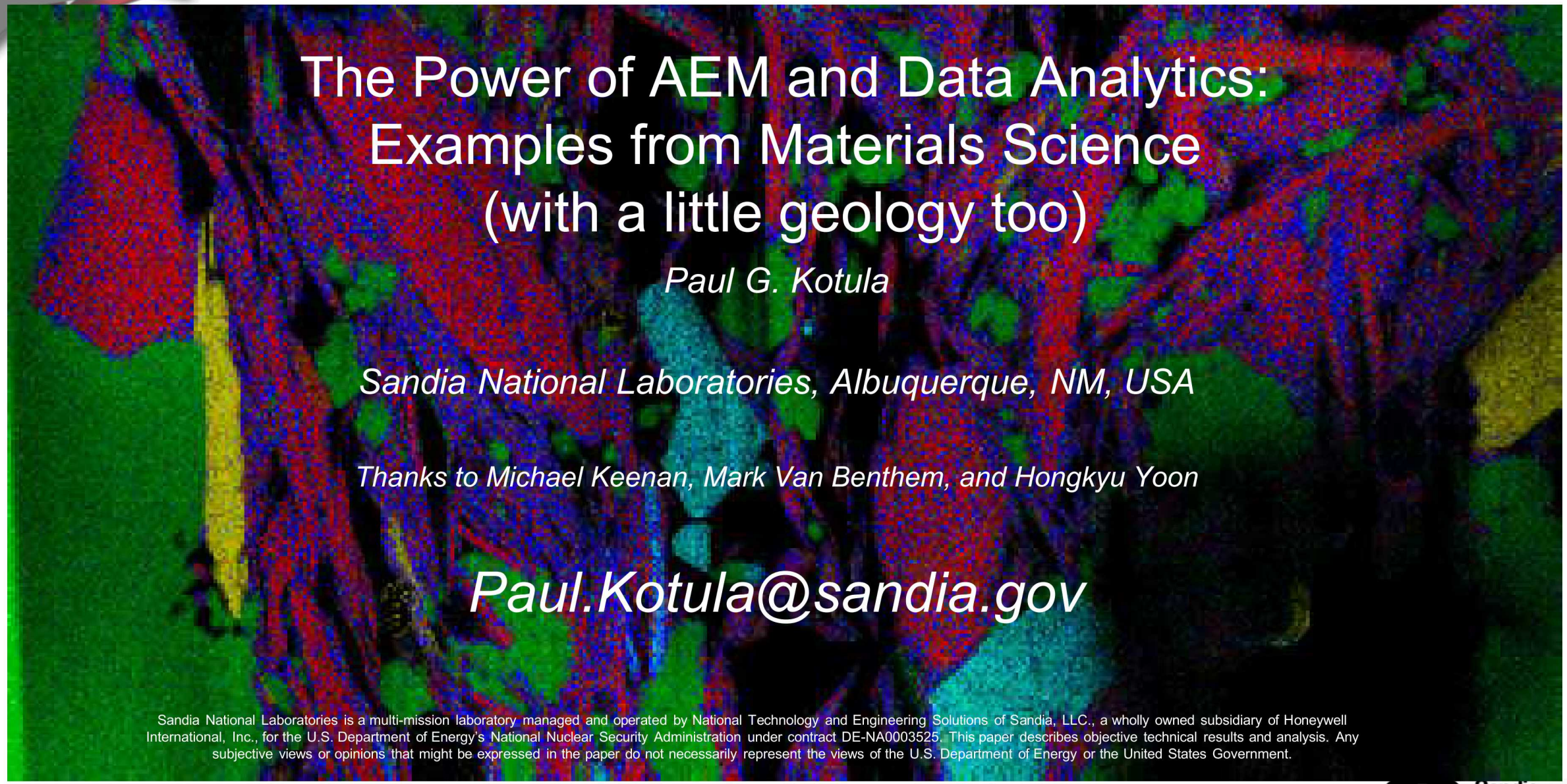
SAND2019-11042C



The Power of AEM and Data Analytics: Examples from Materials Science (with a little geology too)

Paul G. Kotula

Sandia National Laboratories, Albuquerque, NM, USA

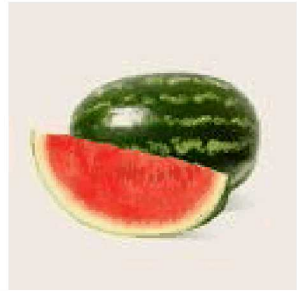
Thanks to Michael Keenan, Mark Van Benthem, and Hongkyu Yoon

Paul.Kotula@sandia.gov

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

NNSA National Nuclear Security Administration

Sandia National Laboratories

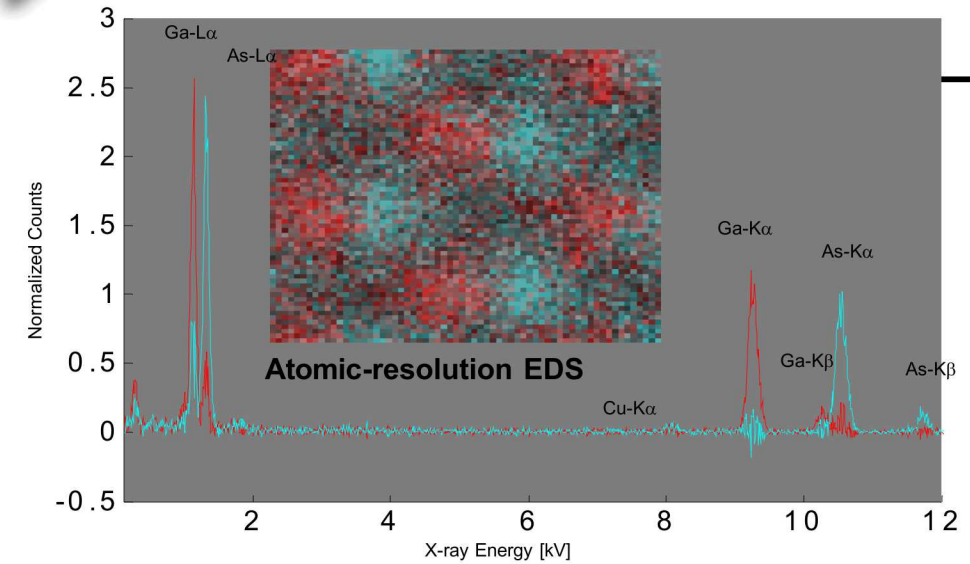
Why are we called Sandia?  ?

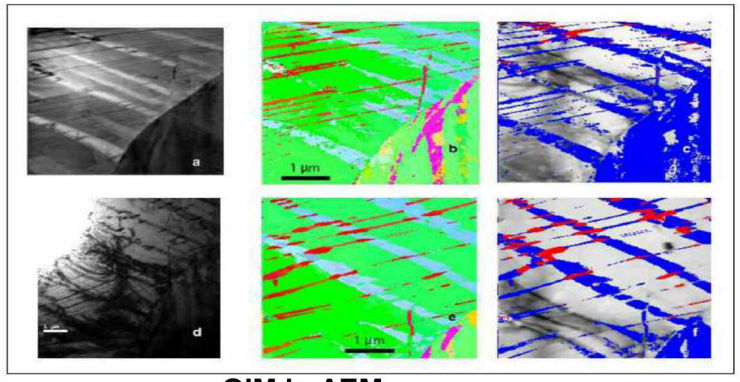
- Largest National Laboratory in the US with over 13,000 employees
- Originally a division of Los Alamos Scientific Laboratory
- Named after the Sandia Mountains near Albuquerque
- Those mountains were named by the early Spanish settlers in ~1540
  - From a distance the Sandia's look like a watermelon on its side
  - The Spanish settlers mistook gourds being grown by the natives for watermelons

Sandia Mountains, Albuquerque, NM, USA, Courtesy USDA-NRCS

Sandia National Laboratories

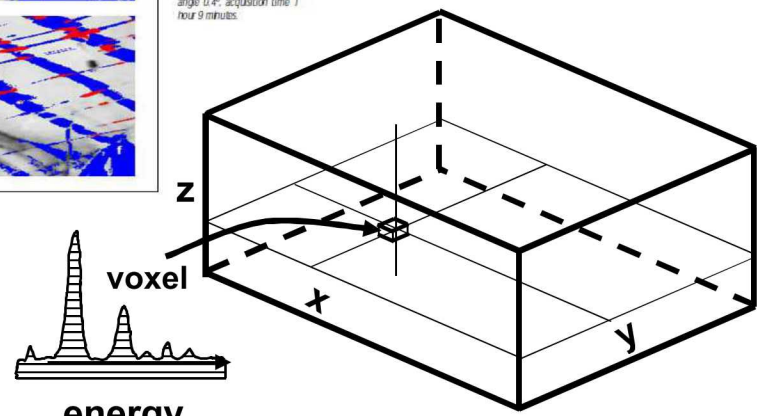
Materials Characterization Tetrahedron



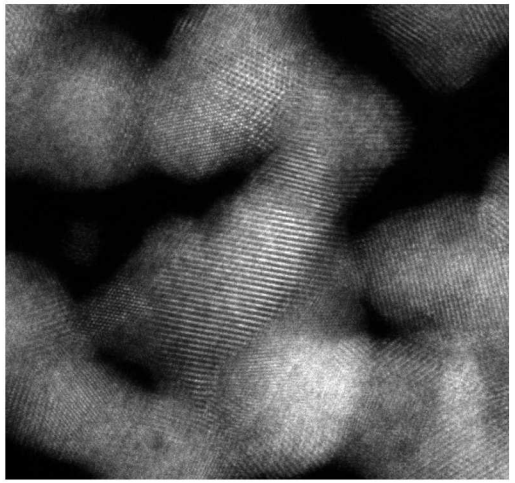


OIM in AEM

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.

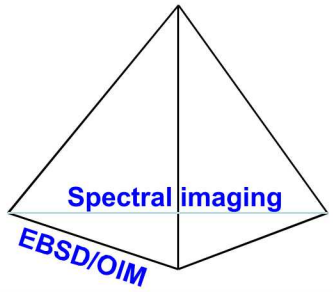


'3D' spectral image



Atomic-resolution STEM image

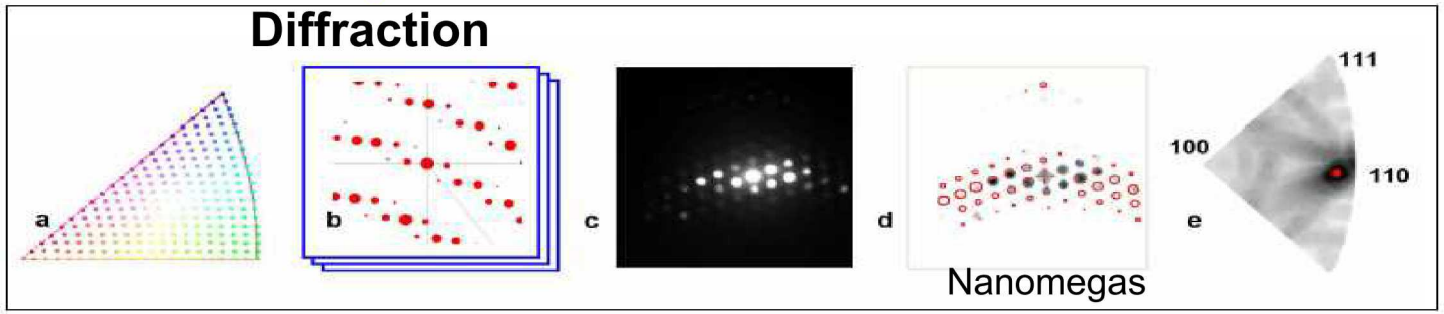
Data Analysis



Imaging

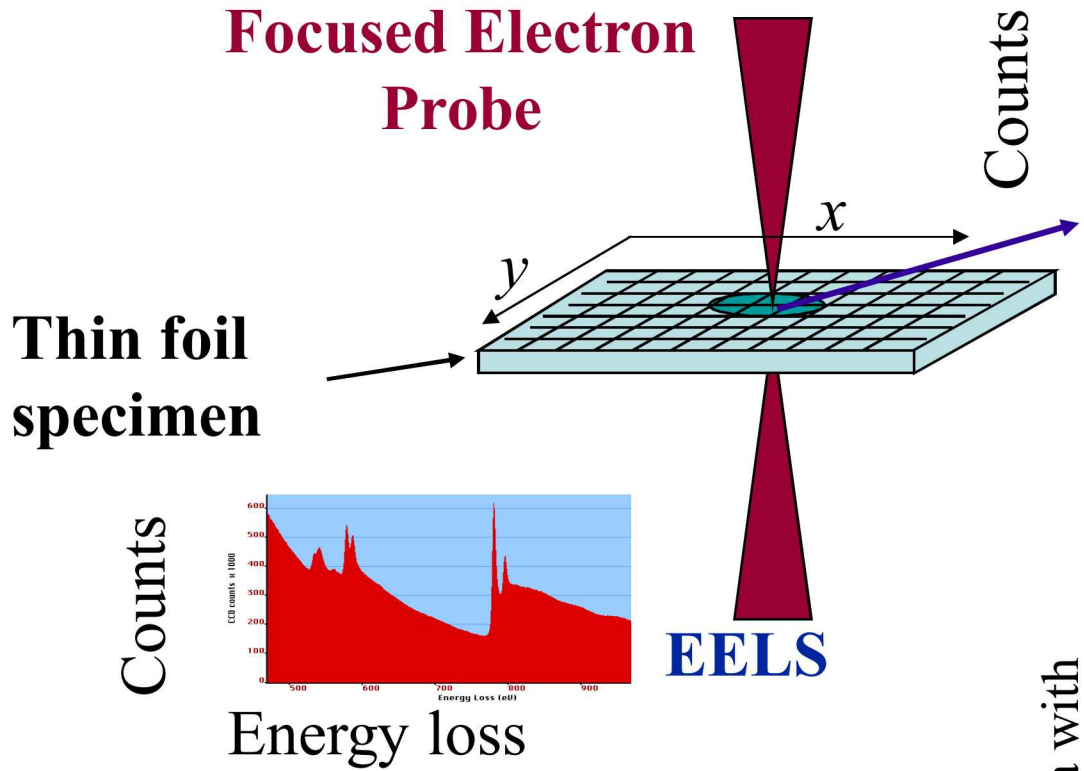
Microanalysis

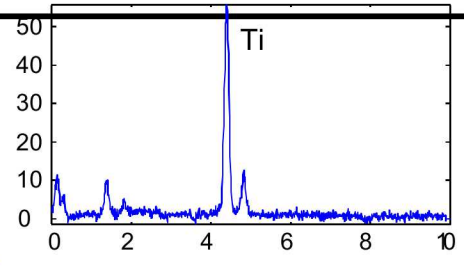
Diffraction

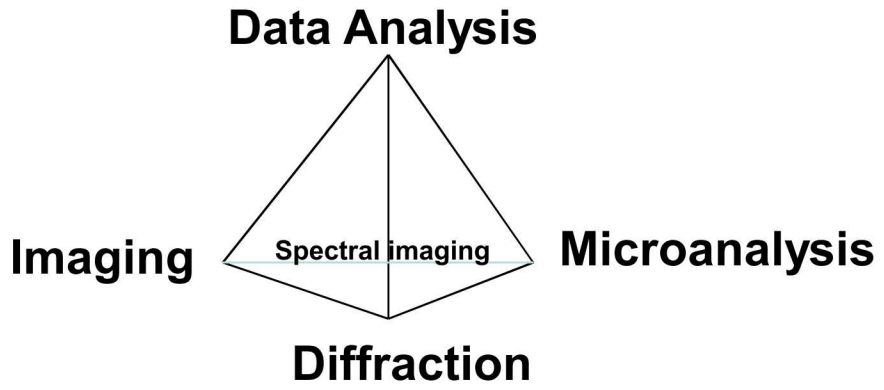


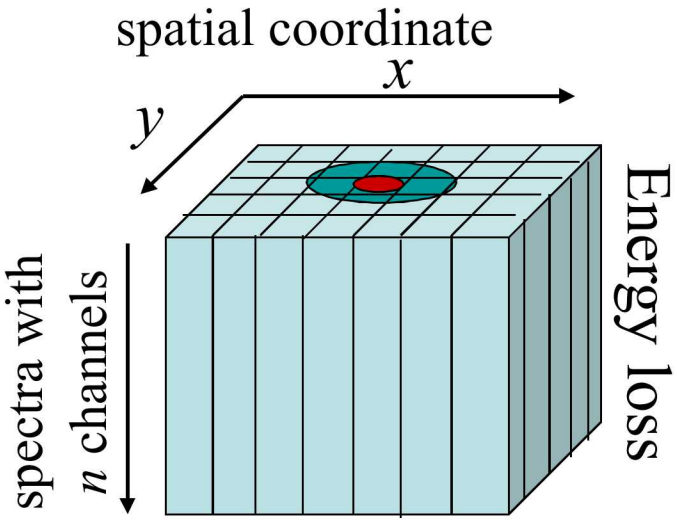
Sandia National Laboratories

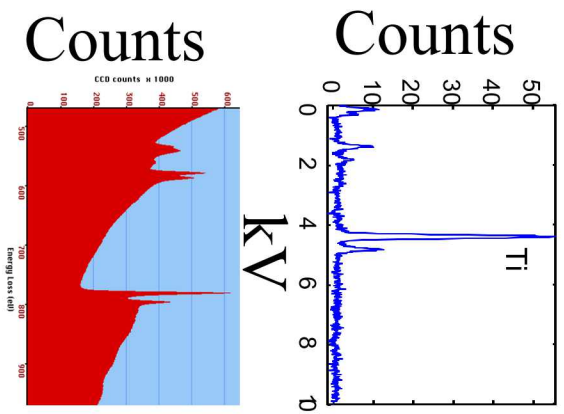
AEM Spectral Imaging





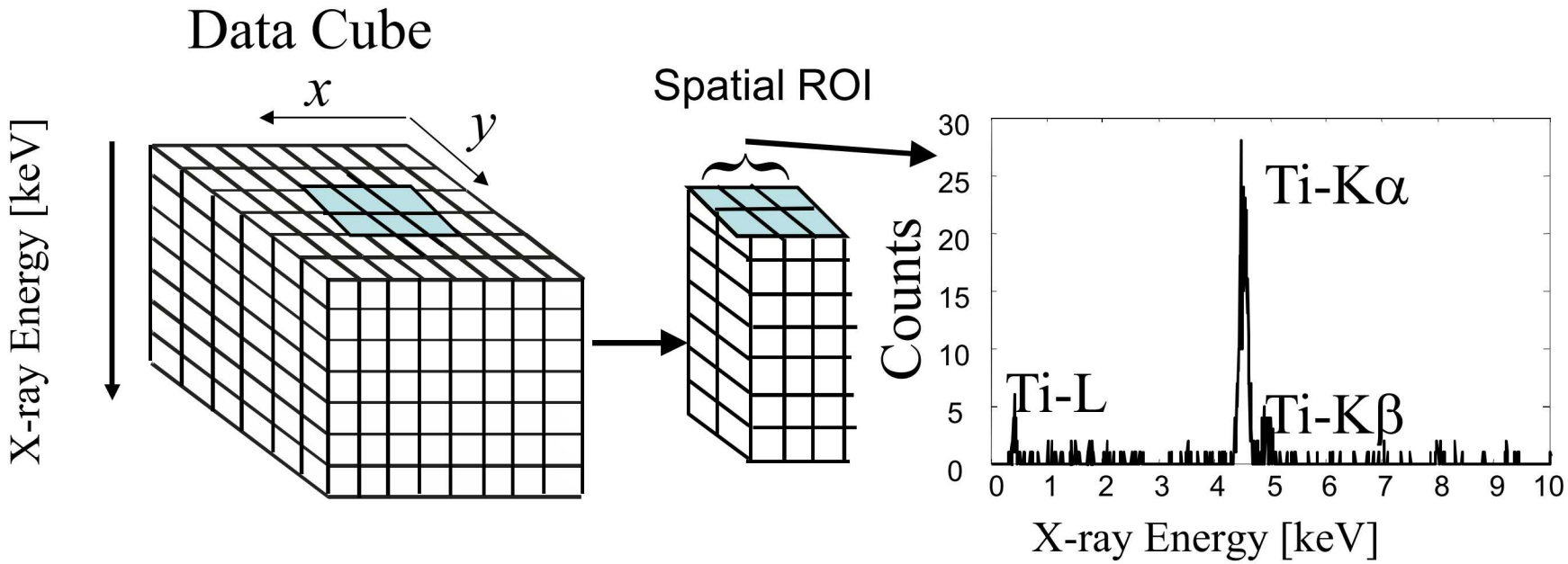


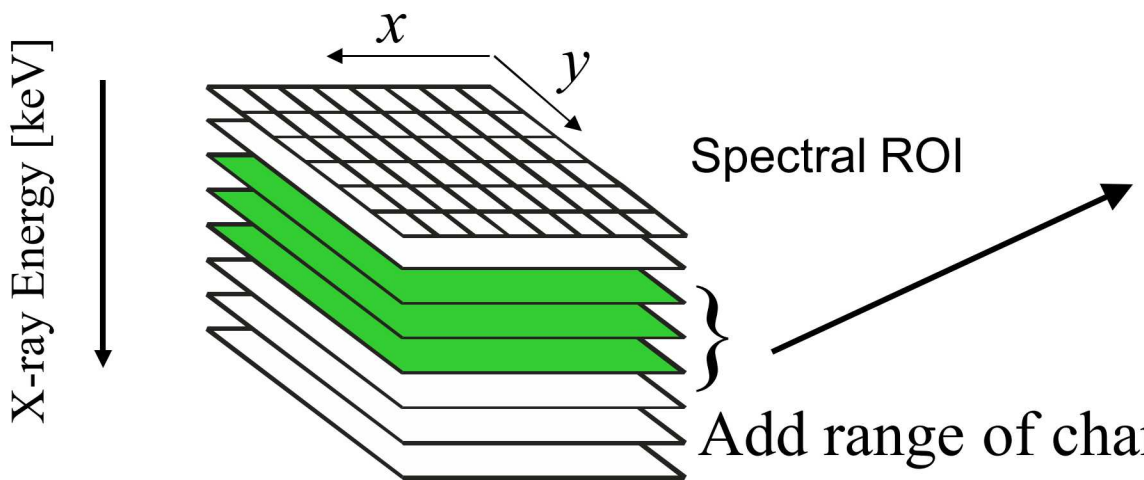


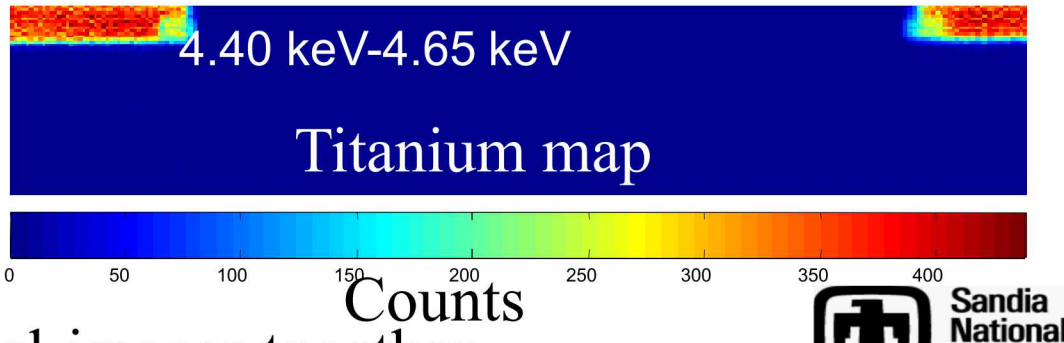


P.G. Kotula, et al. *Microsc. Microanal.* **12** [6] 538-544.

Conventional Data Analysis



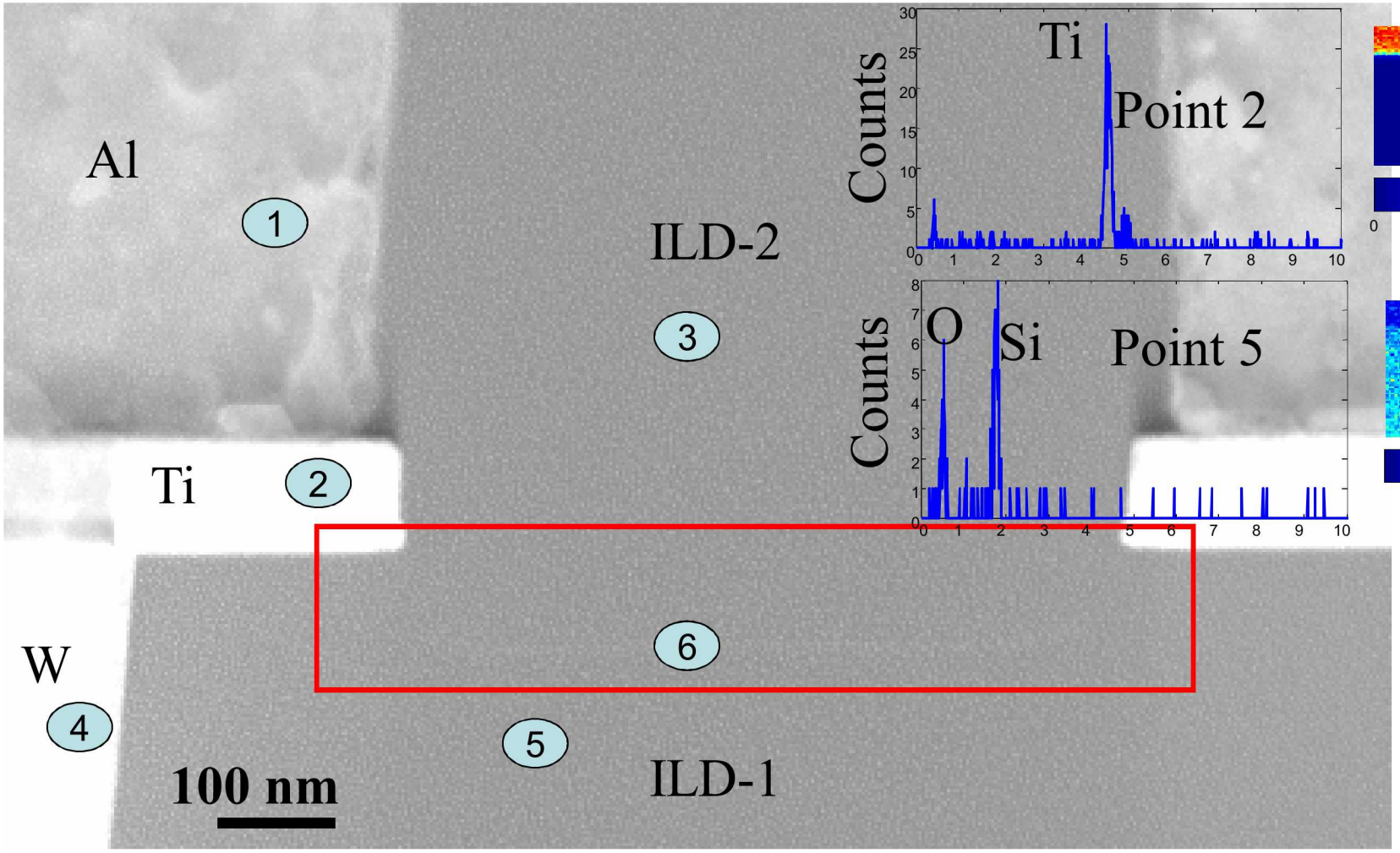


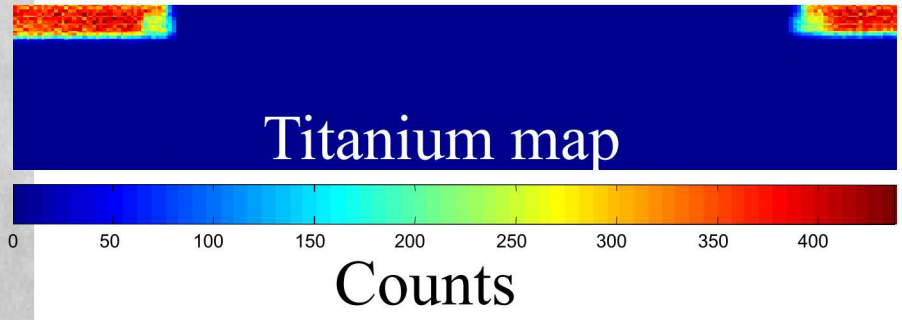


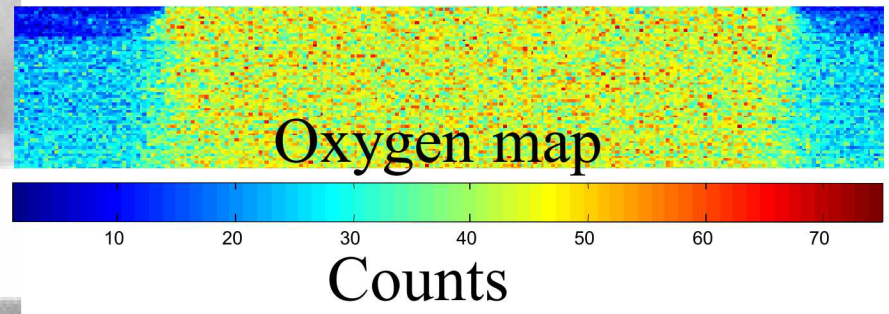
Add range of channel-images together

Sandia National Laboratories

Example of Conventional Analysis



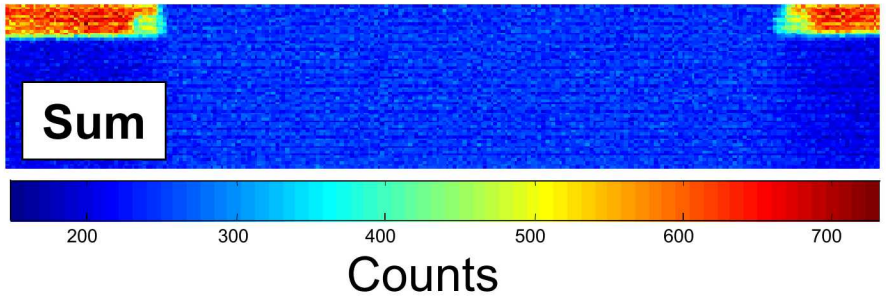


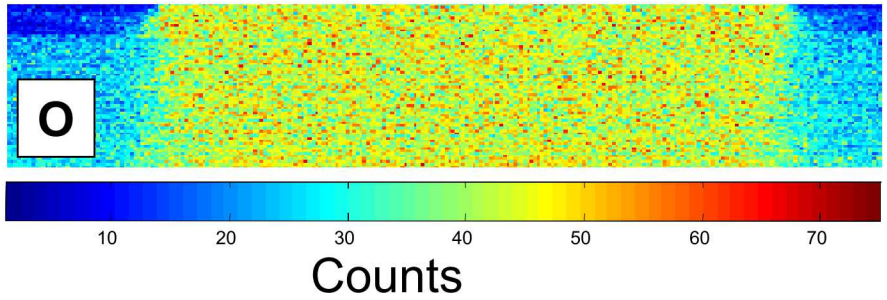


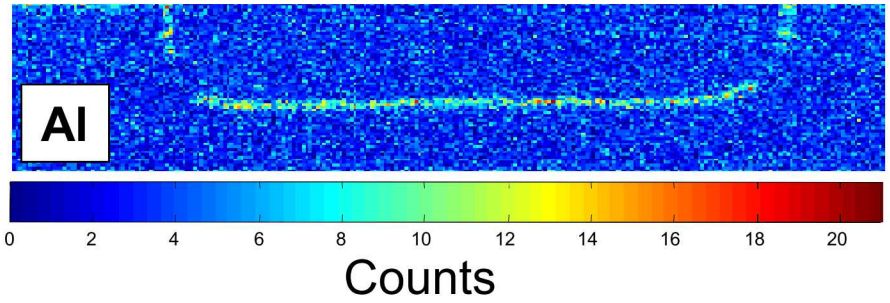
P.G. Kotula, et al. *Microsc. Microanal.* **12** [6] 538-544.

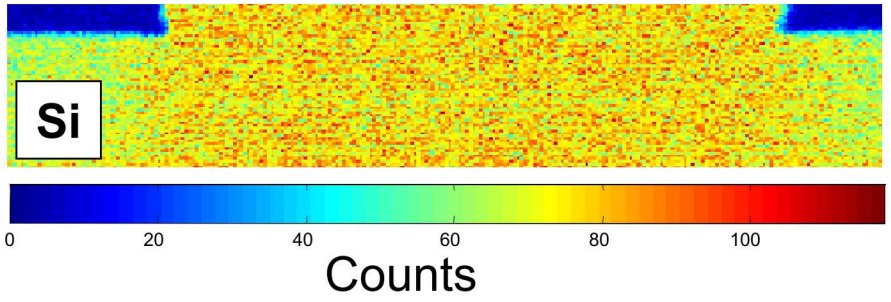
Sandia National Laboratories

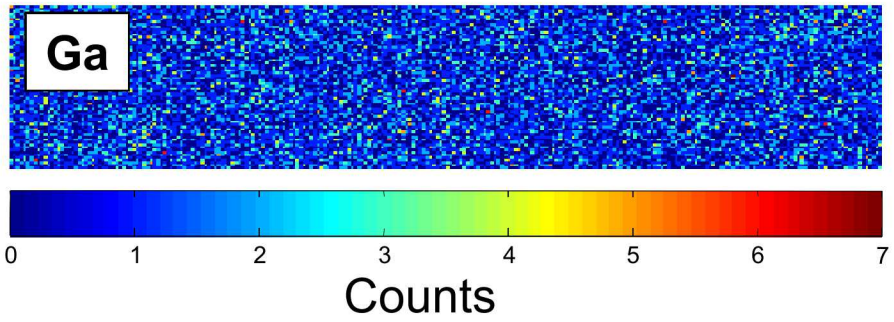
Example of Conventional Analysis

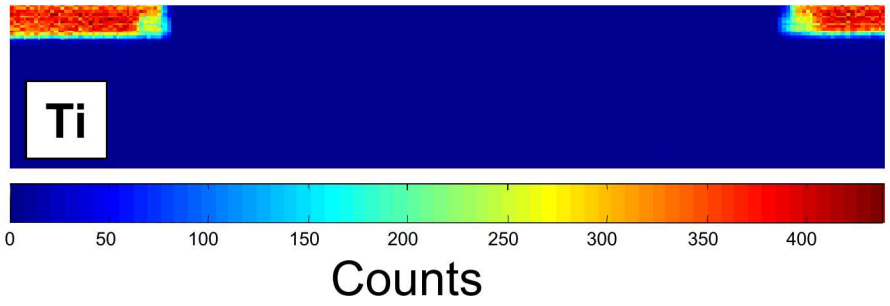








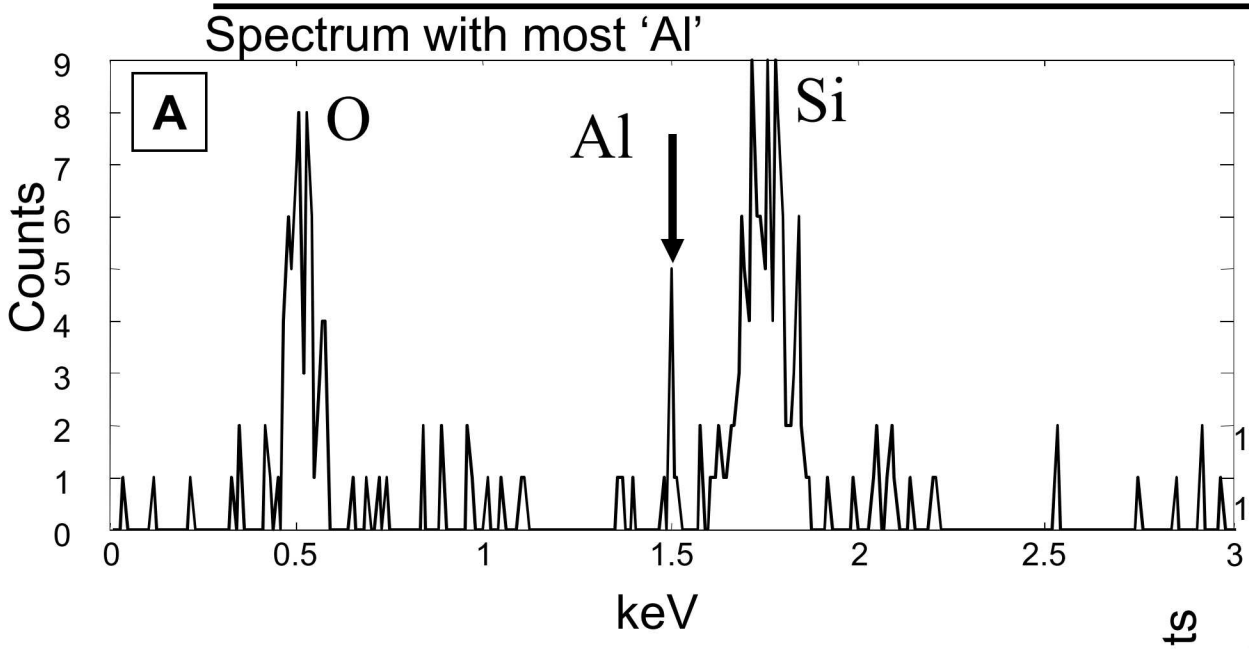


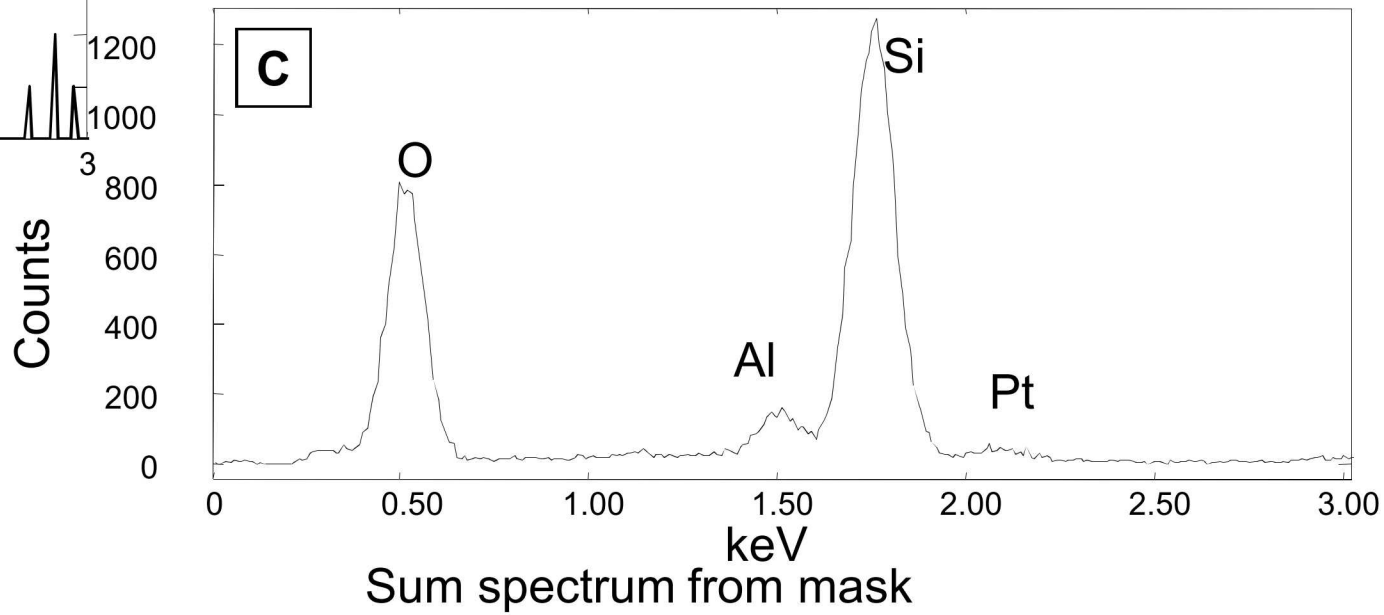


P.G. Kotula, et al. *Microsc. Microanal.* **12** [6] 538-544.

Sandia National Laboratories

Example of Conventional Analysis

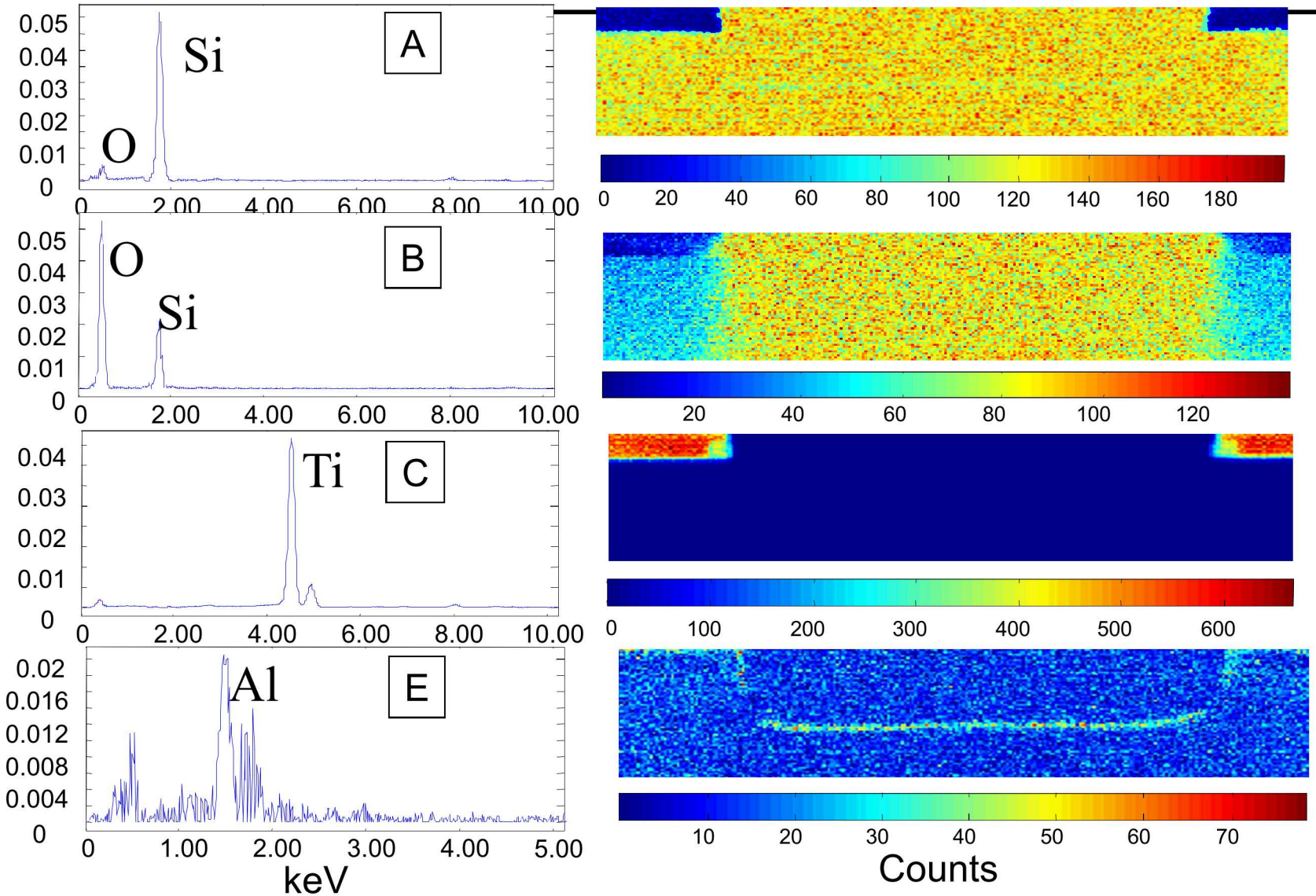




P.G. Kotula, et al. *Microsc. Microanal.* **12** [6] 538-544.

Sandia National Laboratories

Multivariate Statistical Analysis of the same data



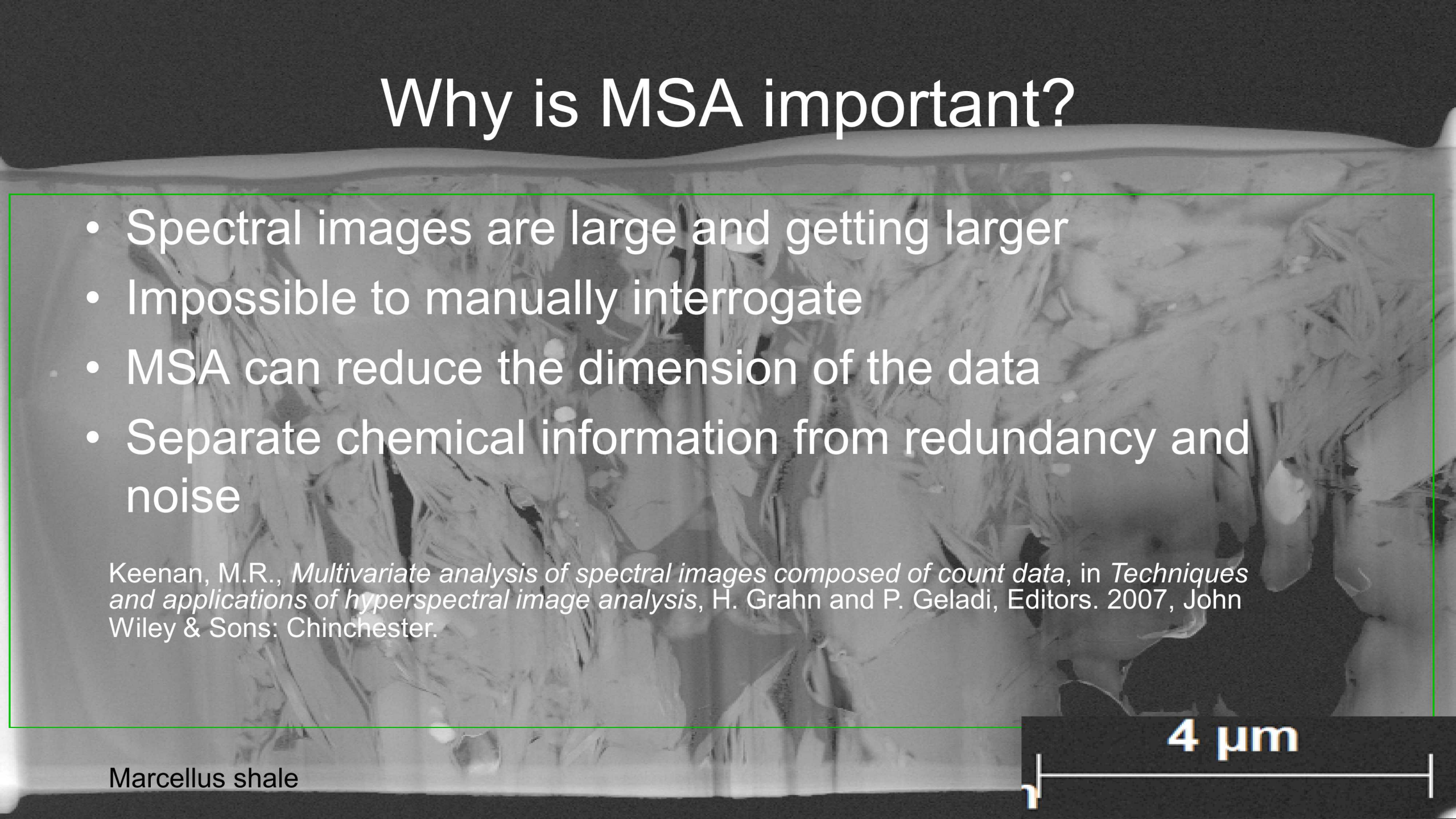
P.G. Kotula, et al. *Microsc. Microanal.* **12** [6] 538-544.

Sandia National Laboratories

Why is MSA important?

- Spectral images are large and getting larger
- Impossible to manually interrogate
- MSA can reduce the dimension of the data
- Separate chemical information from redundancy and noise

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.



Marcellus shale

RGB image

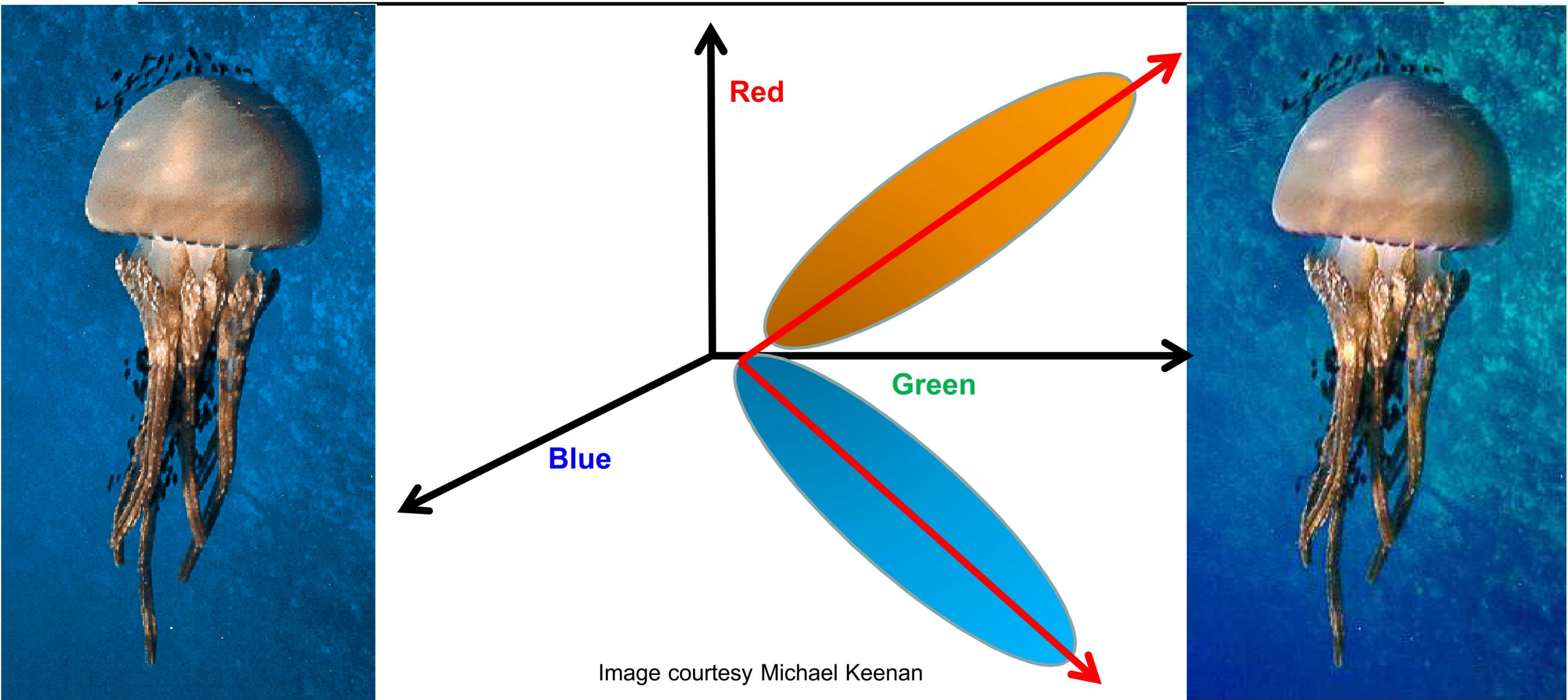
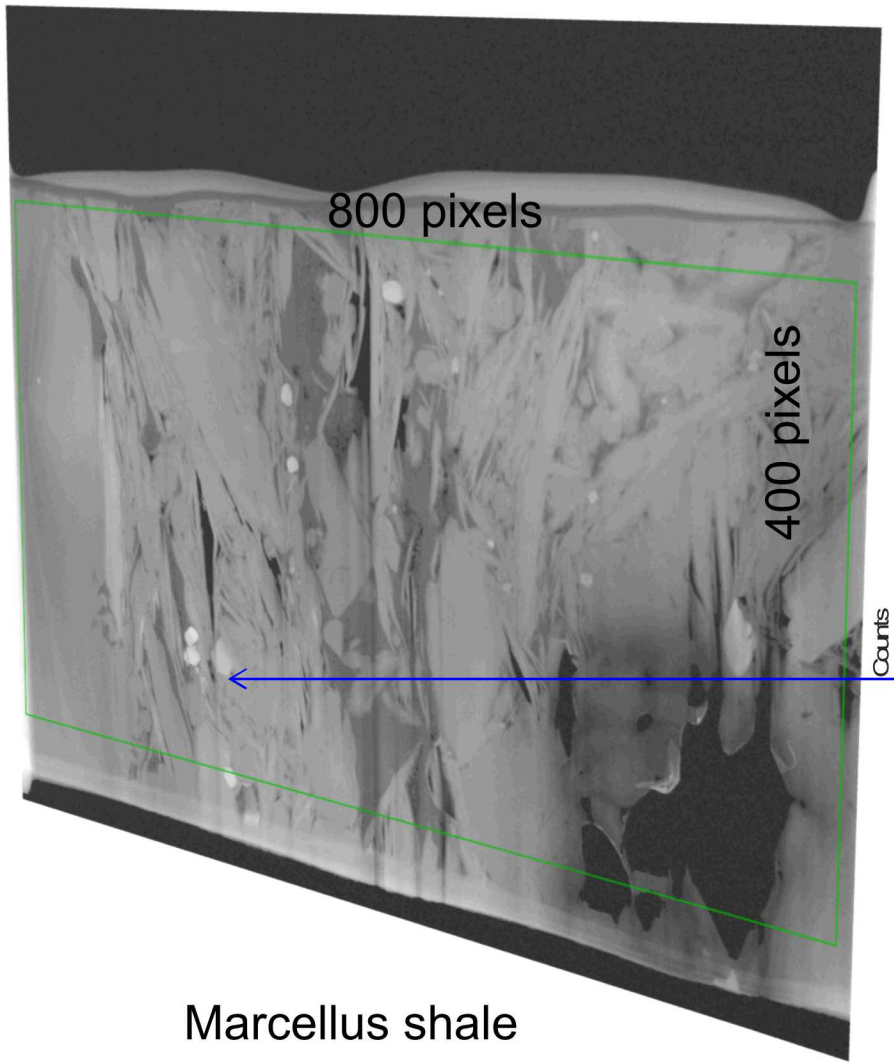


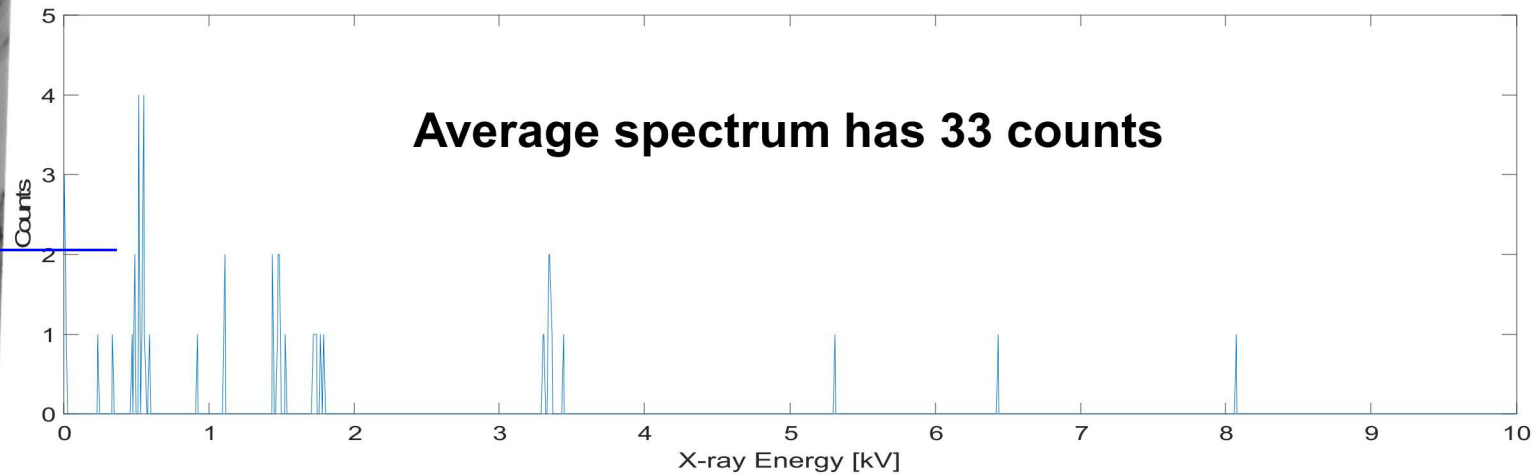
Image courtesy Michael Keenan

The Data Set



Marcellus shale

- A little over 1 hour of AEM data acquisition
- 320,000 spectra each with 2048 channels
- Spectra are noisy
- Can MSA make anything out of this?

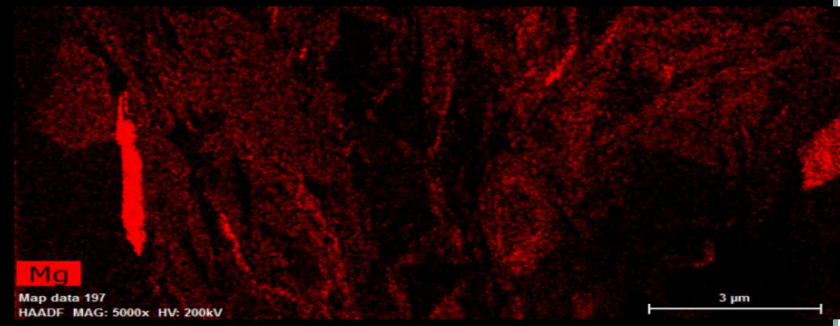


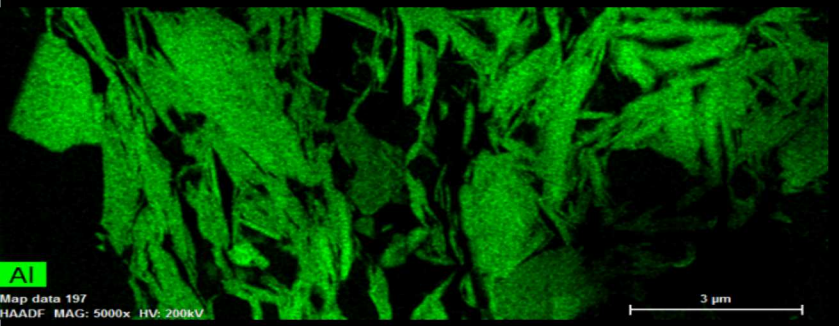
Sandia National Laboratories

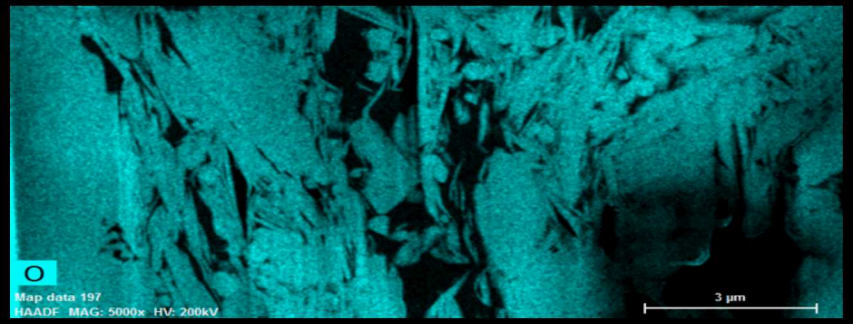
X-ray Maps


HAADF
Map data 197
HAADF MAG: 5000x HV: 200kV
3 µm

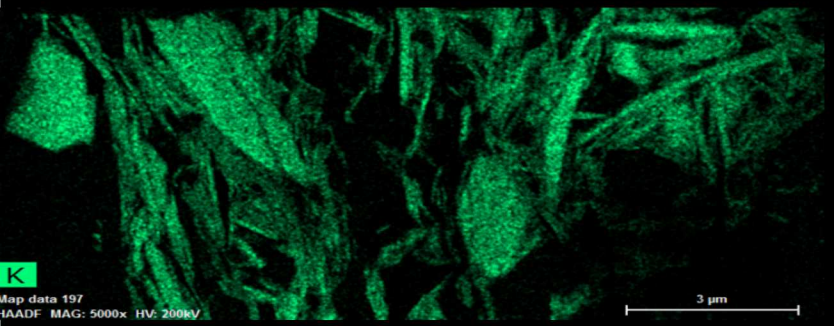

Si
Map data 197
HAADF MAG: 5000x HV: 200kV
3 µm


Mg
Map data 197
HAADF MAG: 5000x HV: 200kV
3 µm

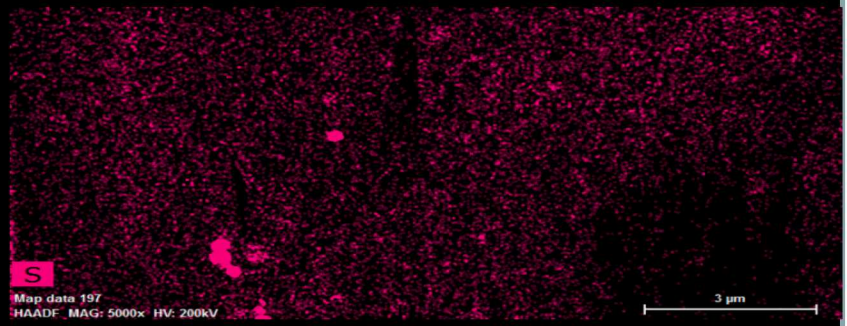

Al
Map data 197
HAADF MAG: 5000x HV: 200kV
3 µm

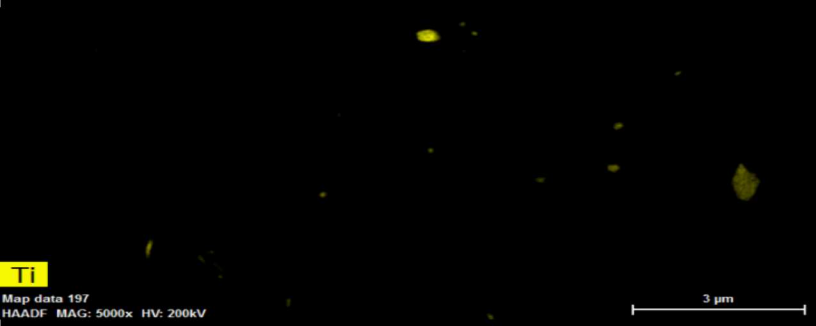

O
Map data 197
HAADF MAG: 5000x HV: 200kV
3 µm

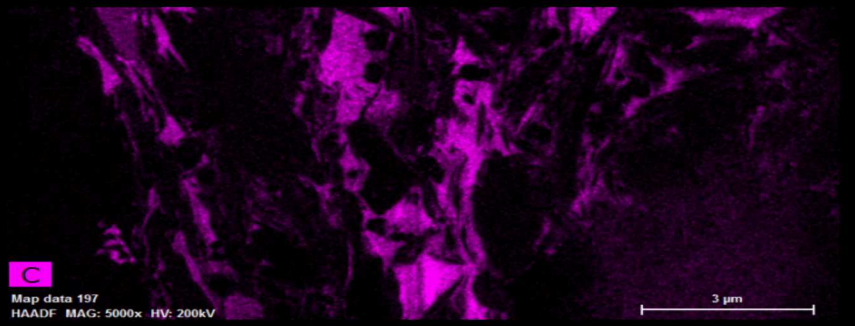

Fe
Map data 197
HAADF MAG: 5000x HV: 200kV
3 µm

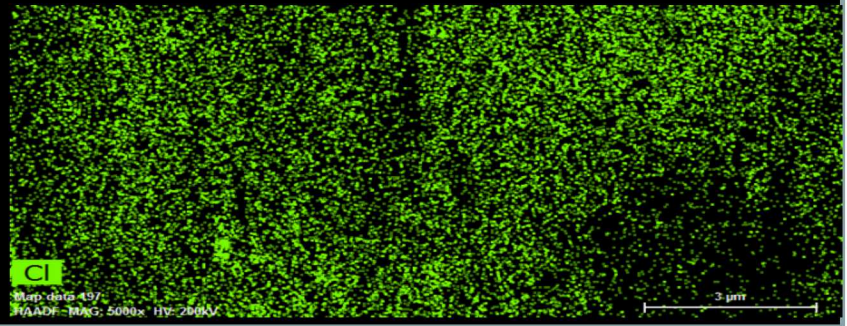

K
Map data 197
HAADF MAG: 5000x HV: 200kV
3 µm


Ca
Map data 197
HAADF MAG: 5000x HV: 200kV
3 µm

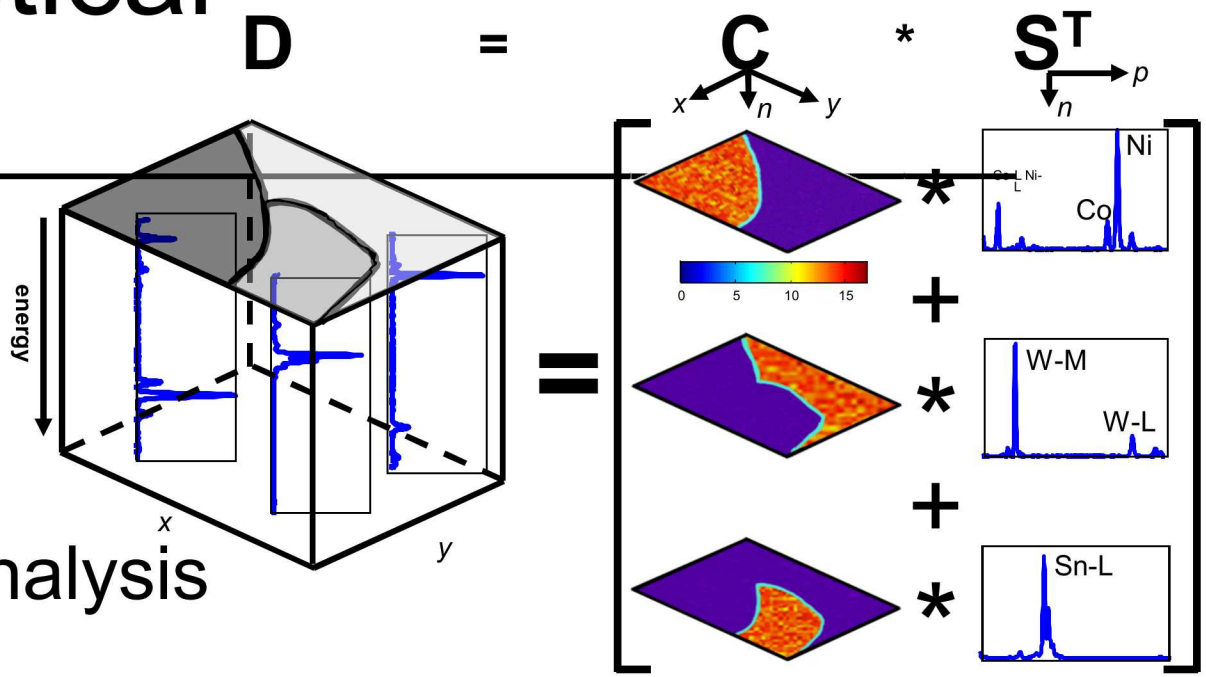

S
Map data 197
HAADF MAG: 5000x HV: 200kV
3 µm


Ti
Map data 197
HAADF MAG: 5000x HV: 200kV
3 µm

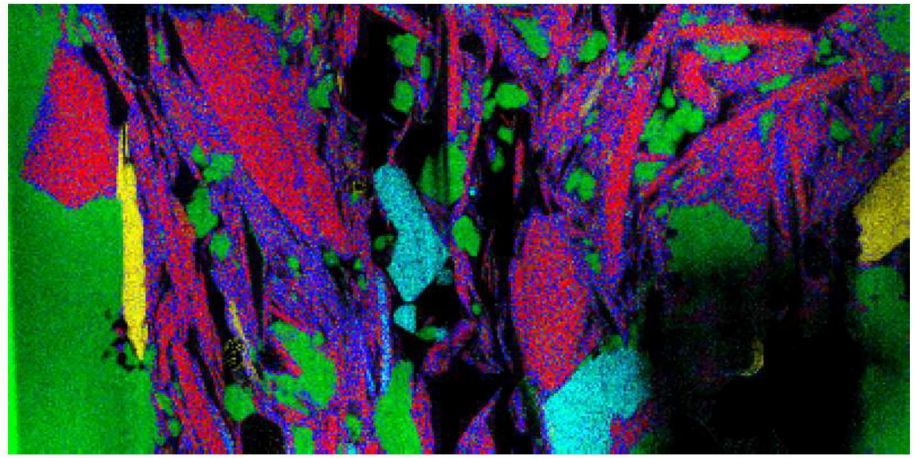

C
Map data 197
HAADF MAG: 5000x HV: 200kV
3 µm


Cl
Map data 197
HAADF MAG: 5000x HV: 200kV
3 µm

Multivariate Statistical Analysis

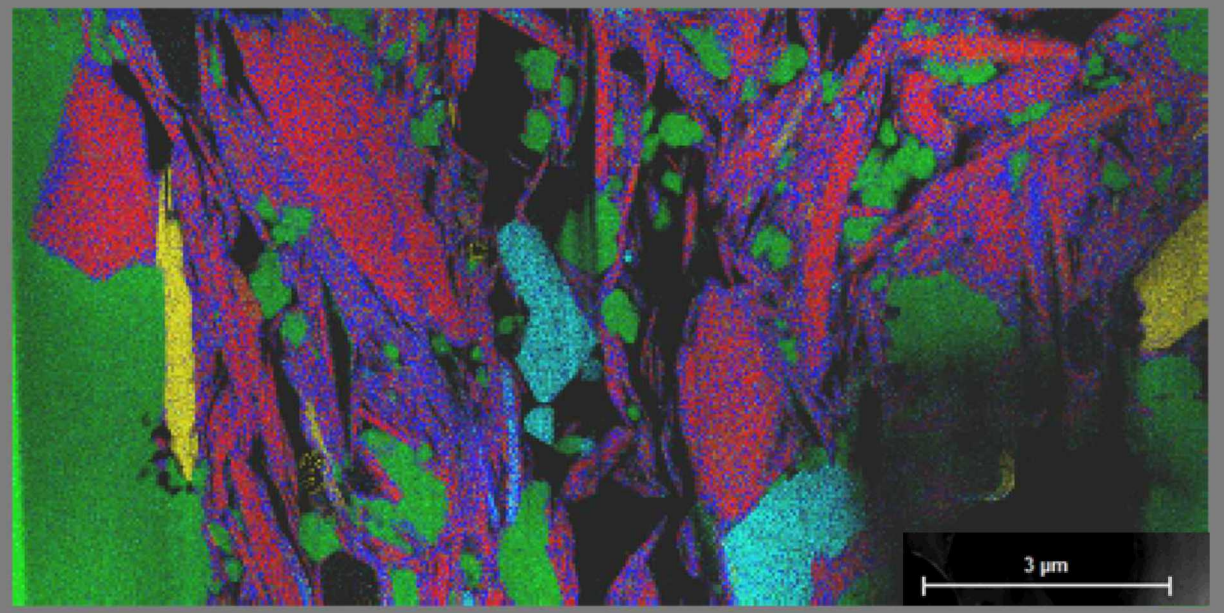


- **$D=CS^T$**
- **Compress** data to get more than 100 counts/new pixel
- **Normalize** for Poisson noise (Eigenanalysis for rank determination…13)
- Compute **Principal Components**
- **Rotate** to simple **spatial** or spectral structure
- Apply **non-negativity** constraint
- **Inverse normalization** for noise
- **25 seconds later…ready for interpretation**



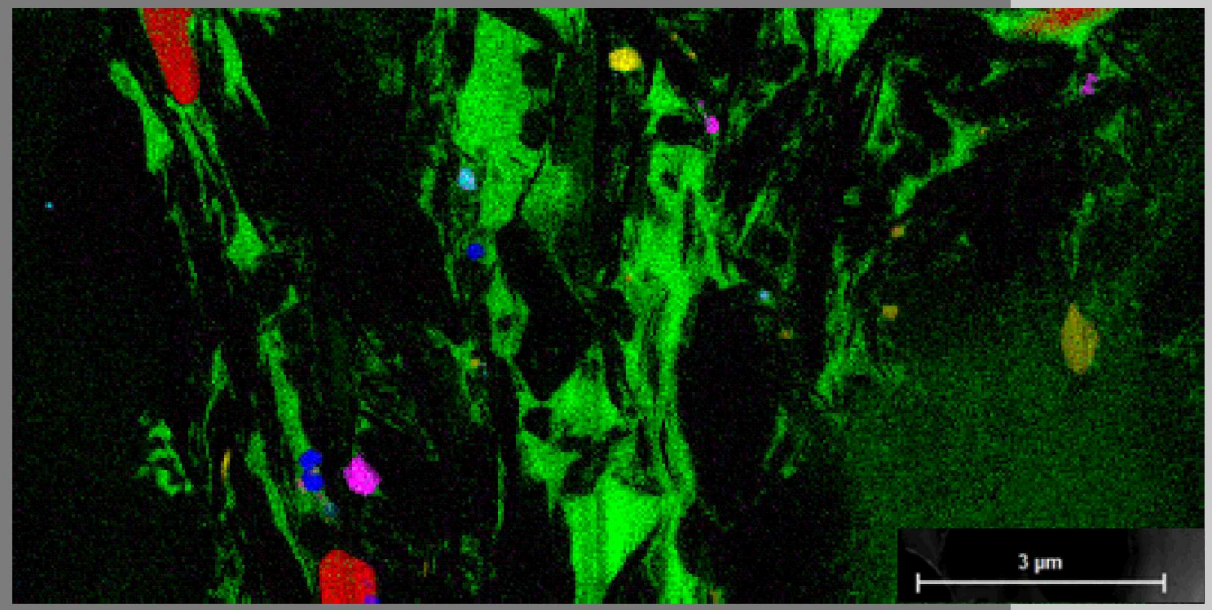
Sandia National Laboratories

Silicates



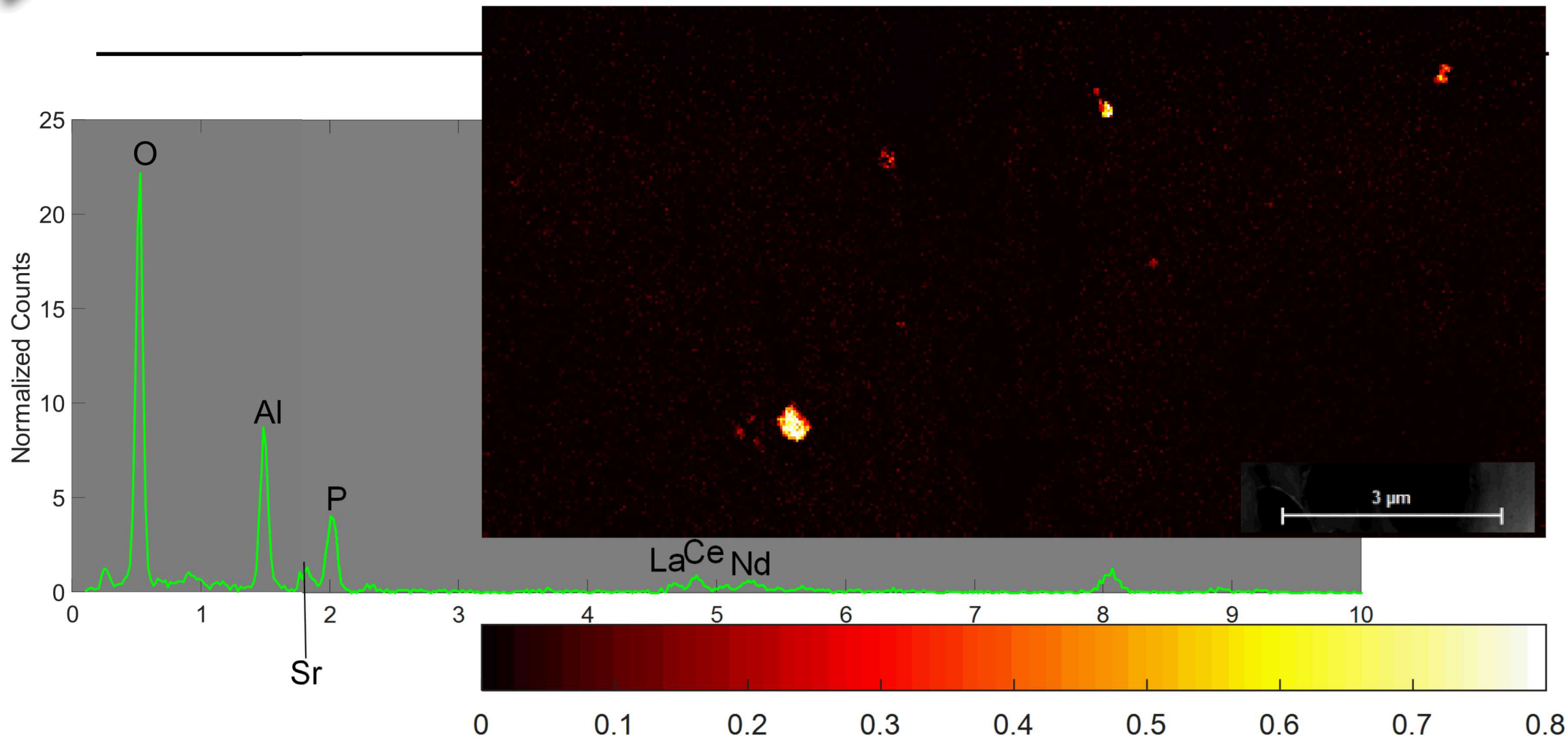
Red = Si-Al-Fe-K-O
Green = Si-O
Blue = Si-Al-K-O
Cyan = Si-Al-Na-O
Yellow = Fe-Si-Al-Mg-O
Black = Non-silicates/hole

Non-Silicates



Red = Ca-C-O
Green = C-O-Ca-K-S-Cl
Blue = Fe-S
Cyan = Zr-Si-O (U?)
Magenta = Al-Sr-P-O-(La-Ce-Nd)
Yellow = Ti-O
Black = Silicates

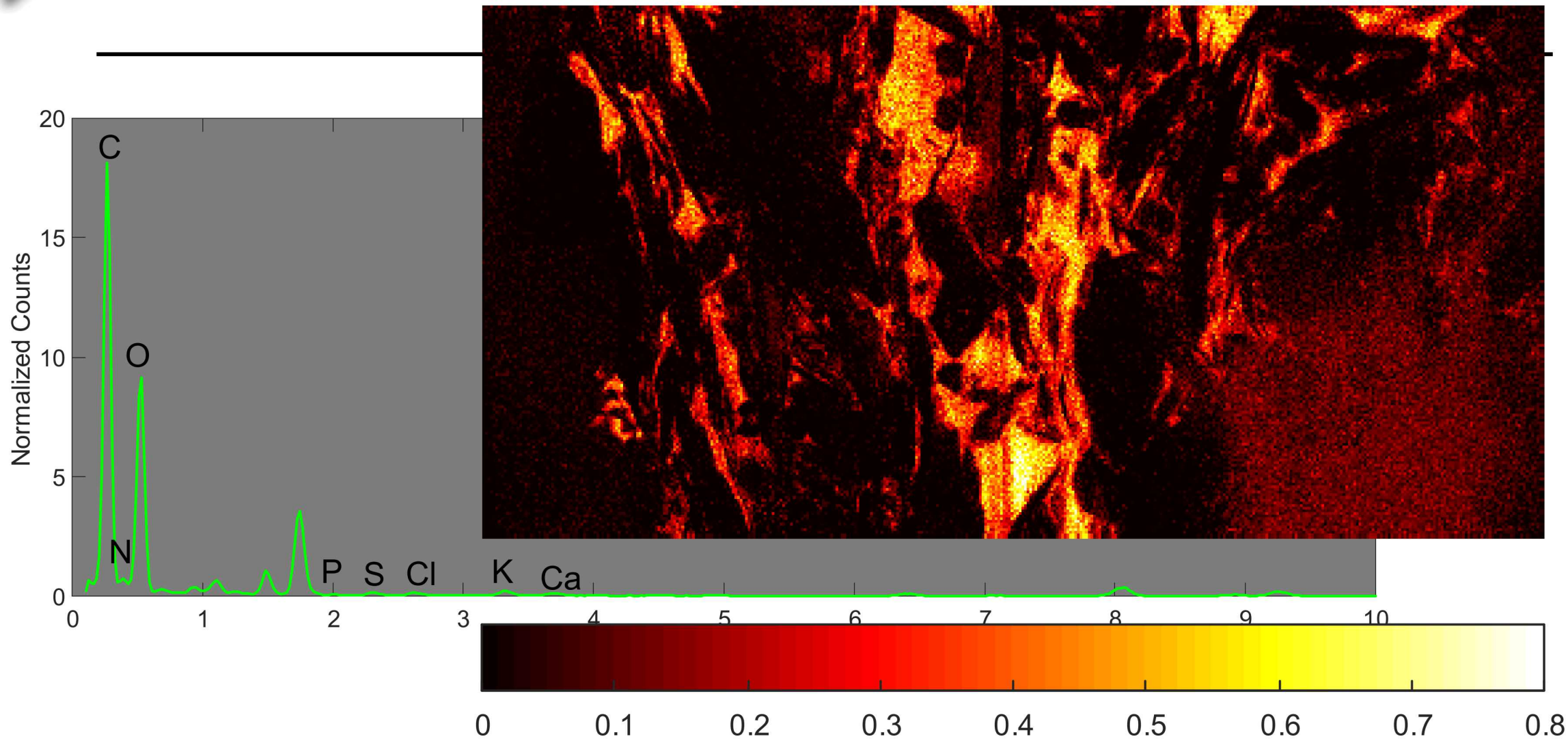
Interesting RE-containing phase



The power of statistics!

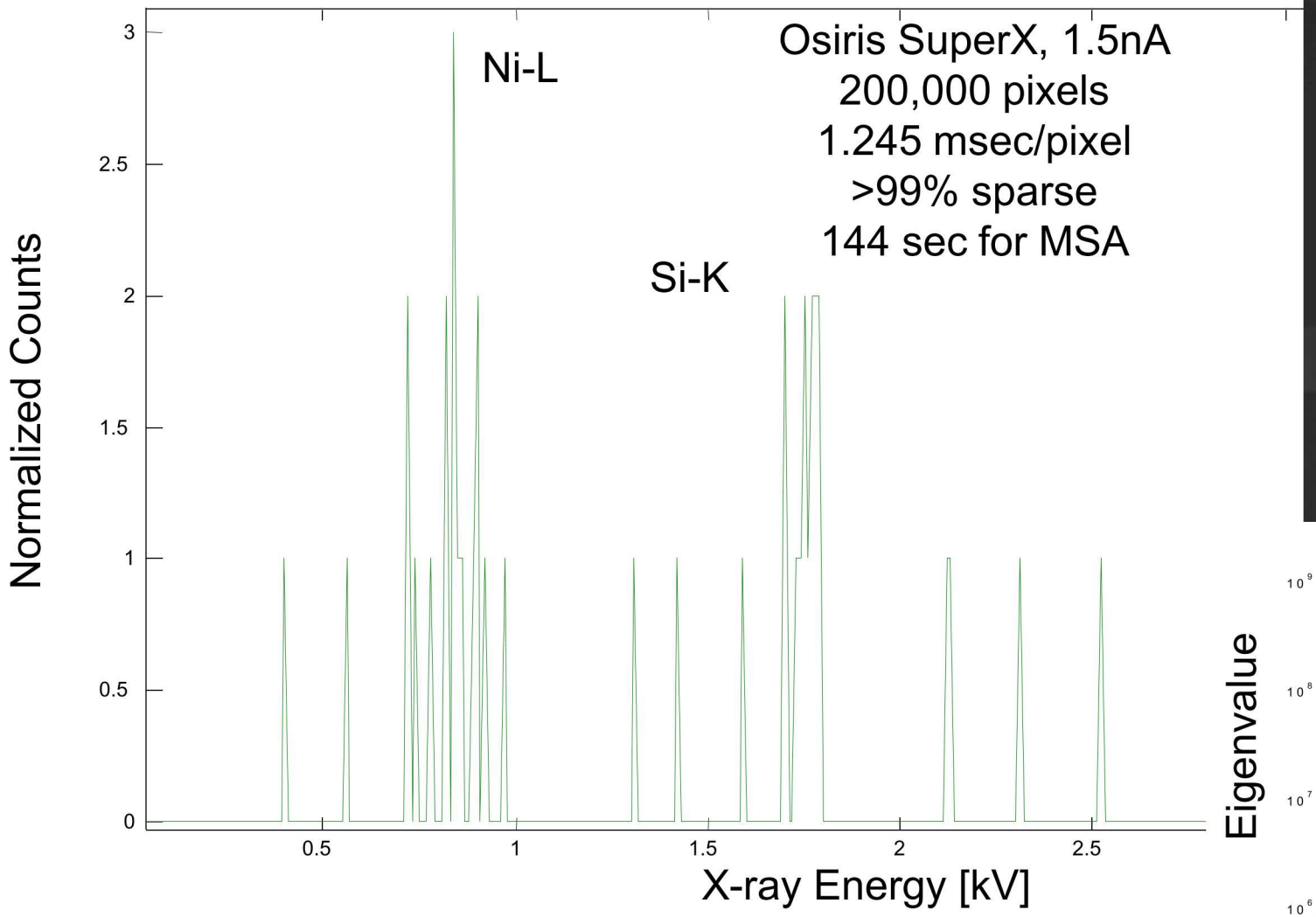
Sandia National Laboratories

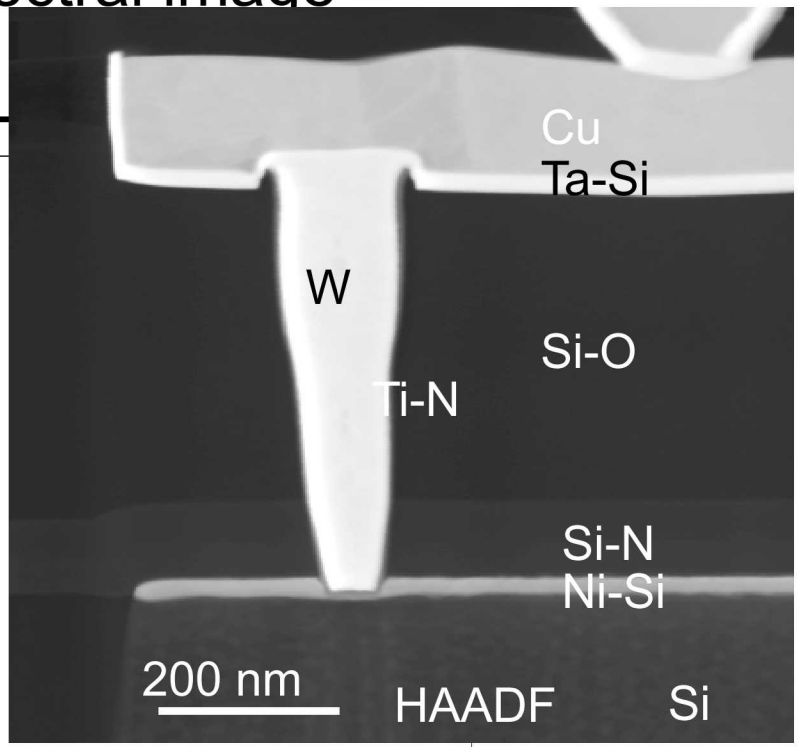
Carbon-containing material

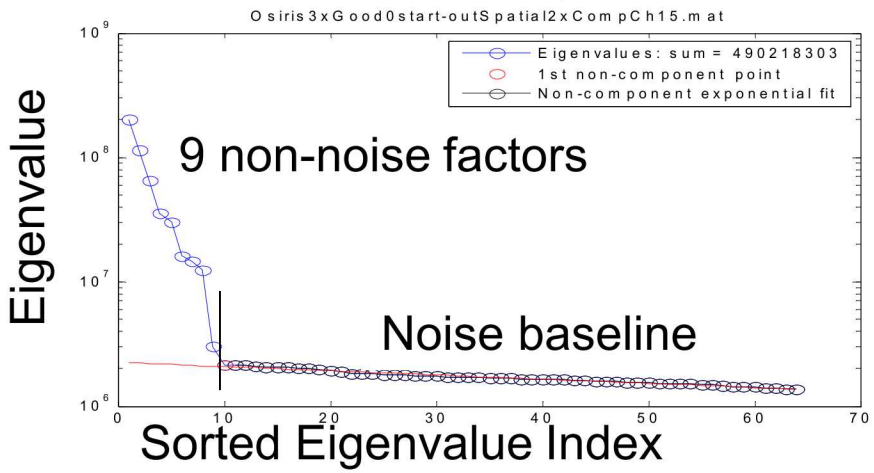


Sandia National Laboratories

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

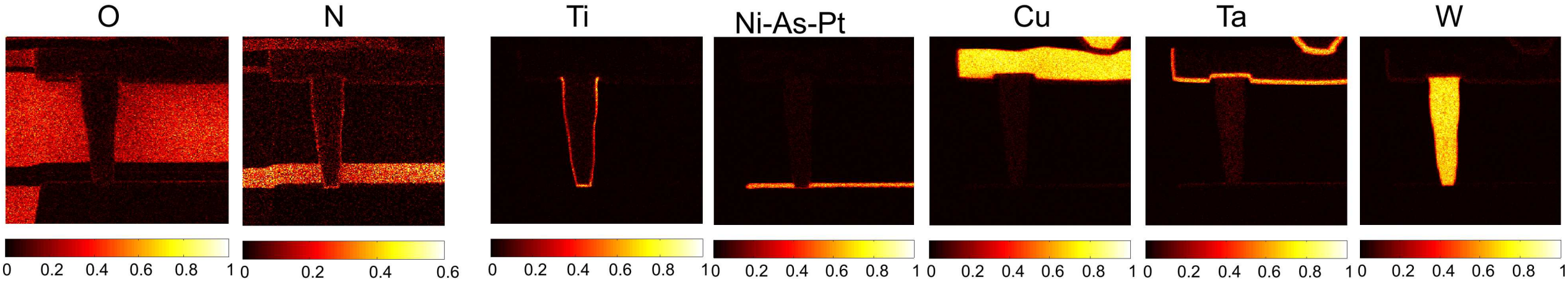


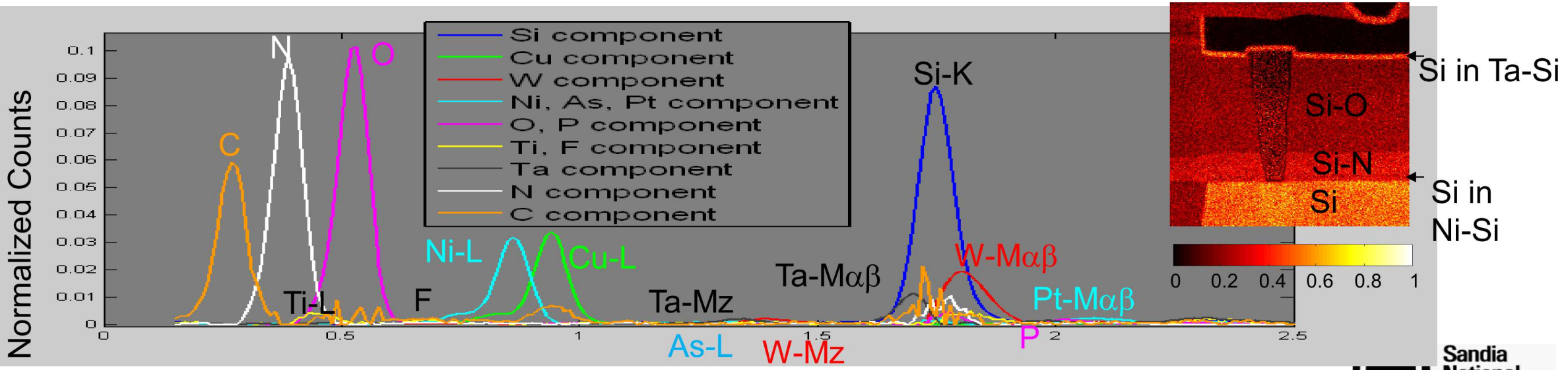




Data courtesy Dmitri Klenov, FEI on sample provide by SNL

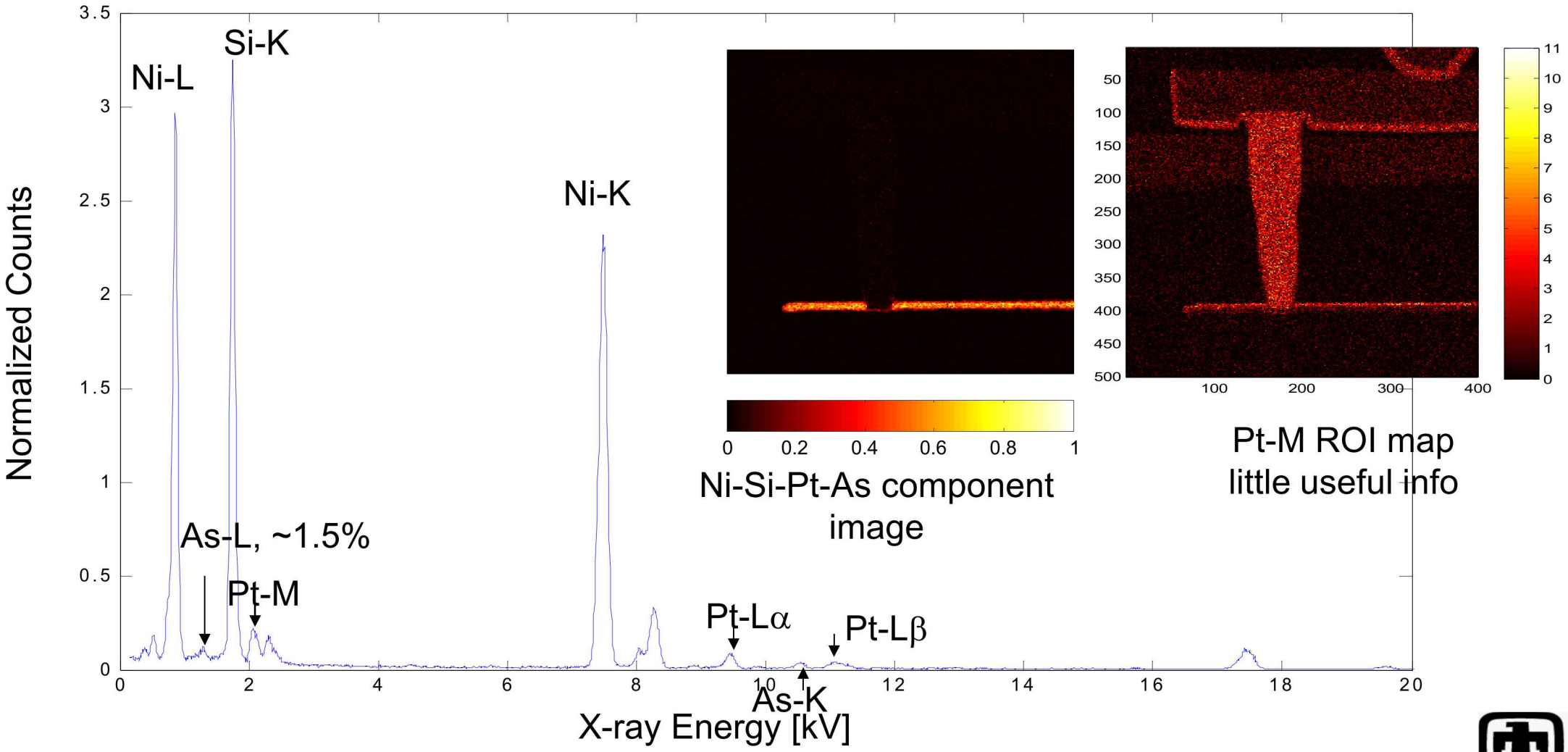
Low end, Spectral-Domain Simplicity
Best Spectral or Elemental 'Contrast'





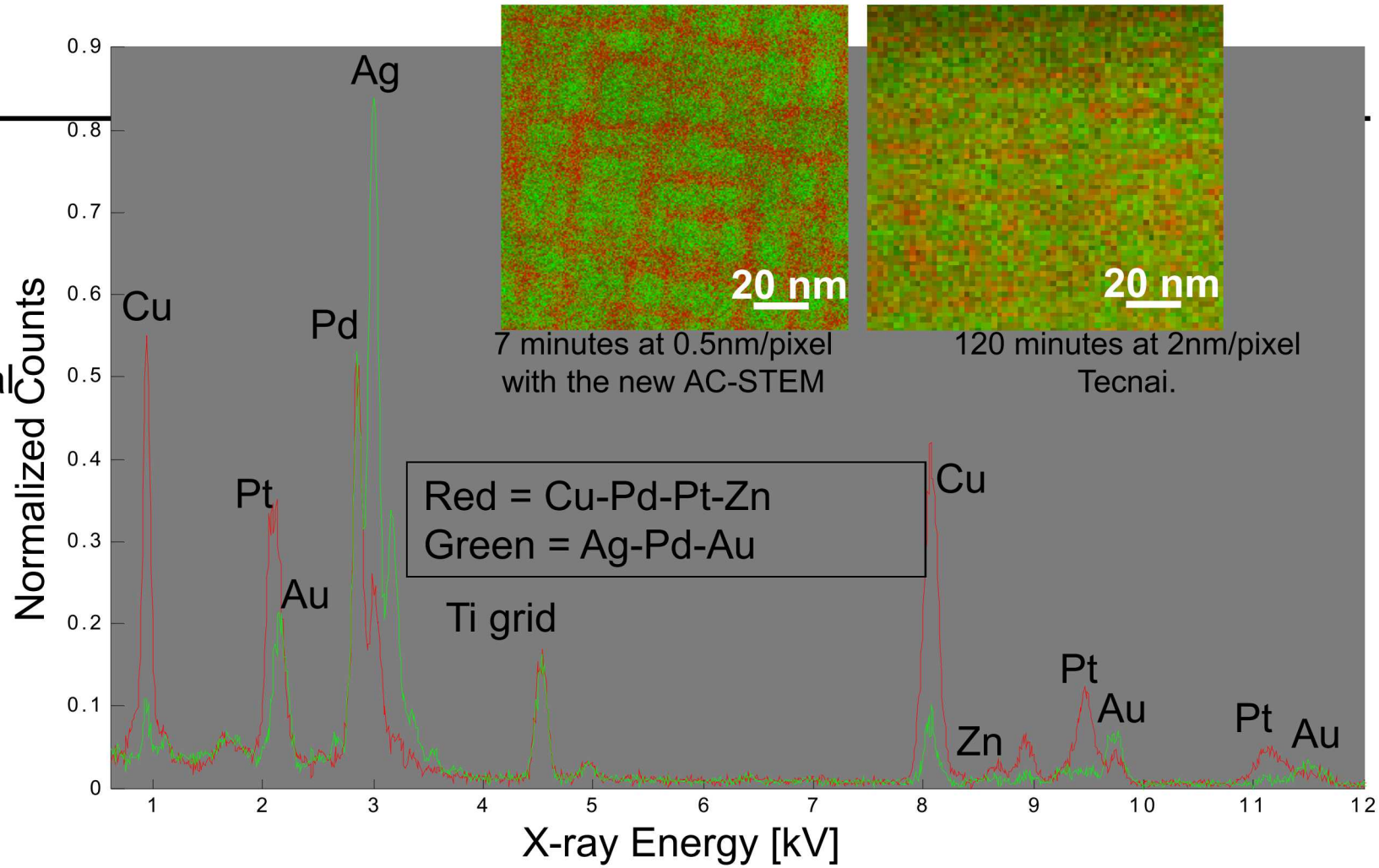
Sandia National Laboratories

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



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.

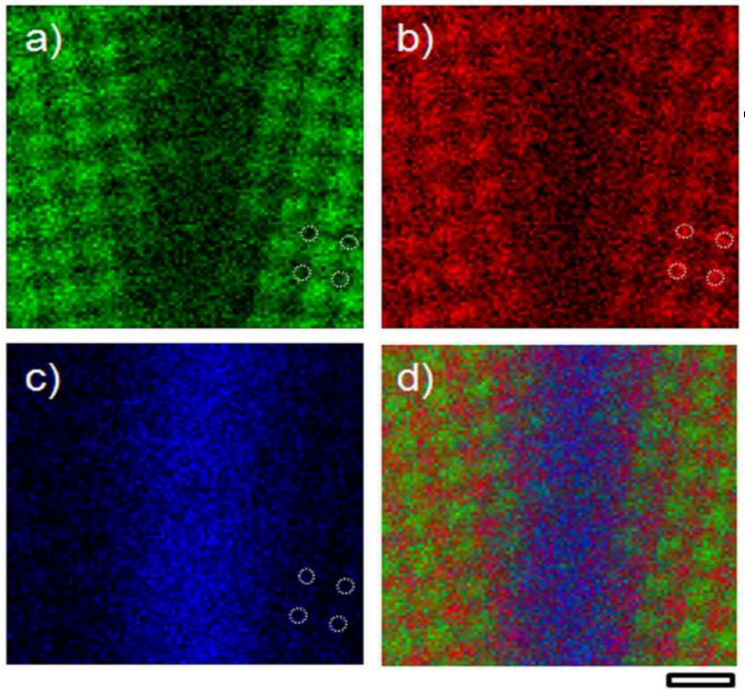
Collaborative work with Don Susan and Zahra Ghanbari of Sandia

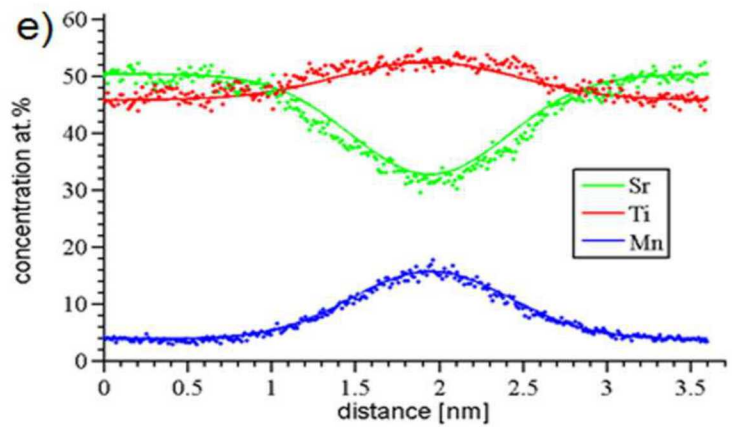
Sandia National Laboratories

Analysis of Mn-doped STO Σ=13 Boundaries

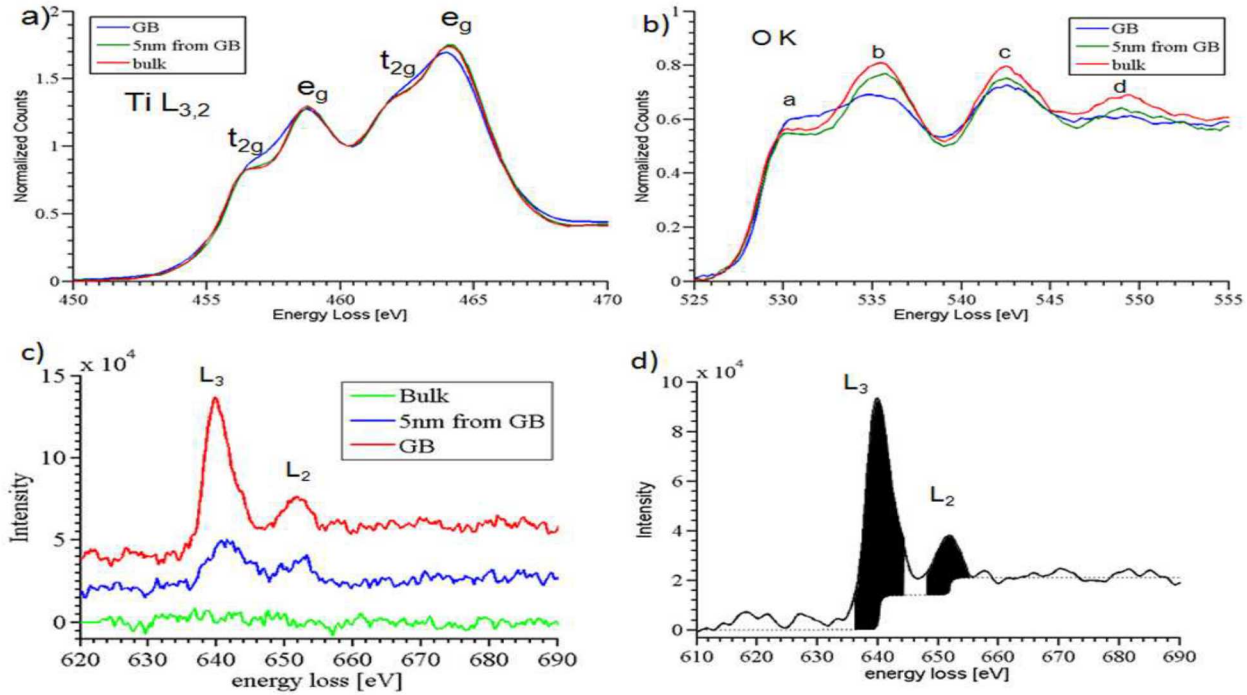
∑13 (510)/[001]

Quantitative EDS and EELS





FWTM enrichment at the boundary less than 2nm



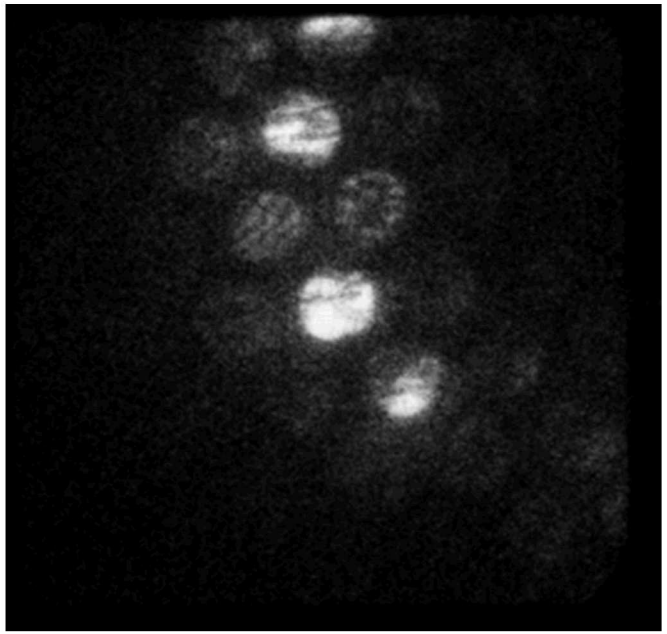
Mn^{+2} at boundary
Mn^{+4} in bulk near boundary
(subsitutional with Ti)

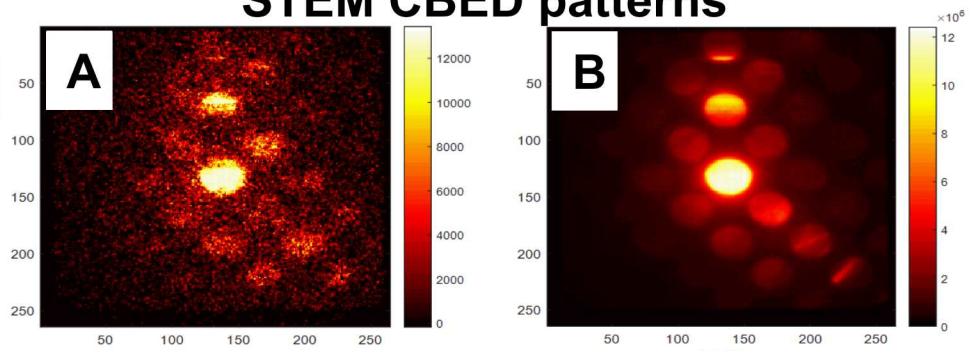
Hao Yang, Paul G. Kotula, Yukio Sato, Yuichi Ikuhara, Nigel D. Browning. "Segregation of Mn^{2+} Dopants as Interstitials in $SrTiO_3$ Grain Boundaries," Submitted (2013).

Sandia National Laboratories

4D-STEM
STEM-CBED and MSA…A Tale of Big Data

- Titan G2 80-200 STEM
- pnCCD mounted below the projection chamber
- 4.8 mrad convergence angle in probe with 30 pA
- 256x256 real-space pixels
- 264x264 reciprocal-space pixels
- $4x10^9$ data elements as summed
- No “small” dimension





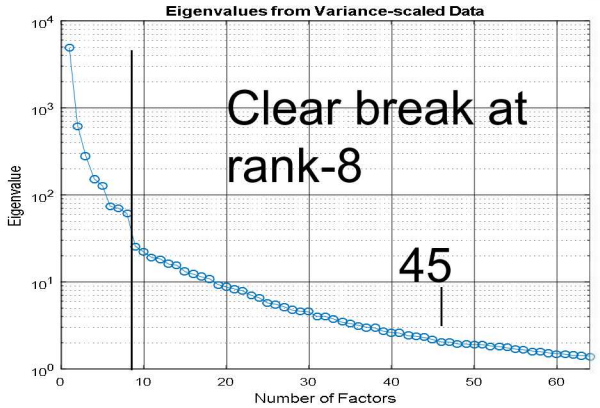
1 msec (1 frame)

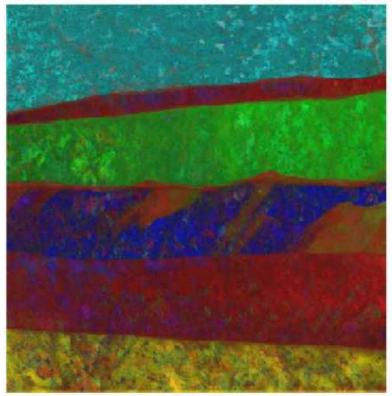
20 msec
(replicates summed)

Sandia National Laboratories

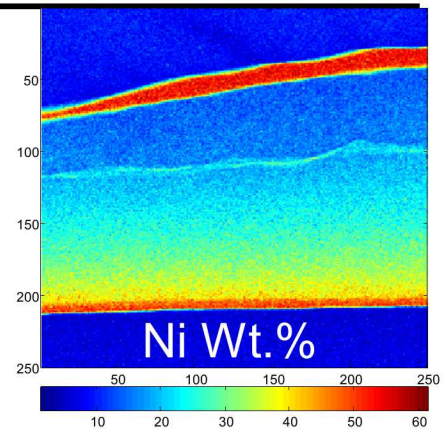
STEM-CBED and MSA…Real-space simplicity

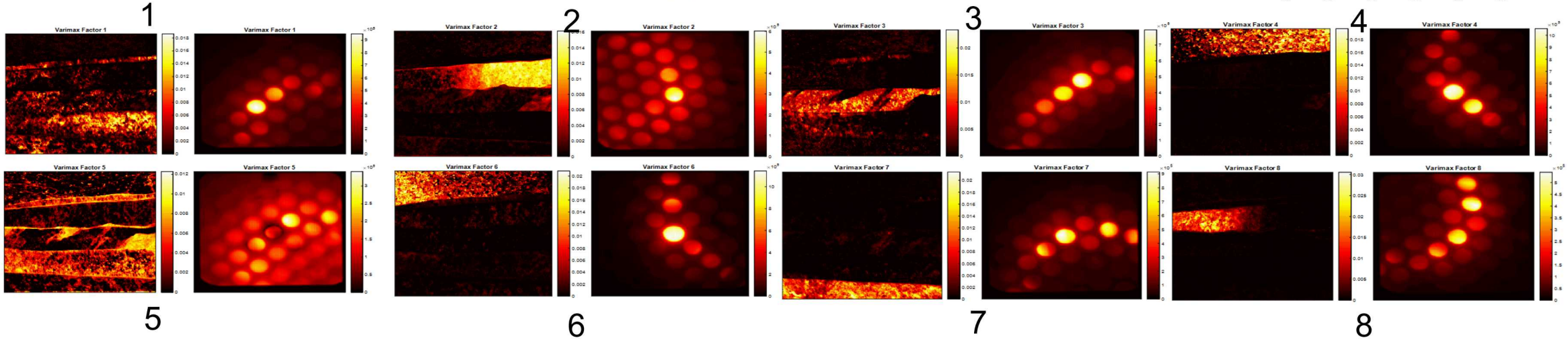
38 Gbyte in, 9 Mbyte after MSA, Compression factor of ~21000





Red = 1+5 (fcc)
Green = 2+8 (fcc)
Blue = 3 (fcc)
Cyan = 4+6 (bcc)
Yellow = 7 (bcc)



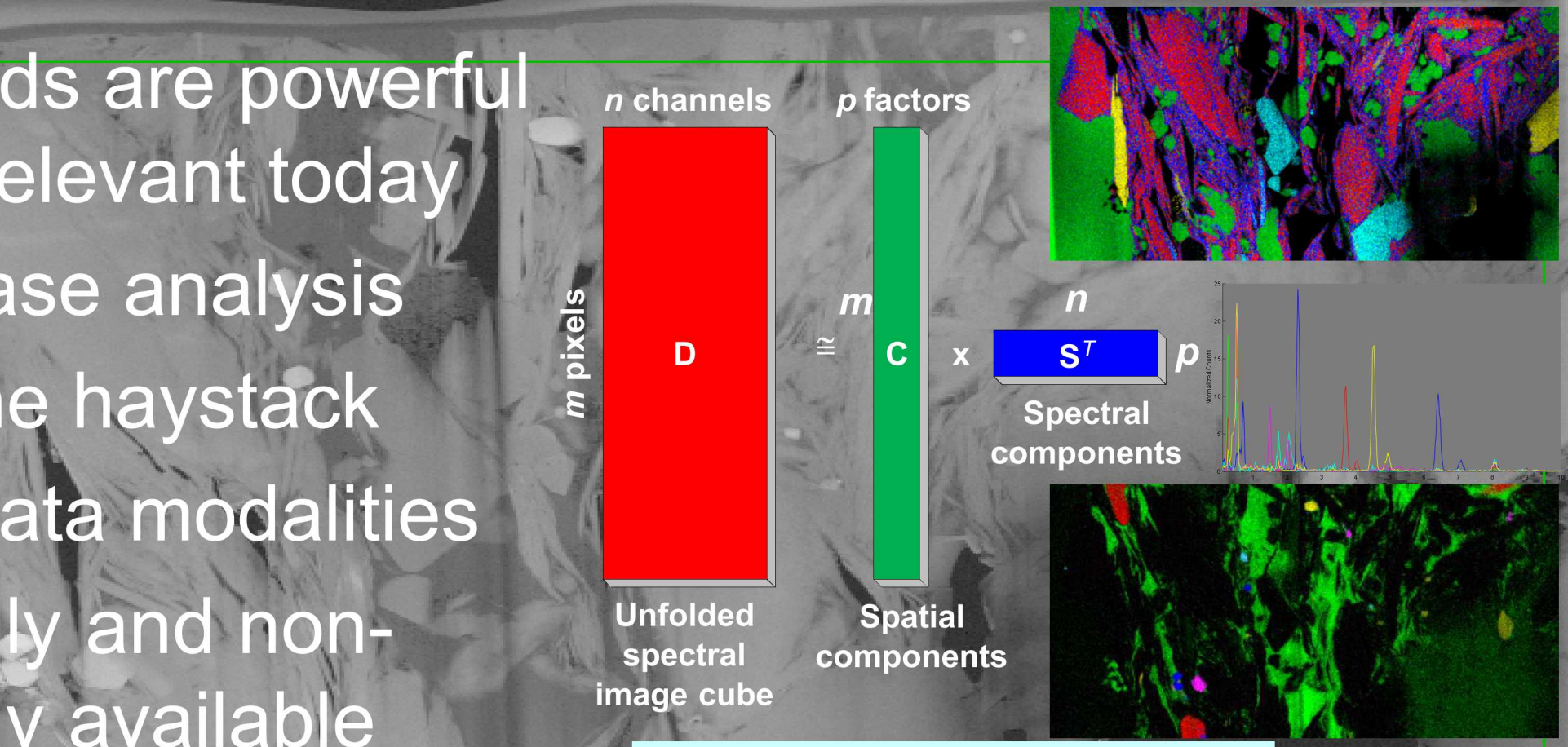


First-pass MSA breaks out largely by crystallographic phase/orientation

Sandia National Laboratories

Conclusions

- MSA methods are powerful and highly relevant today
- General phase analysis
- Needle in the haystack
- Additional data modalities
- Commercially and non-commercially available
- Paul.Kotula@sandia.gov



Analysis goal: Obtain an easily interpretable representation of the data