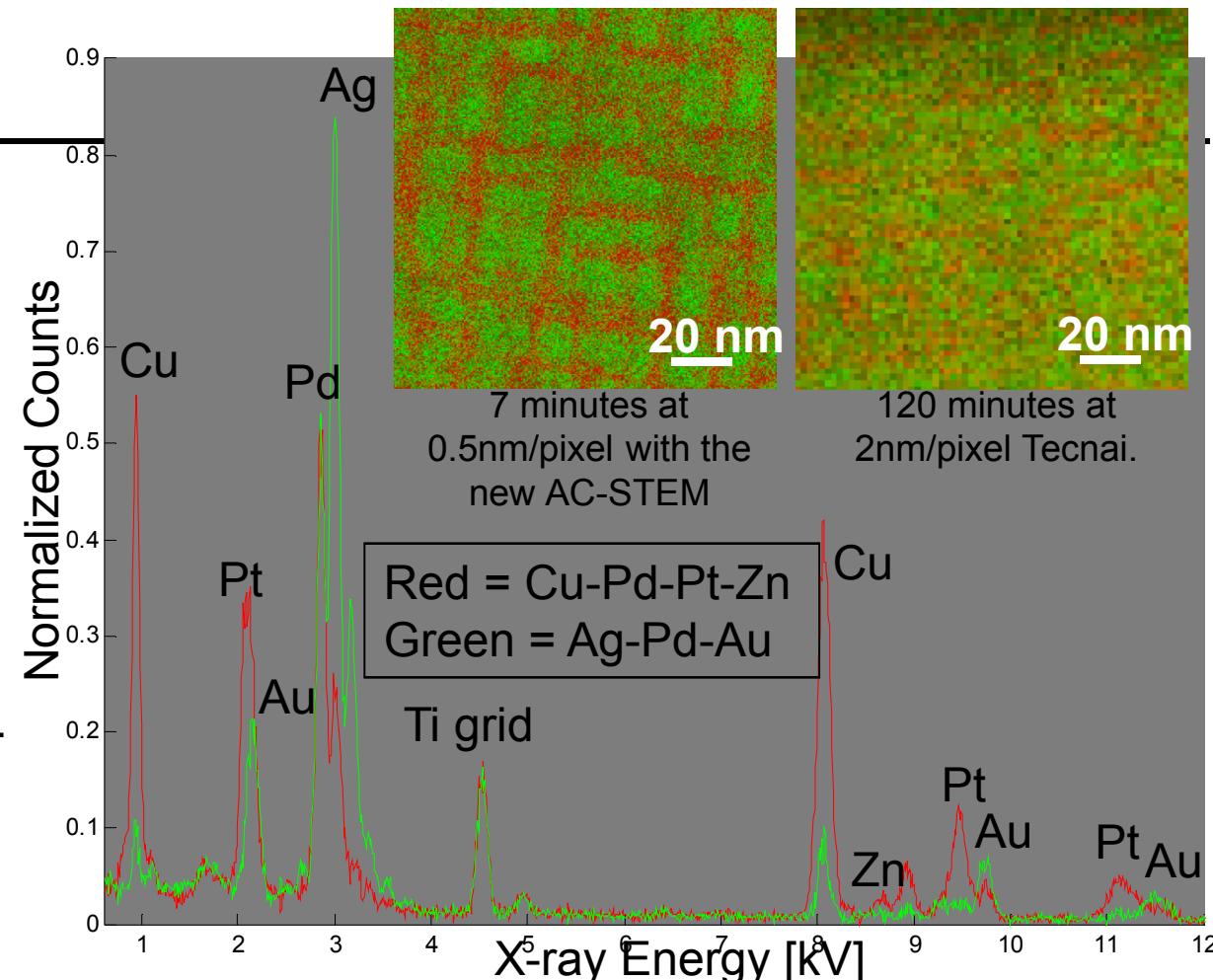
# Low end, Spatial-Domain Simplicity Ni-silicide contact, MSA shows minor elements



# Sub-nm microanalysis of electrical contact materials

Titan G2 80-200 Cs  
probe corrected  
with ChemiSTEM  
(SuperX)  
MSA analysis

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

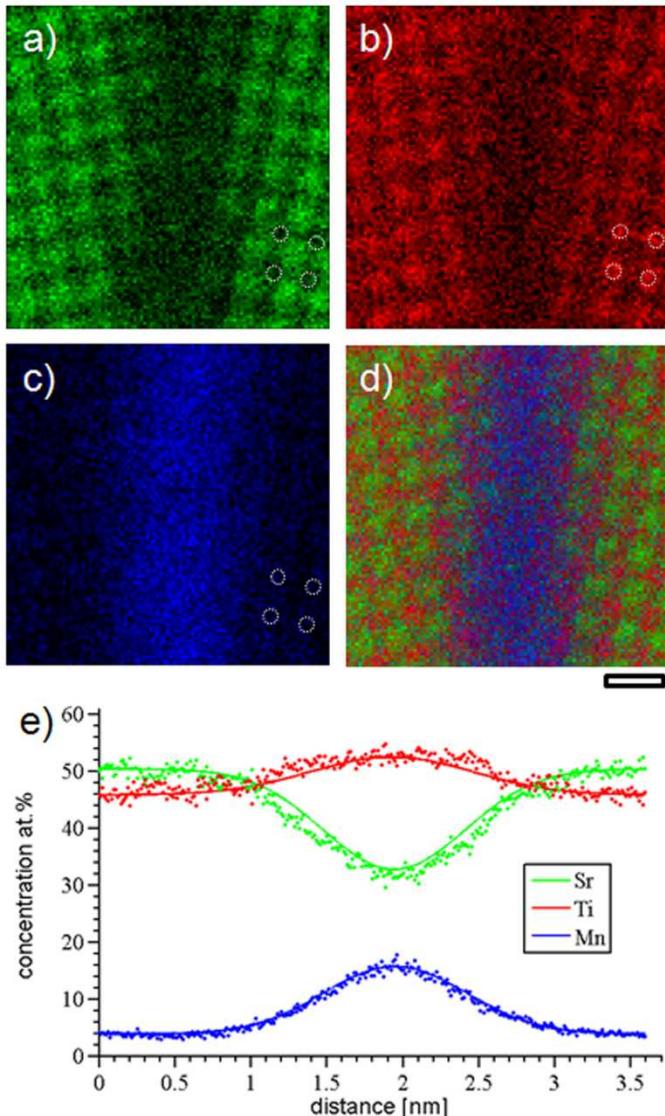


The new AEM is at least **70x** better than our older AEM  
(Philips/FEI Tecnai F30-ST)

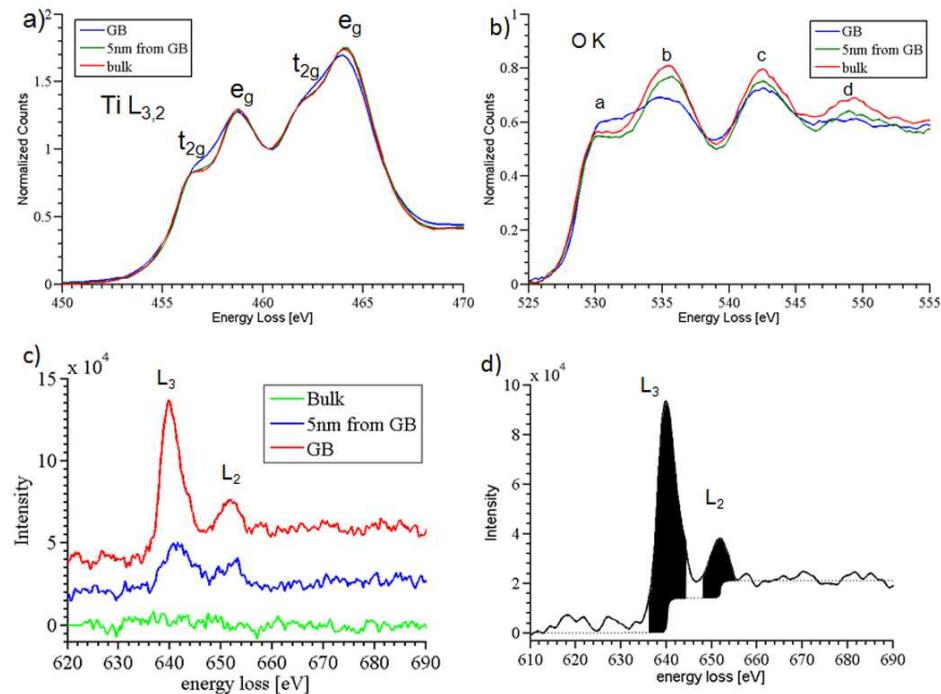
# Analysis of Mn-doped STO $\Sigma=13$ Boundary

## $\Sigma 13 (510)/[001]$

### Quantitative EDS and EELS



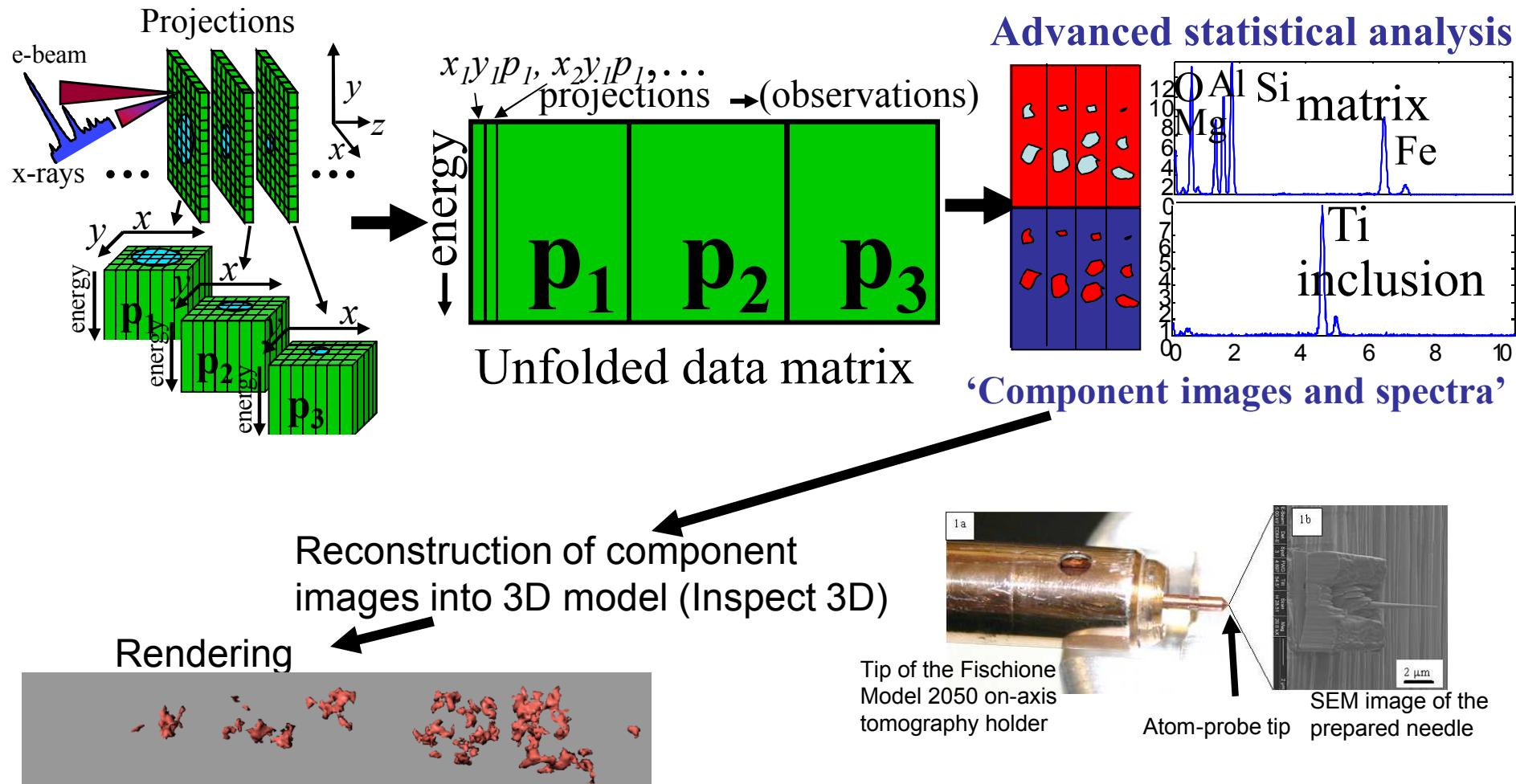
FWTM enrichment at the boundary less than 2nm



$\text{Mn}^{+2}$  at boundary  
 $\text{Mn}^{+4}$  in bulk near boundary  
(substitutional with Ti)

H. Yang, P.G. Kotula, Y. Sato, Y. Ikuhara, N.D. Browning. *Materials Research Letters* (2013). DOI: 10.1080/21663831.2013.856815

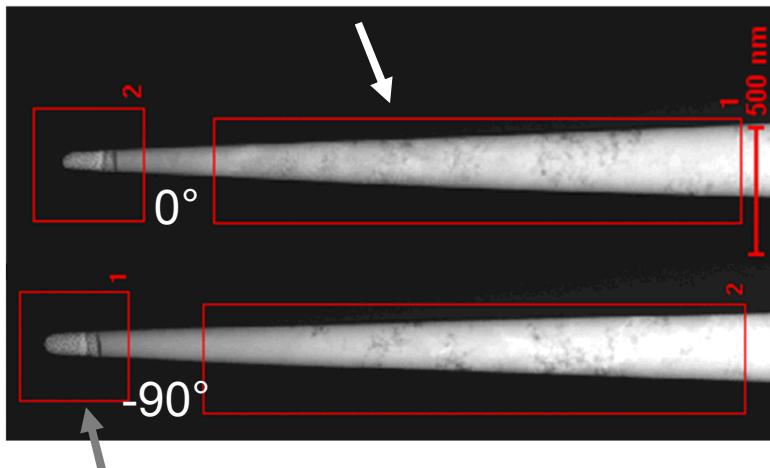
# Tomographic Spectral Imaging and Multivariate Statistical Analysis



# MSA of the entire projection series

FEI Tecnai F30-ST, 0.1sr

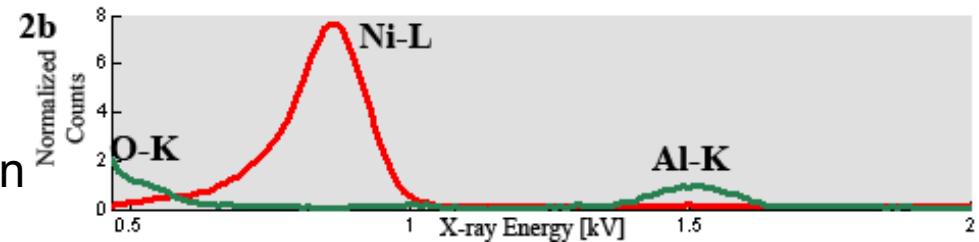
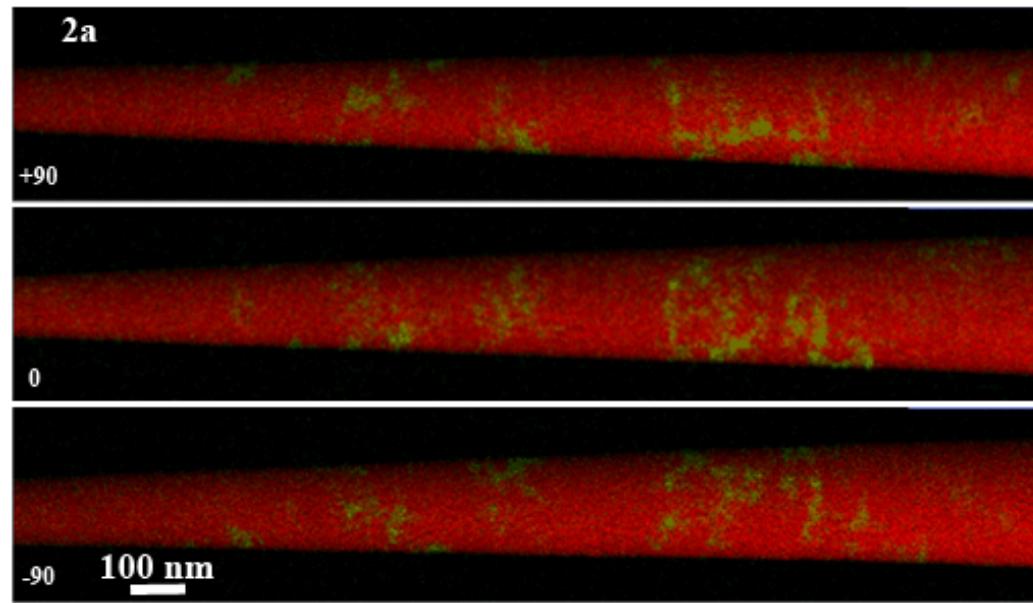
Region of spectral  
images 2000nm x 400nm



Drift-correction region

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

Color overlays of component images



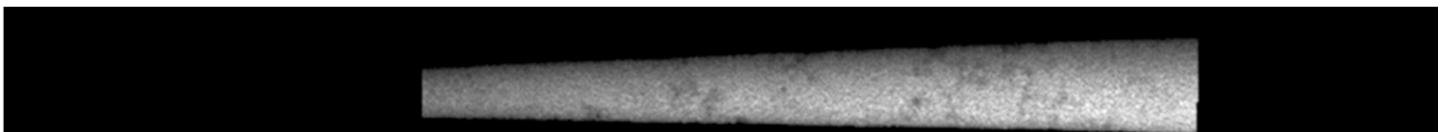
Then, reconstruct component projection  
images into 3D model (Inspect 3D)



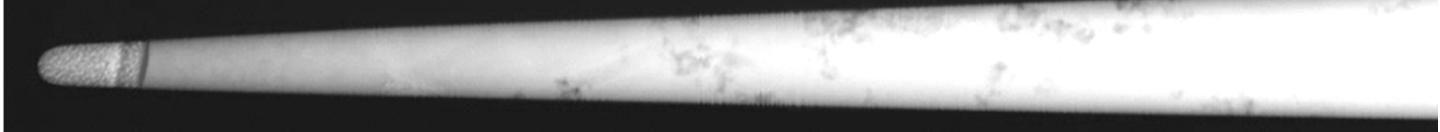
# Raw tomography series

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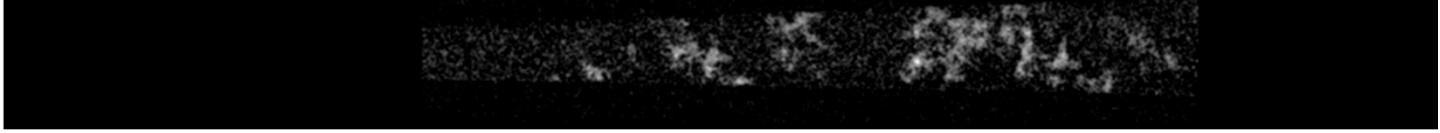
Ni

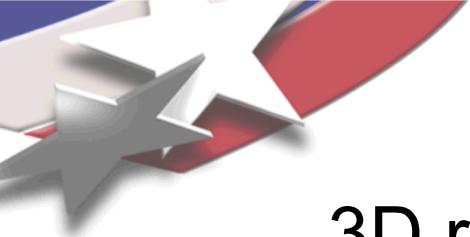


HAADF



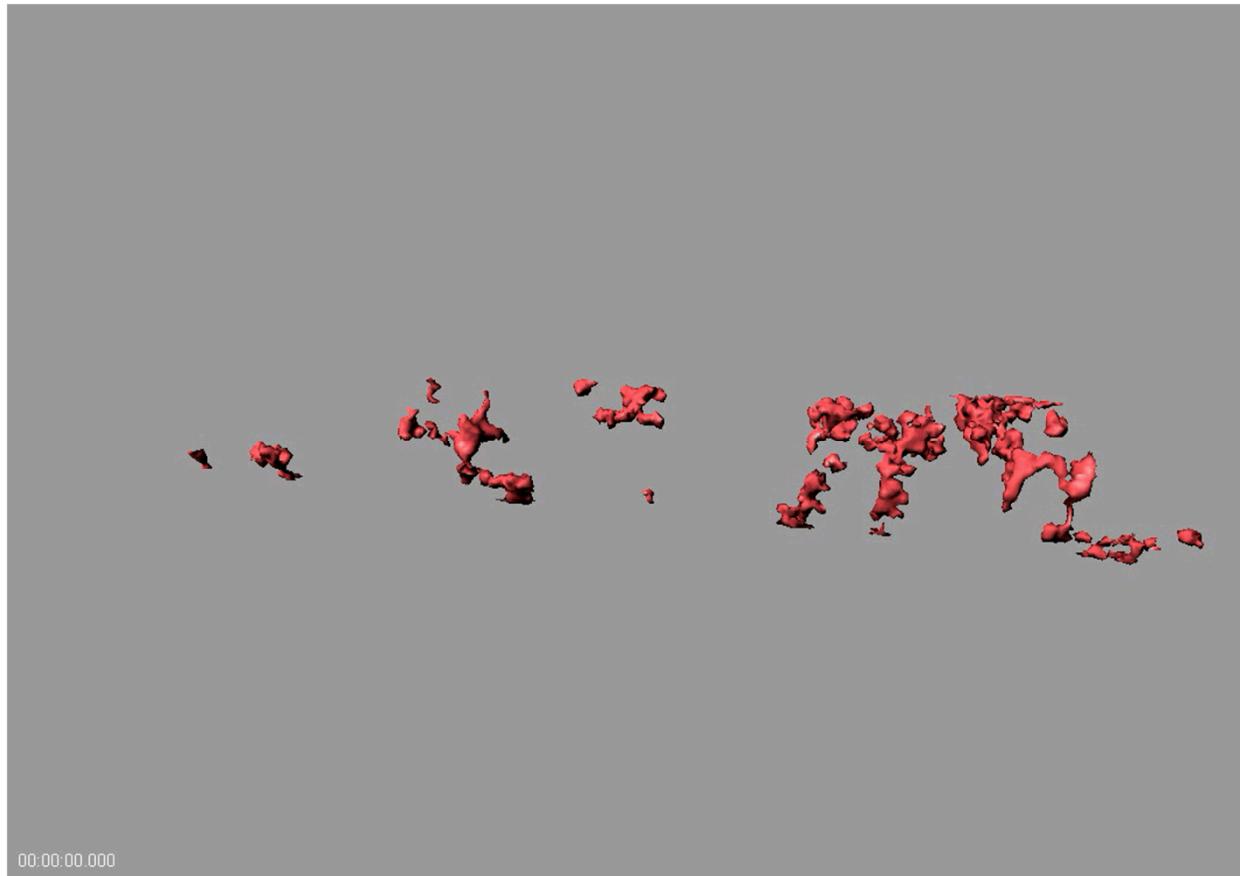
Al-O





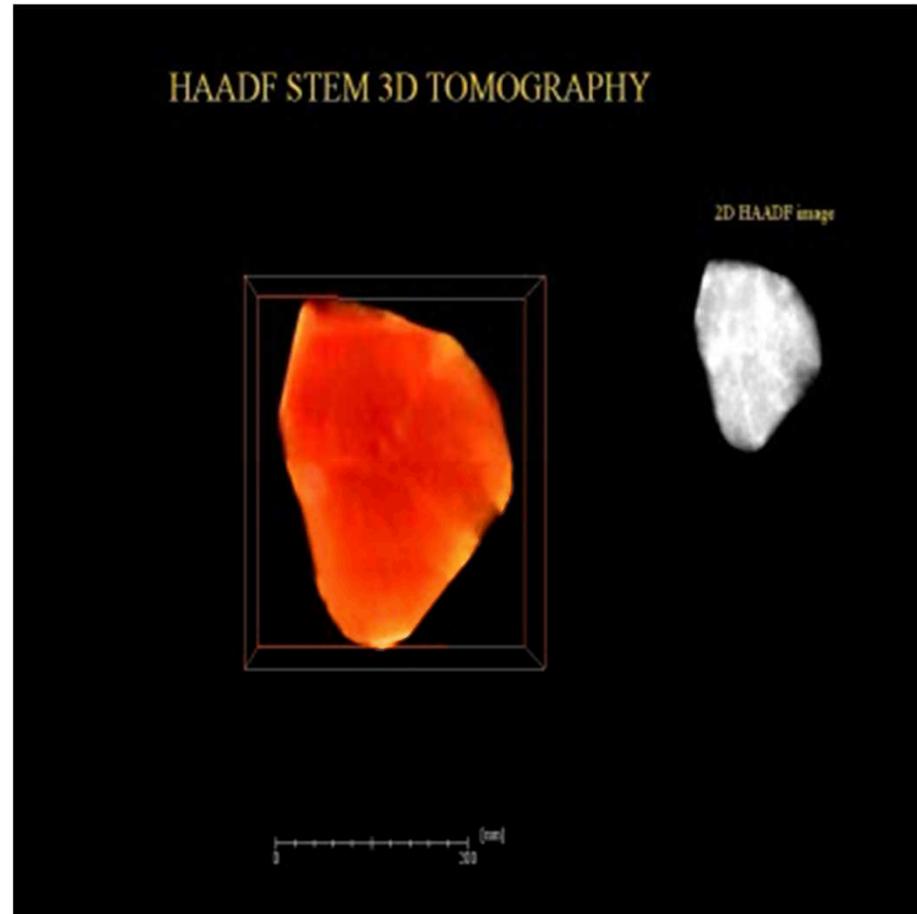
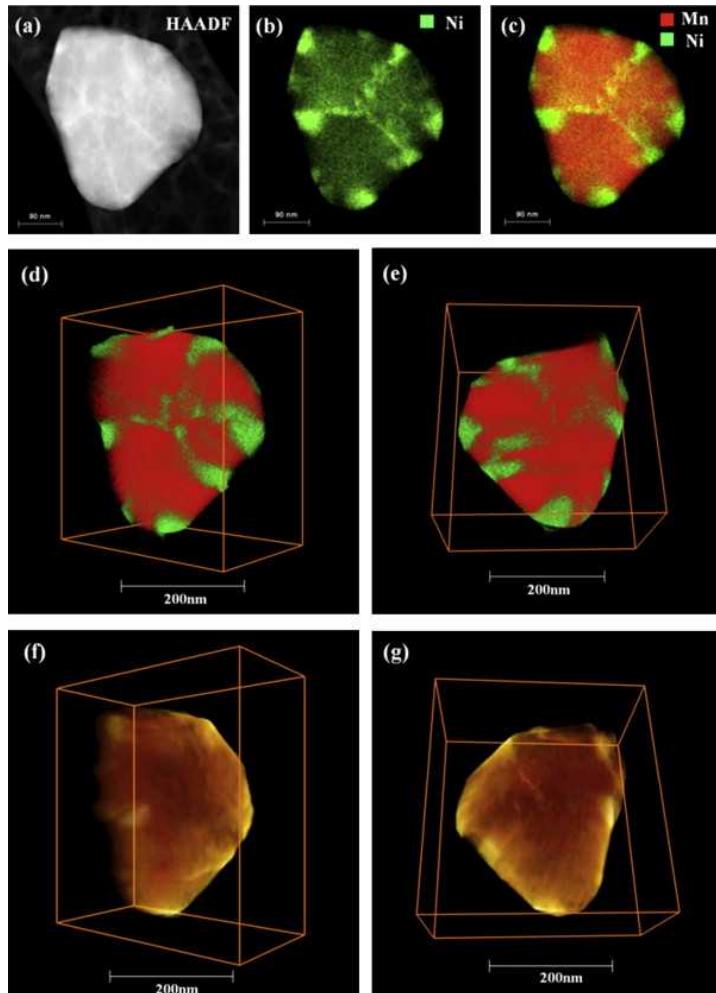
# 3D reconstruction for alumina nanoparticles

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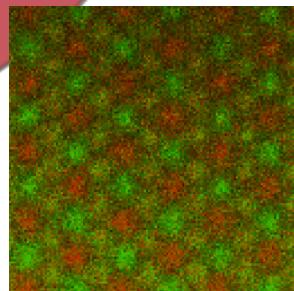


P.G. Kotula, et al. *Microsc. Microanal.* 13  
(Suppl 2), 2007 1324CD-1325CD

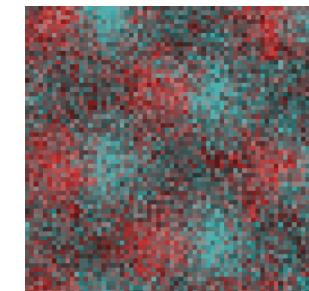
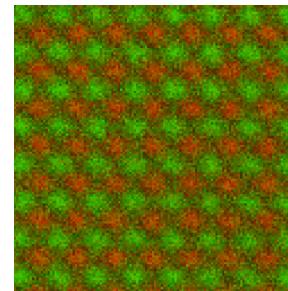
# 3D chemistry of a nanoparticle



A Genc, et al., (2013) "XEDS STEM tomography for 3D chemical characterization of nanoscale particles," *Ultramicroscopy* **131** 24-32.



# Conclusions



- In the last 10 years SDDs have come into their own and enabled huge gains in analytical speed and sensitivity making comprehensive 2- and 3-D microanalysis both possible as well as faster and better (FIB-SEM-EDS and AEM)
- New analytical electron microscopes are 100 times better than the last generation...faster, higher resolution, more sensitive.
  - Practical 3D microanalysis via computed tomography
- MSA methods are very useful for simplifying the analysis of large, complex data sets
  - Unbiased analysis powerful for materials science, etc. Needle in the haystack....
  - Quantification can them be performed with added knowledge
- All of these developments have depended upon the availability of inexpensive and powerful computers