SAND2006-6156C

Recent Developments in Spectral Image Analysis

Future Technologies Conference II

Track 4: Future Trends in Analysis and Characterization

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Sandia National Laboratories

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under contract DE-AC04-94AL85000.

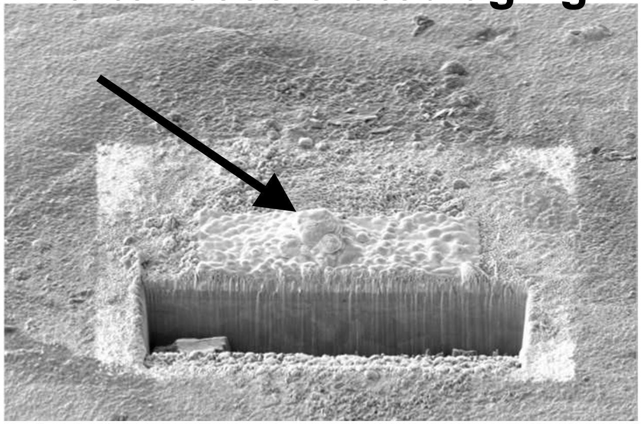
Outline of the Problem

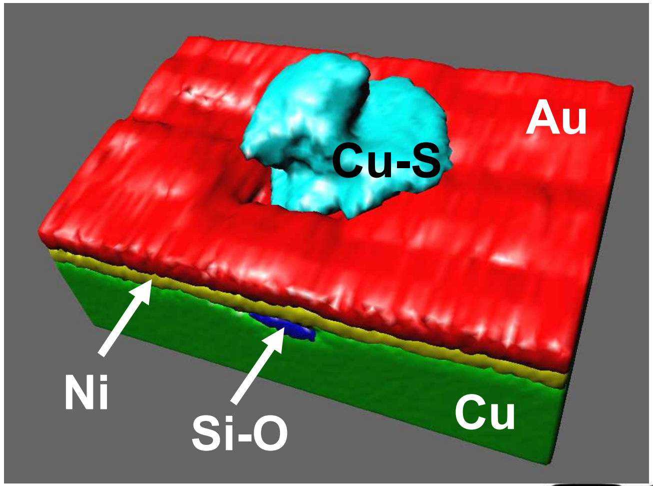
- Materials performance, failure and degradation are often governed by local chemistry
  - Corrosion
  - Interfacial adhesion
  - Impurities, etc.

- Spectral imaging is quickly becoming the tool of choice for comprehensive materials characterization from the nano- to micro- scales

- How do we extract the chemical information from the mountain of spectral data?

Analysis of corrosion product after accelerated aging





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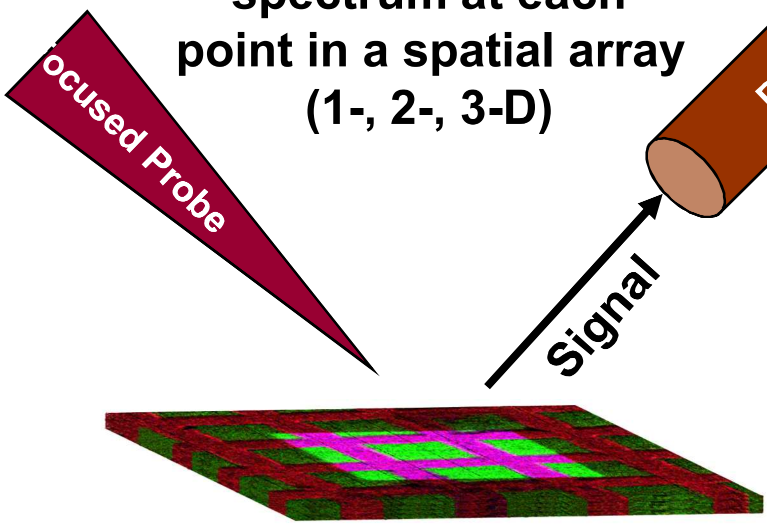
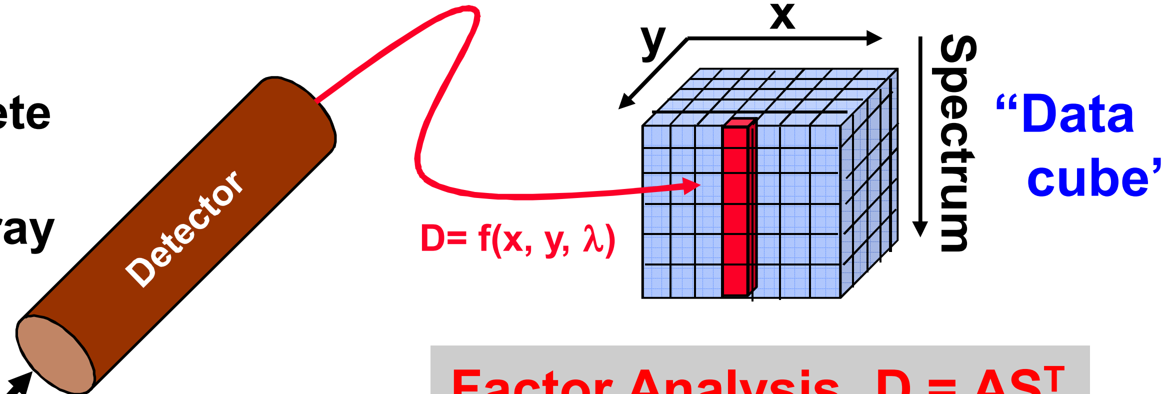
Goals of Spectral Image Analysis

- Unbiased, comprehensive, rapid, routine analysis
  – Find all sources of chemical variation
    - Major phases to single-pixel impurities
  – No foreknowledge of constituents
  – Computation time ~ data acquisition time
  – Use commonly available lab computers
- Easily interpretable representation of the data
  – Spectral pure components look like spectra, etc.
  – Useful to the non-expert (non-chemometrician)
  – Solve the chemical problem at hand

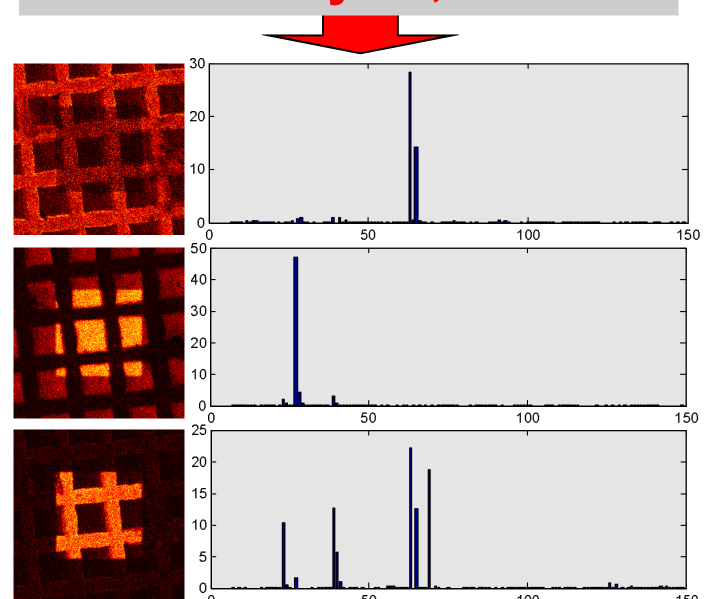
Spectral imaging and Factor Analysis

A spectral image comprises a complete spectrum at each point in a spatial array (1-, 2-, 3-D)





Factor Analysis, $D = AS^T$

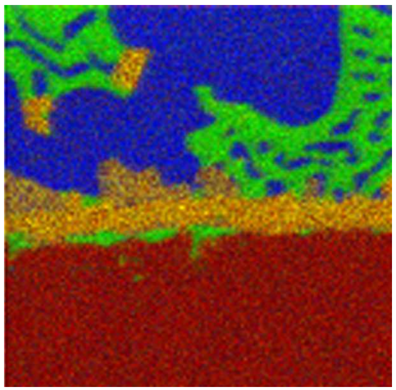


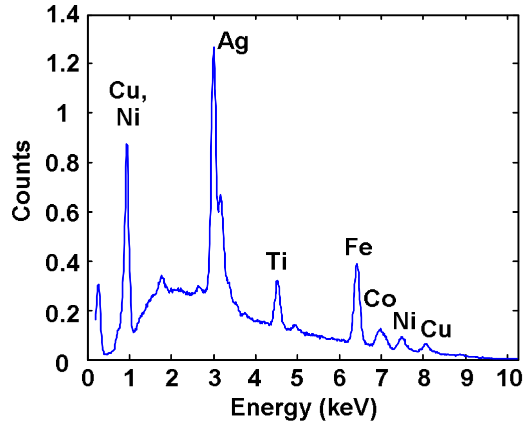
The goal of FA it to estimate:

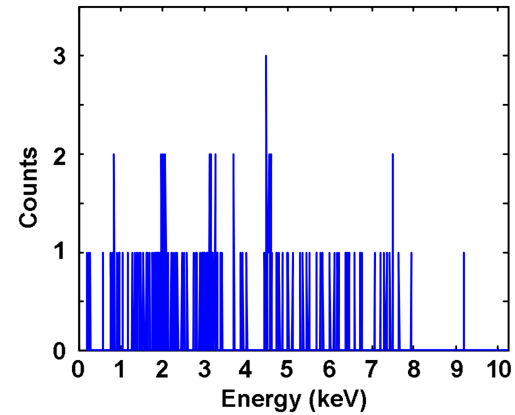
- p, "how many components?"
- S, "what are they?"
- A, "where are they and how much?"

Spectral images are often acquired with low S/N, statistical aggregation is essential

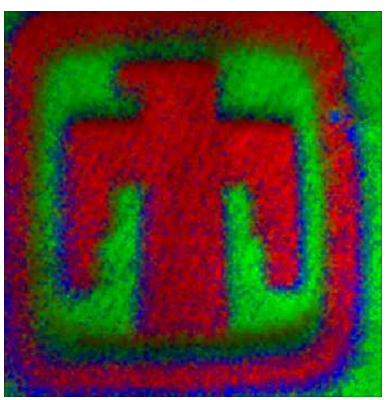
Energy Dispersive X-ray Spectroscopy (EDS)

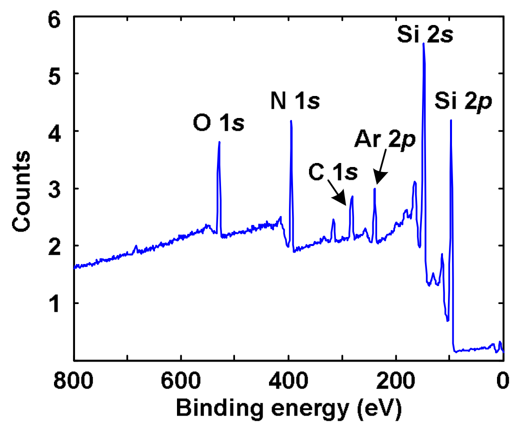


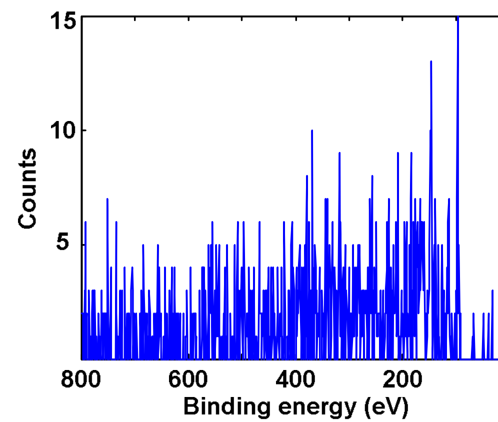




X-ray Photoelectron Spectroscopy (XPS)







Analysis accounts for Poisson Statistics

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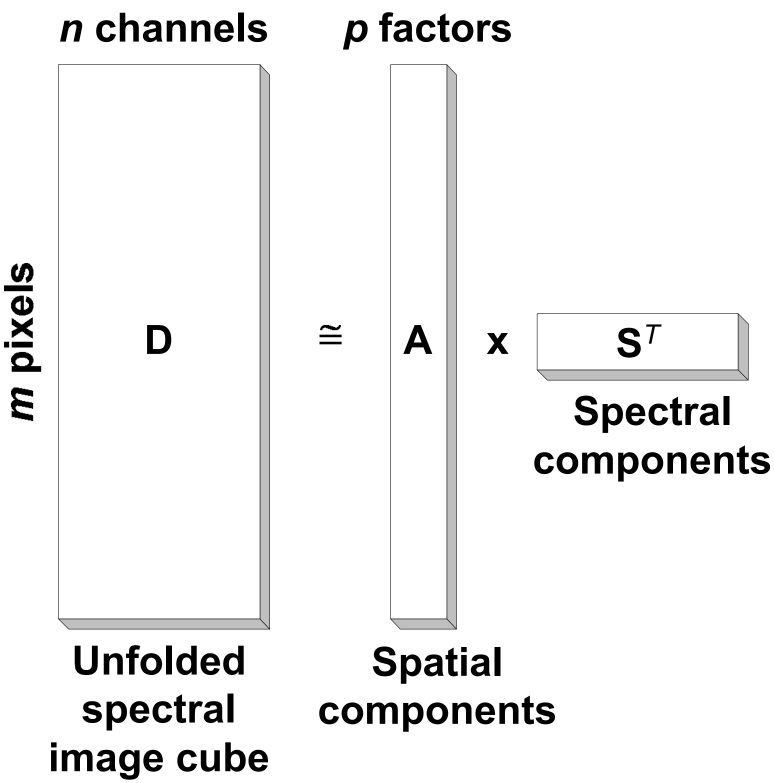
Factor models suffer "rotational ambiguity," additional criteria are needed for uniqueness

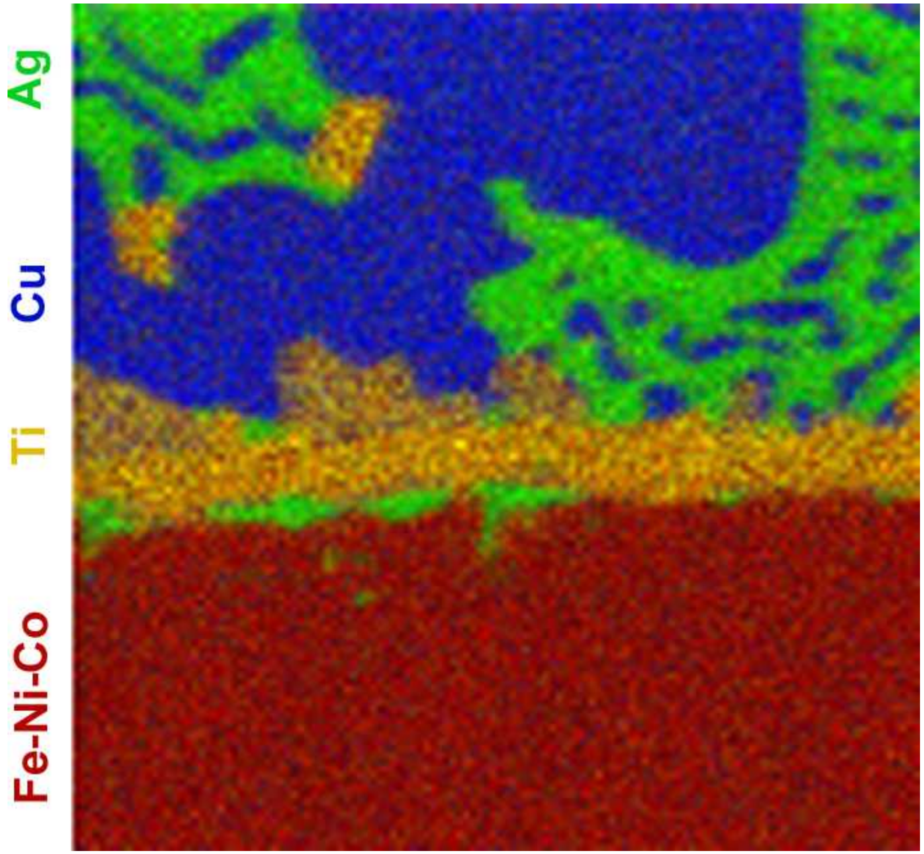


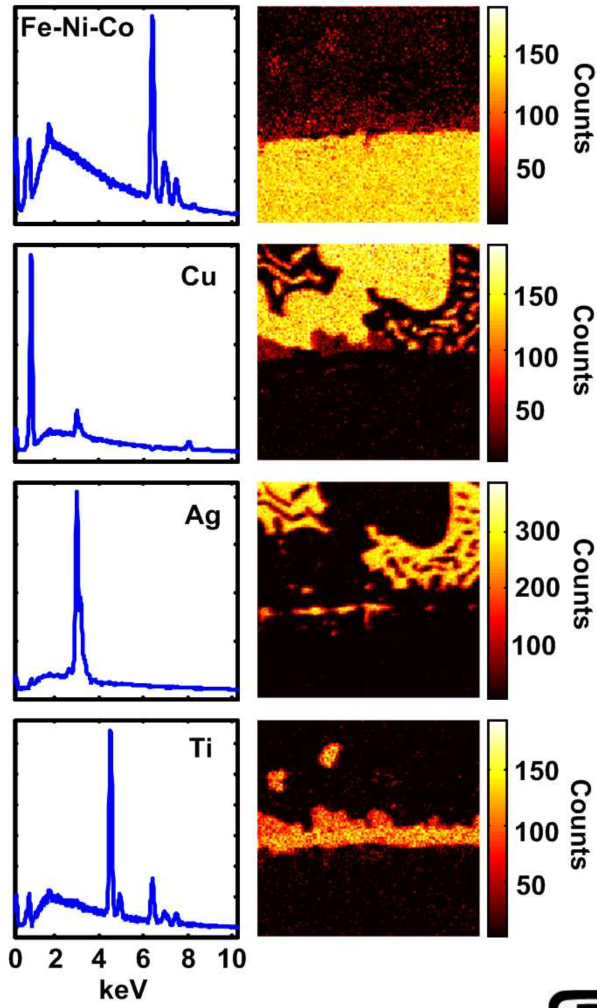
Analysis goal: Obtain an easily interpretable representation of the data

- 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
  - Rotate factors to "simple structure"
- Alternating Least Squares (ALS)
- MCR-ALS
  - Non-negativity of A and/or S
  - Simplicity/sparsity
  - Equality, closure and others

A simple example: Energy Dispersive X-ray Analysis of a Braze Interface

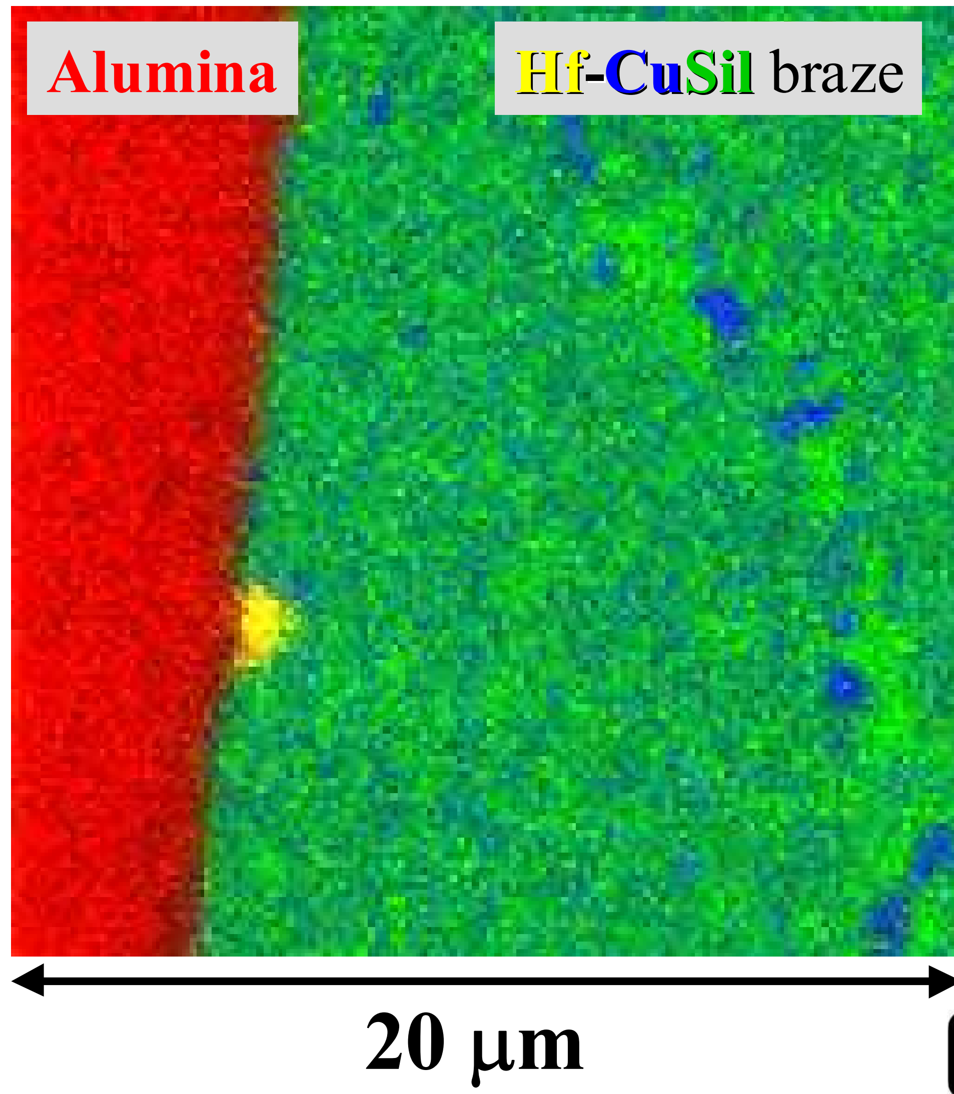
RGB Composite Image



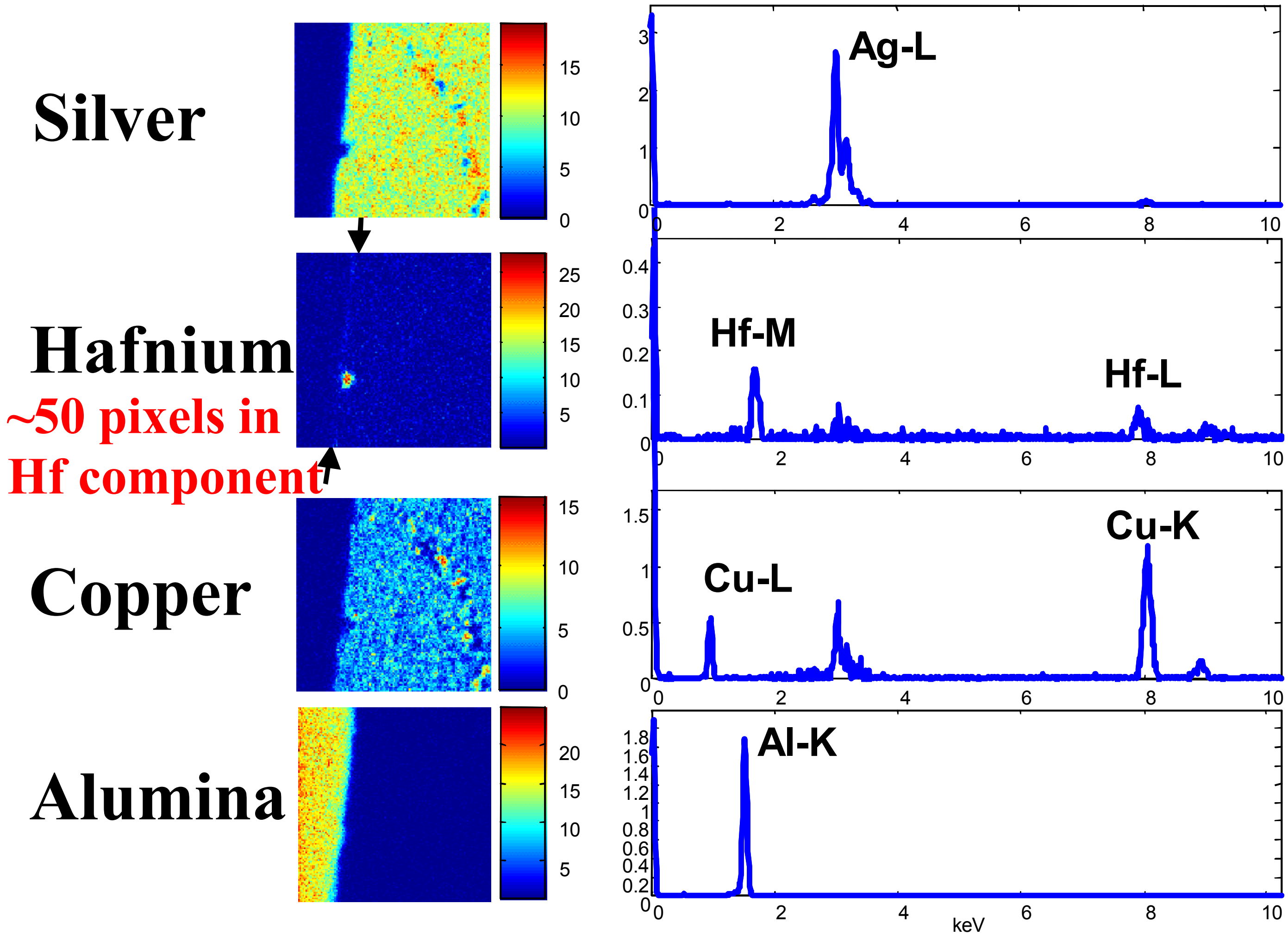


Where’s the Hafnium?

Red=Al_2O_3
Green = Ag
Blue = Cu
Yellow = Hf



Hafnium was found as an interfacial inclusion by spectral imaging



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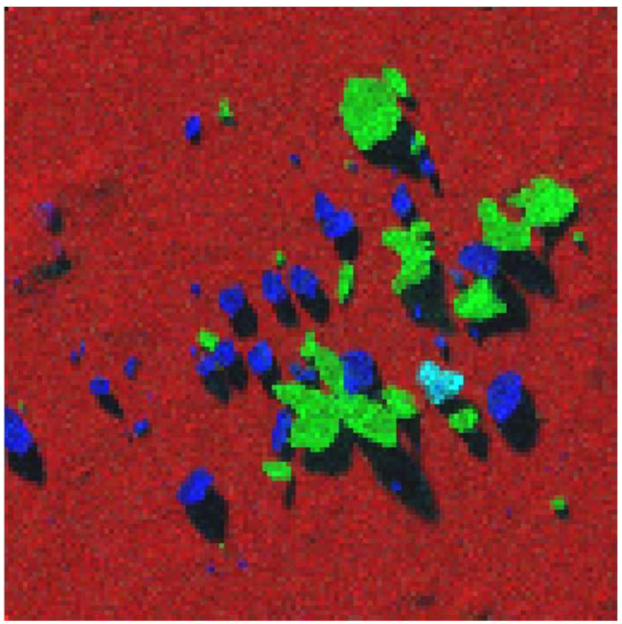
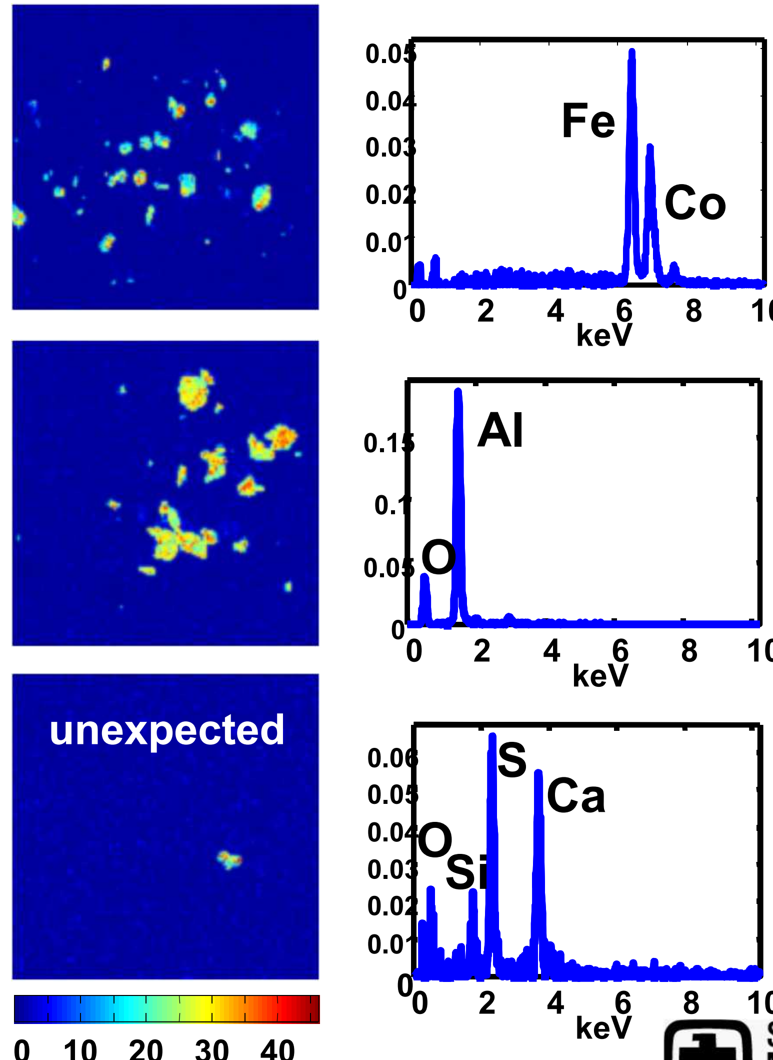
Spectral imaging can solve the “needle-in-a-haystack” problem

Red = C-support
Green = alumina
Blue = FeCo*
Cyan = Ca-S-Si-O
Black = shadowed support

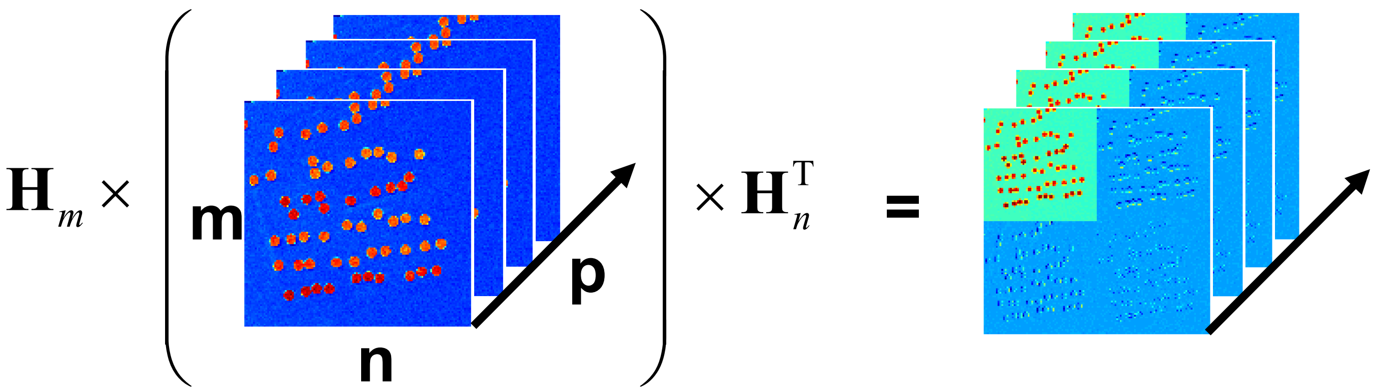


Unexpected Ca-S-Si-O particle is ~40 pixels



Improved performance can be achieved through compression

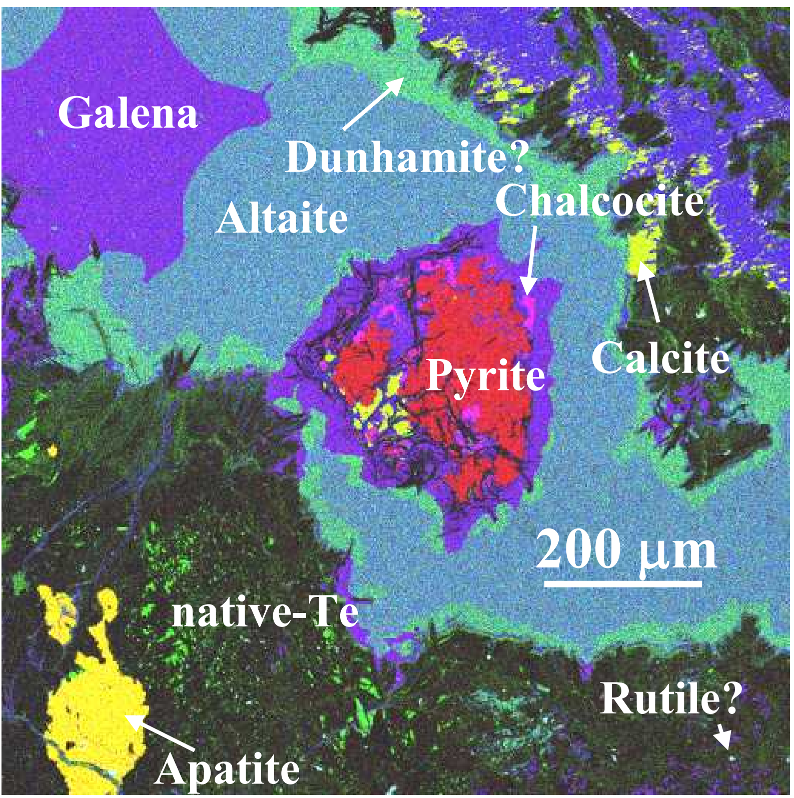
- Spatial compression using wavelets

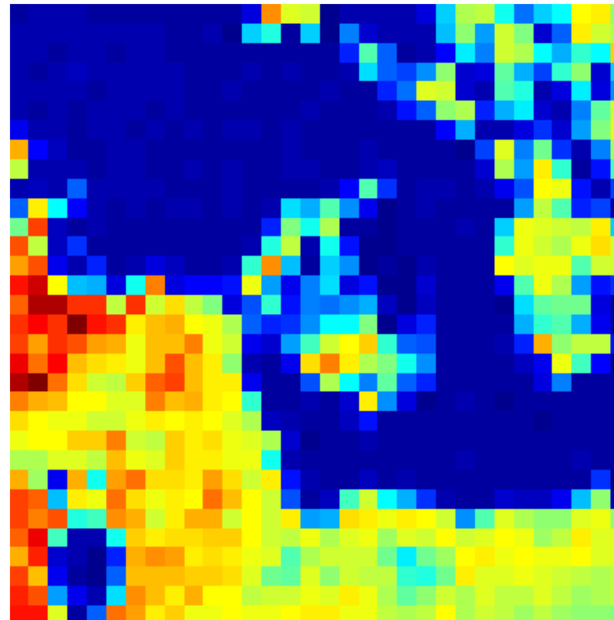


- Spectral compression using principal components
  - ~100-fold compression for chemical images
- Least squares algorithms can be written in terms of the compressed coefficients.
- Larger-than-core-memory data sets can be analyzed
- Compression is a filtering operation which leads to improved S/N and sensitivity

Spatial Compression yields improved performance with no loss of detail

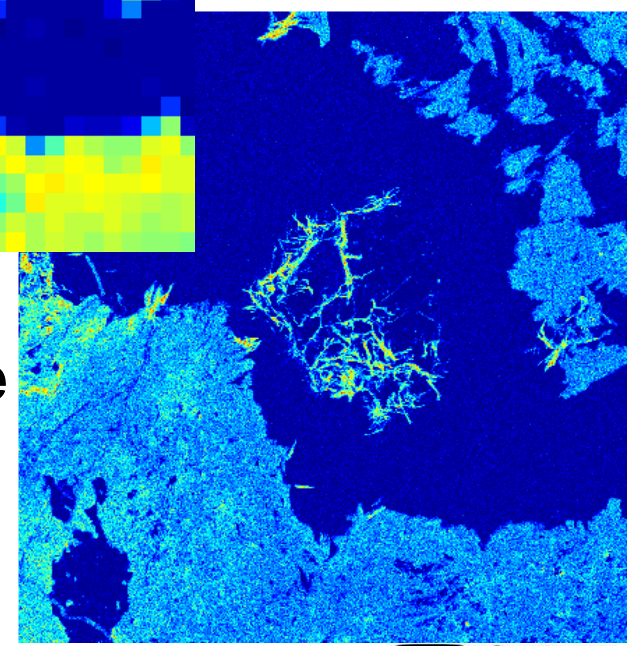
X-ray analysis of tellurium ore





As analyzed (256 X compression)

Final silicate component



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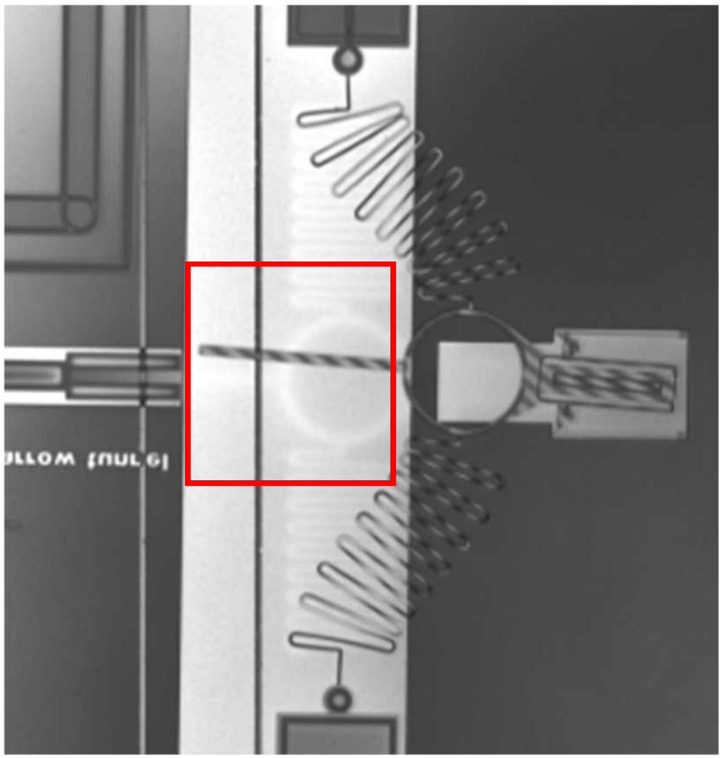
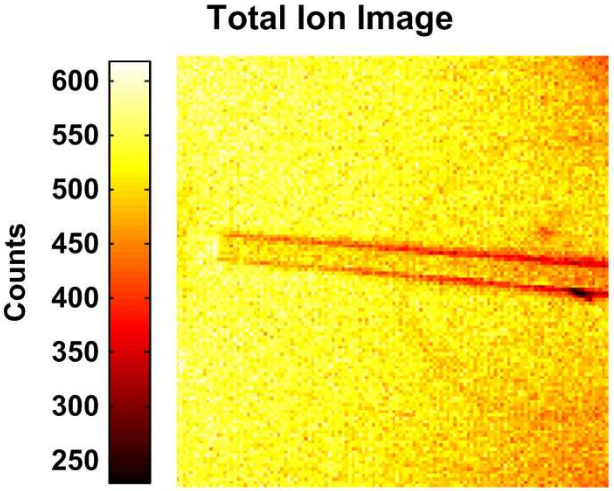
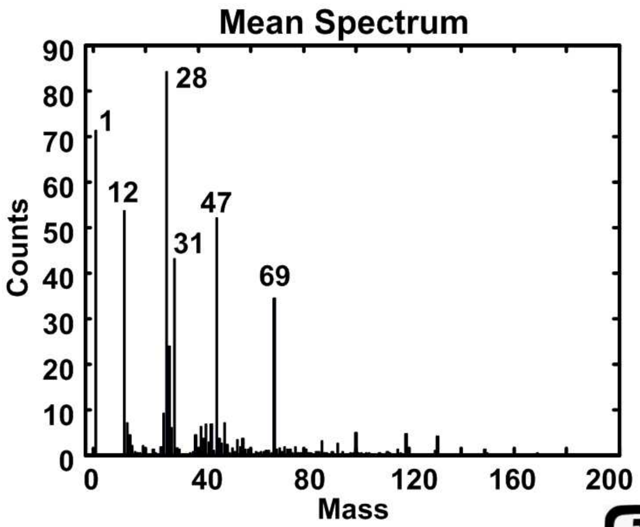
MEMS test device with a beam and an occluded volume (ToF-SIMS)

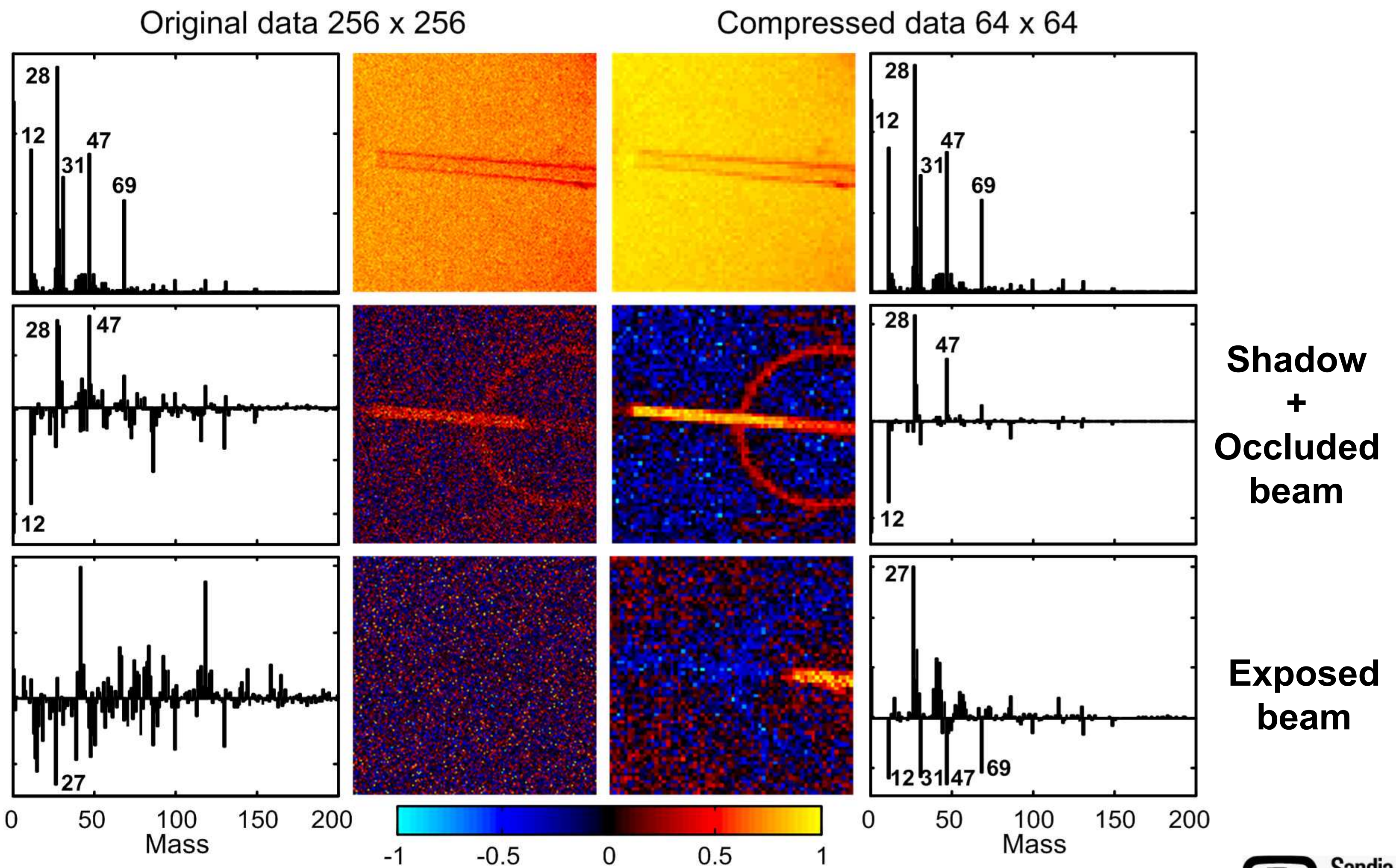






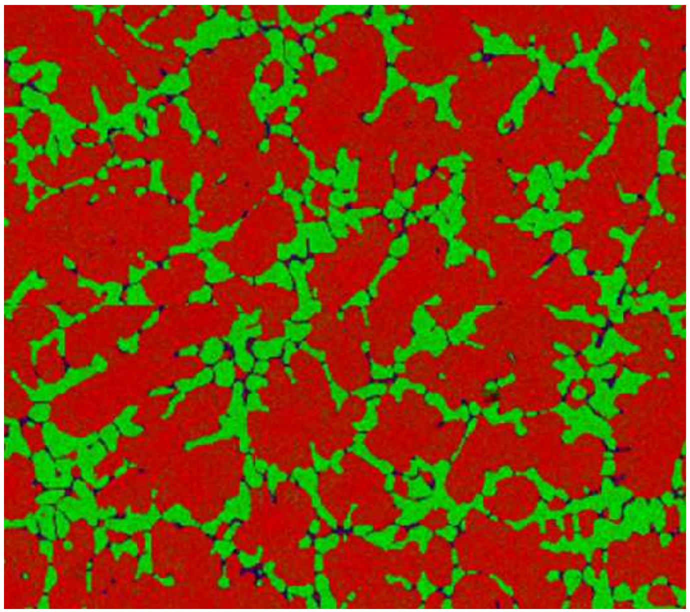
- **Device processed with beam inserted**
- **Device imaged with beam retracted**

16x spatial compression prior to PCA was required to develop chemical contrast



Out-of-core algorithms enable the analysis of data sets that are larger than computer memory

Large-area microstructure of a turbine blade

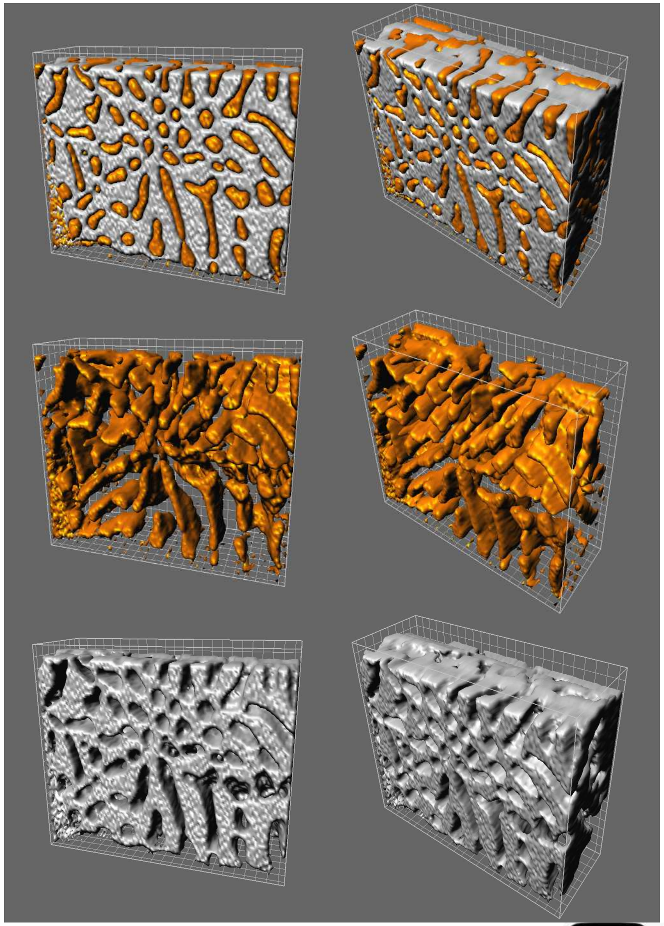


1.2 million pixels x 2048 channels

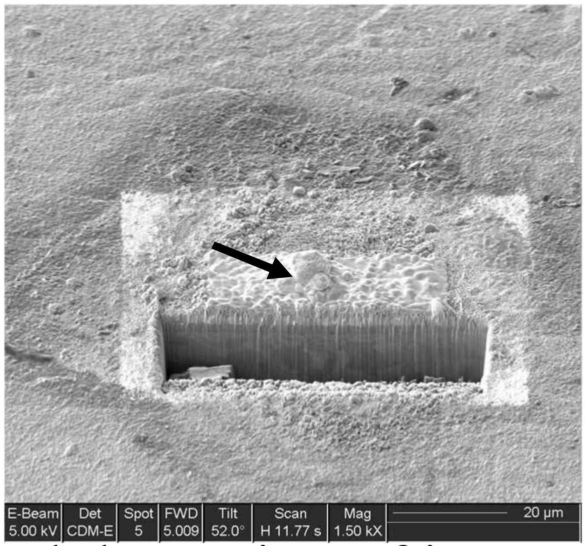
9 GByte data set

12.5 minutes on 4-year-old desktop computer with 2 GByte main memory

3-D microstructure of Cu/Ag eutectic

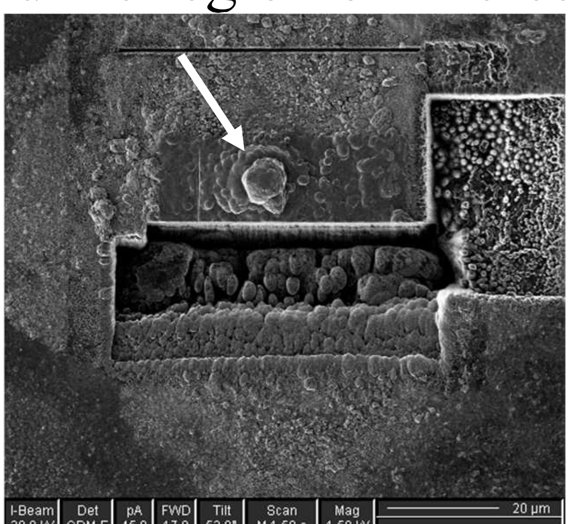


Accelerated Aging of Au-plated Cu Sulfide Bloom on Corrosion Coupon

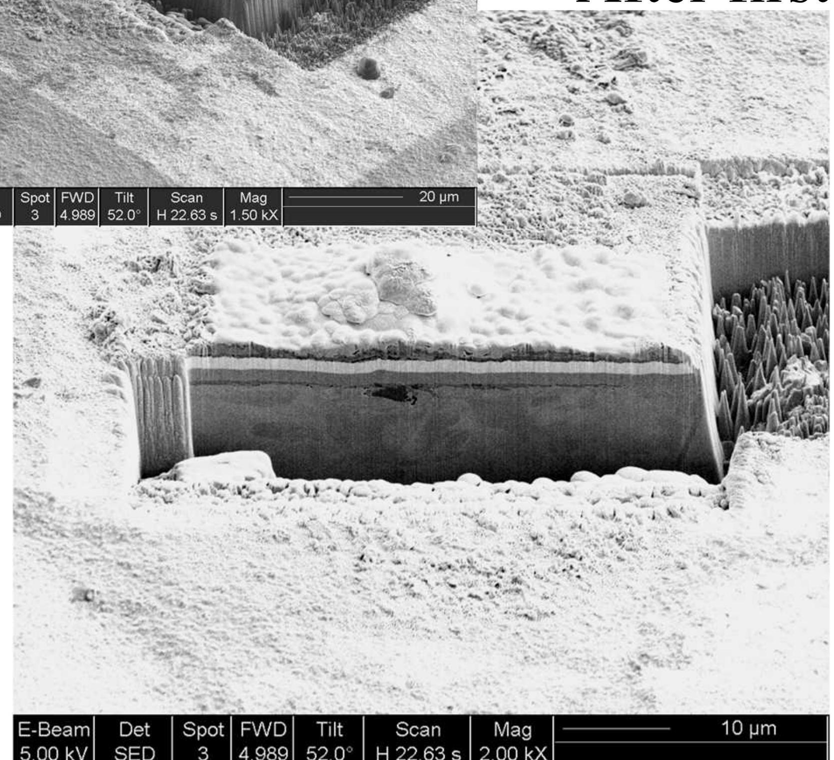


Second trench for x-rays

Find the region of interest



After first cut/polish



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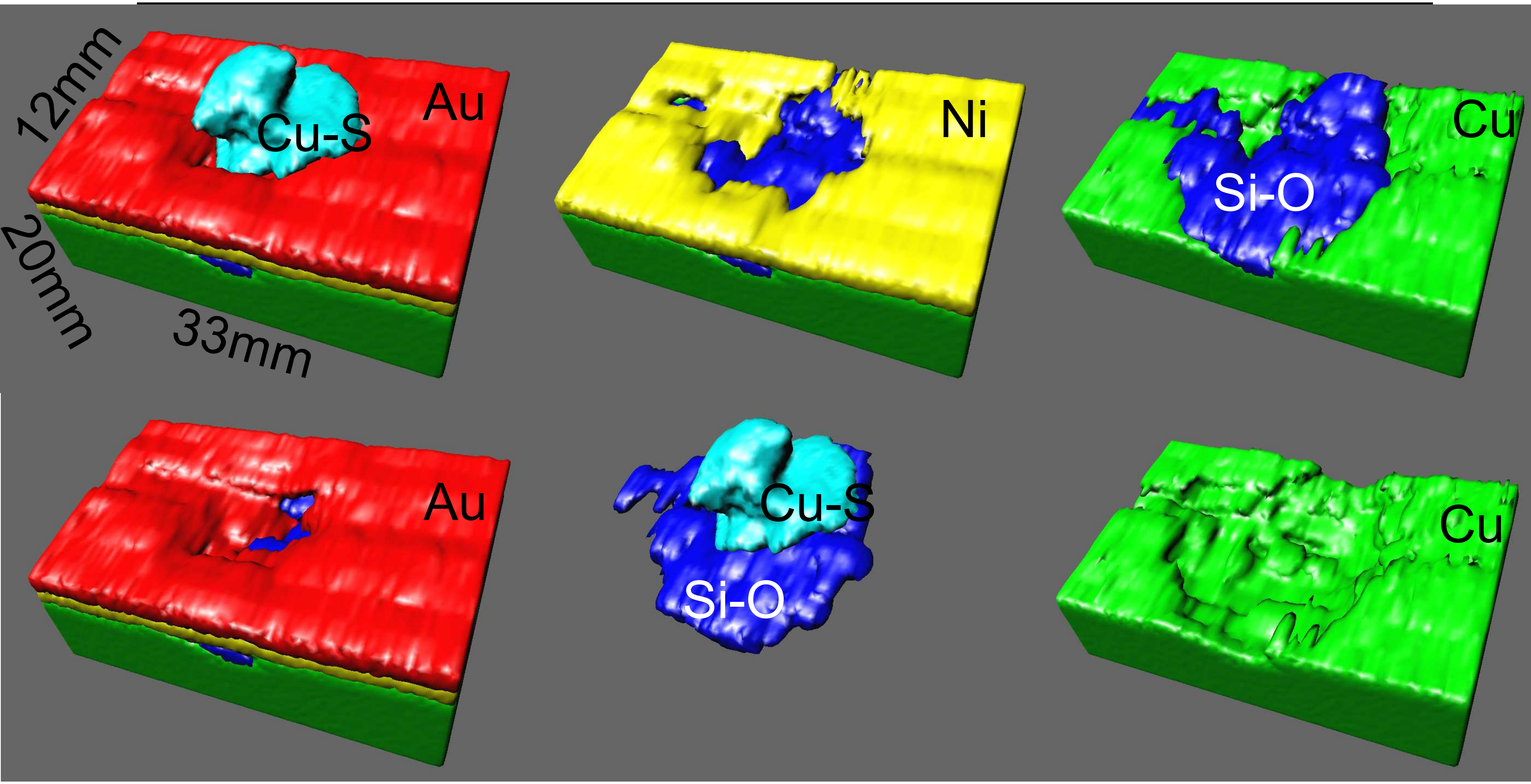
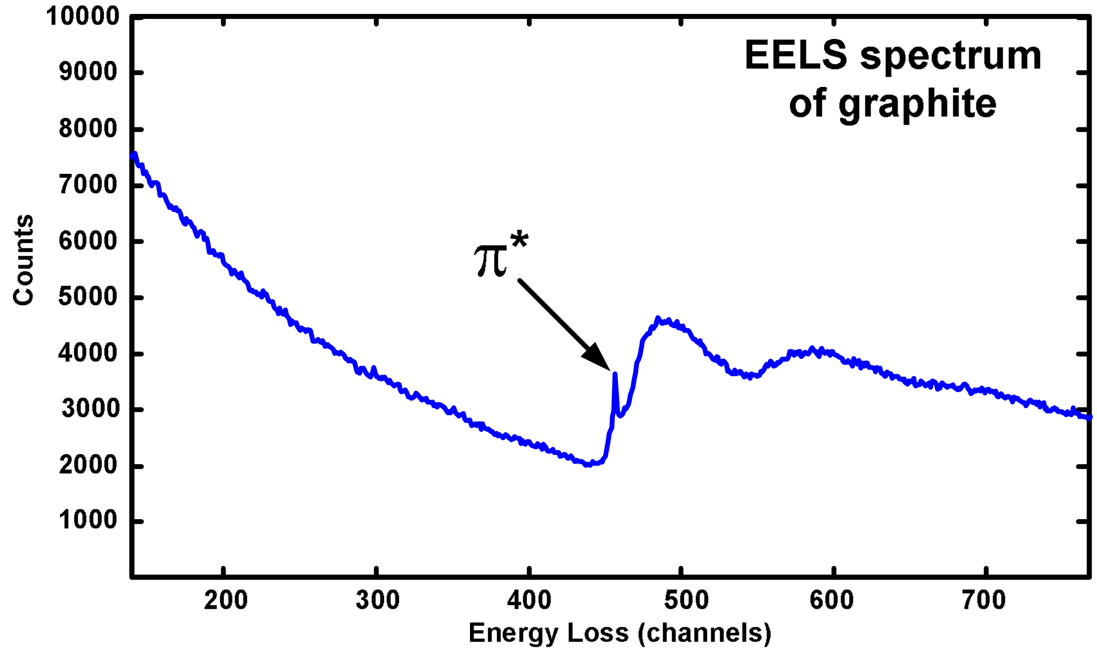
Accelerated Aging of Au-plated Cu
Sulfide Bloom on Corrosion Coupon



Red = Au Green = Cu Blue = Si, O, Cl
Cyan = Cu-S Yellow = Ni

Different spectroscopic problems require different optimization approaches

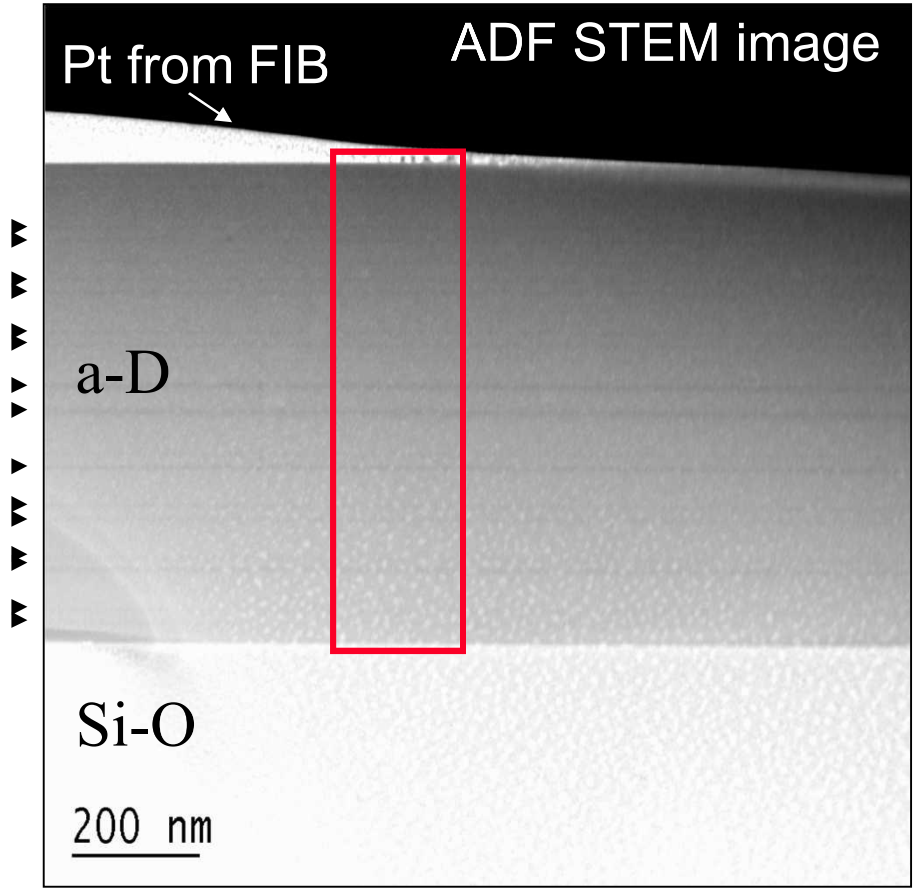


- Observation: many samples are "simple" in the sense that only one or a few chemical components are present at any particular spatial location
- New idea: maximize "spatial simplicity"

EEL Spectral Image Analysis a-Diamond

In collaboration with Tom Friedman
Sandia National Labs, Albuquerque (a-D material)

- **Laser ablation grown a-D**
- **Growth interrupts for annealing**
- **Moving shield in vacuum sys.**
- **Bands of apparently less dense material**
- **FIB Specimen with slight gradient in thickness**
- **Ex-situ lift out sample placed on polymer film**
- **Tecnai F30-ST with TIA (Emispec) spectral imaging**
- **High- and low-frequency high voltage drift/instability**



SI: 200x800 nm, 25x100 pixels
100 msec/pixel

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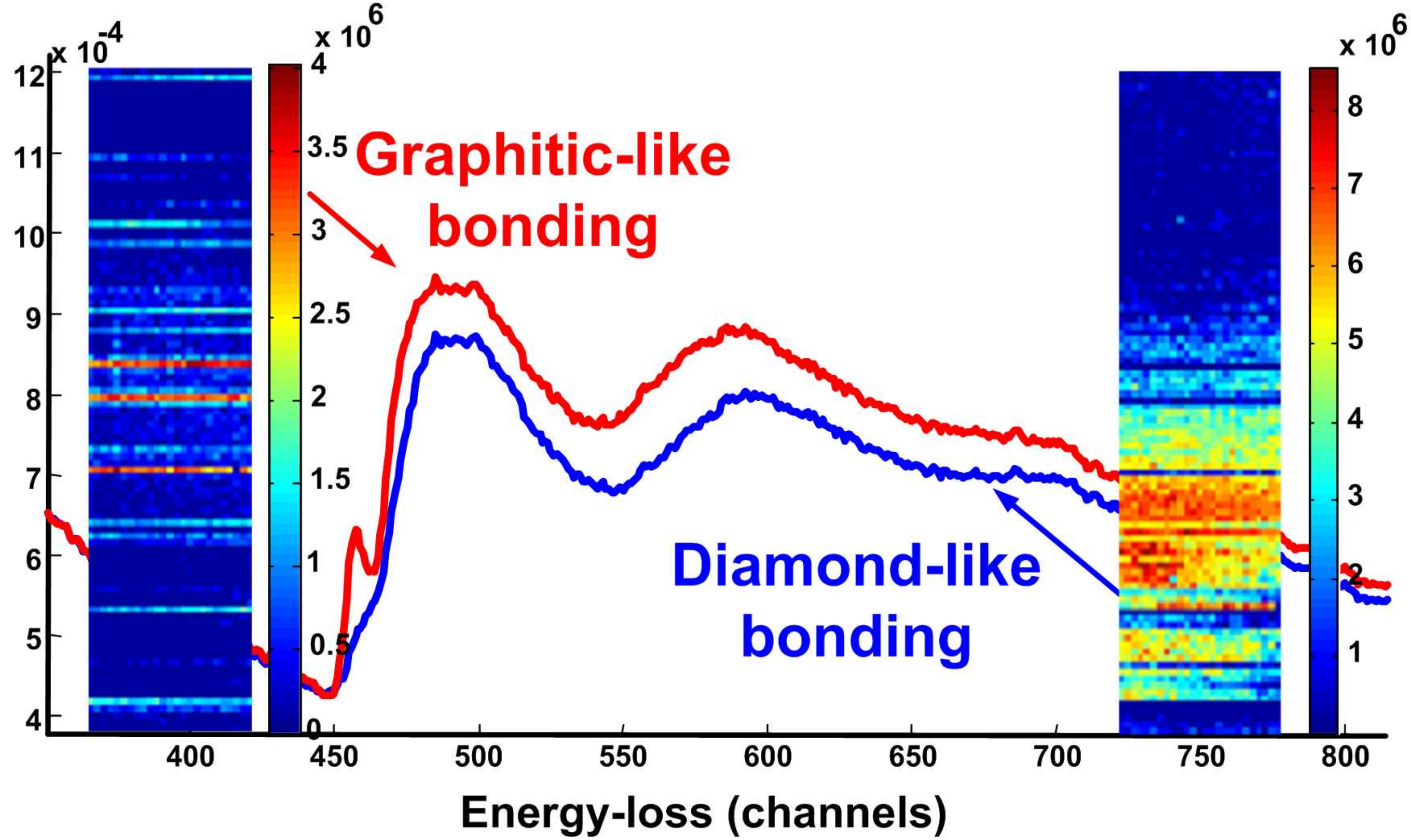
Maximization of “spatial simplicity” enabled identification of graphitic layers



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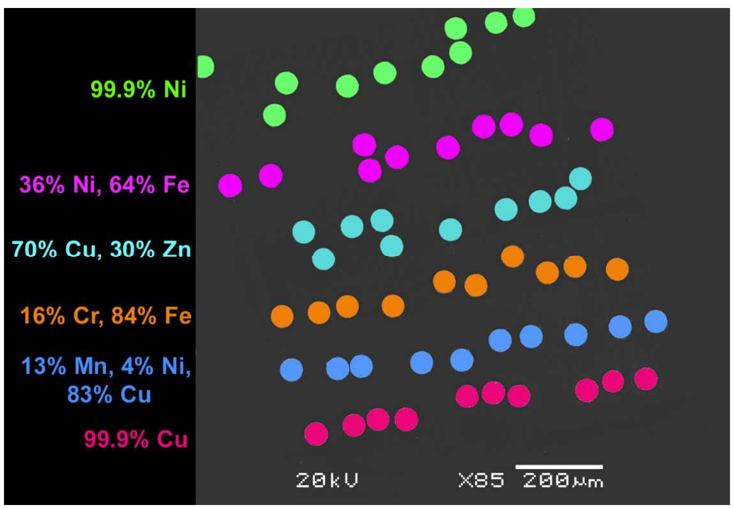
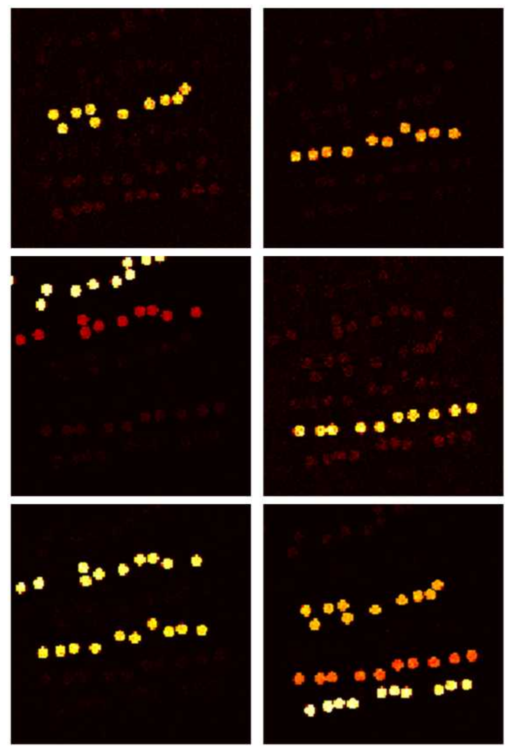
Alternative constraints can yield additional analytical insight

6 different alloys composed of 6 different elements

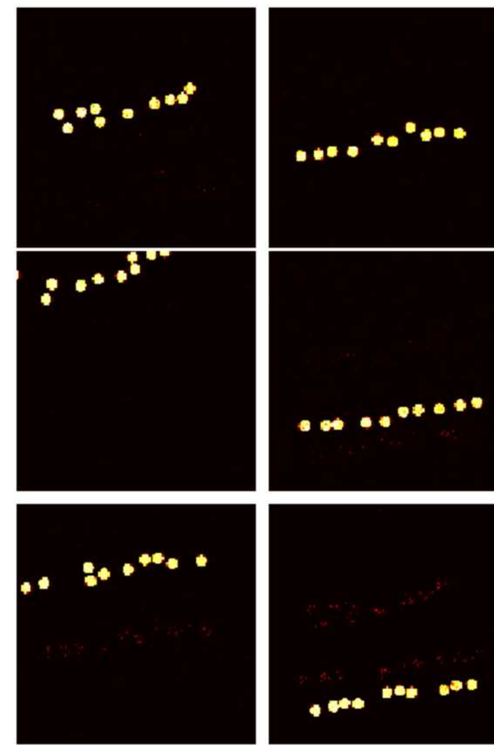
What are the pure components?



NN constraint
Spectrally simple

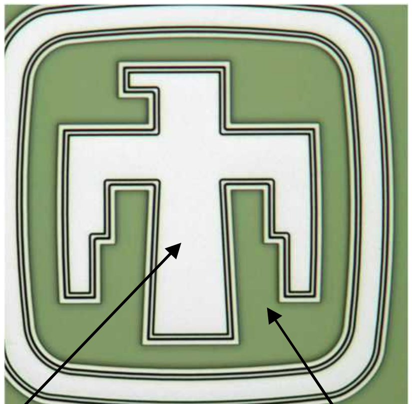


Simplicity constraint
Spatially simple



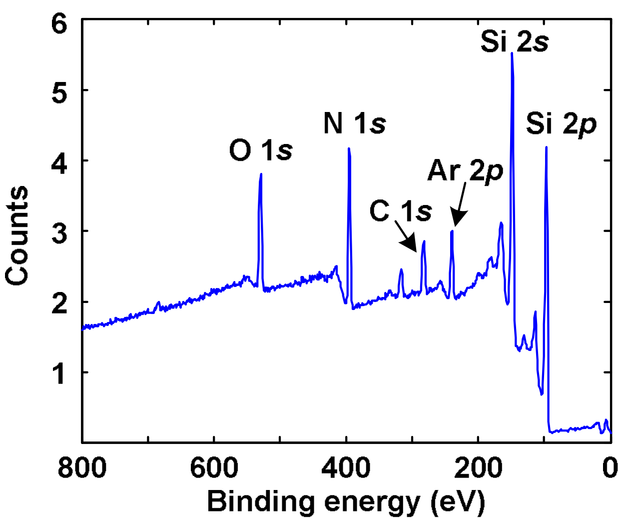
XPS example: putting it all together

Optical Image



Polysilicon

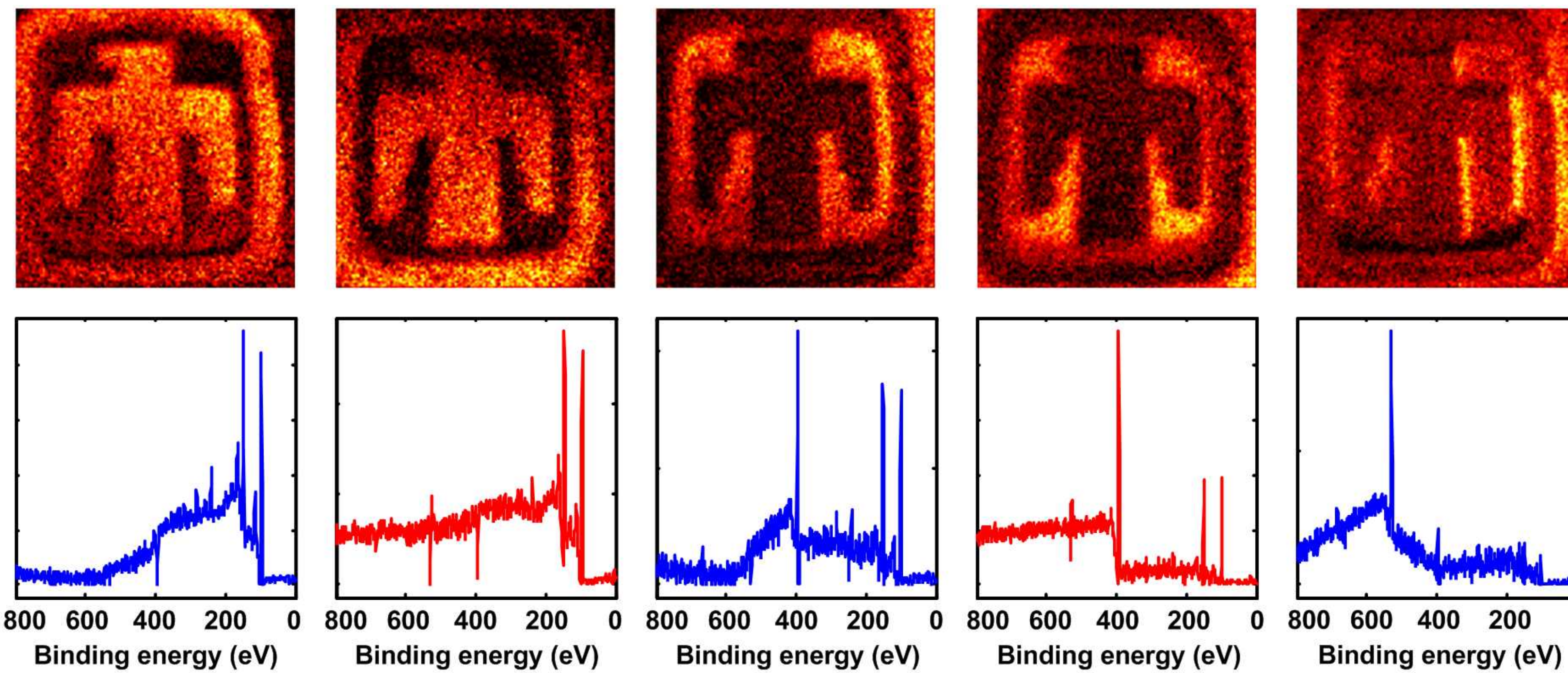
Silicon Nitride

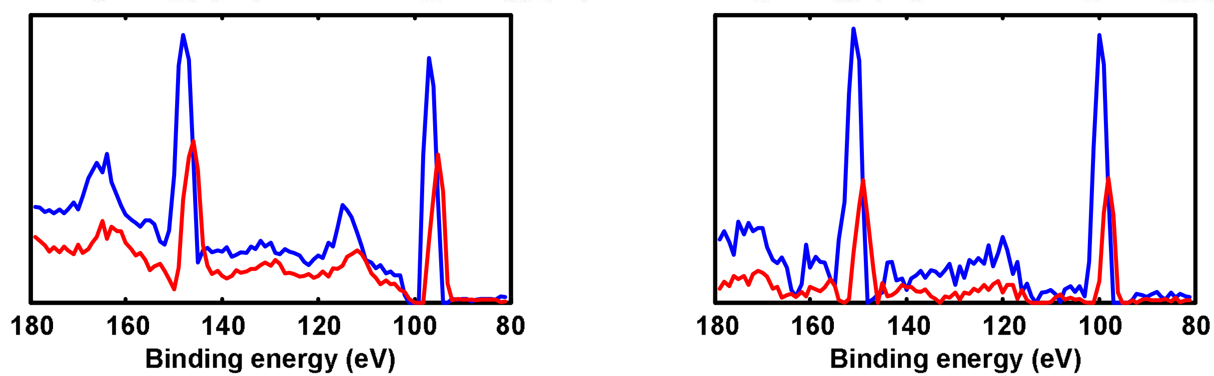


- Polysilicon on silicon nitride MEMS device
- Sputtered with Ar ions to remove surface oxide
- Has 3-D structure
- Some edges are shadowed

SEM view from ion gun

Standard MCR-ALS yields results that are more difficult to interpret than expected





The major effect is a spatially correlated energy shift

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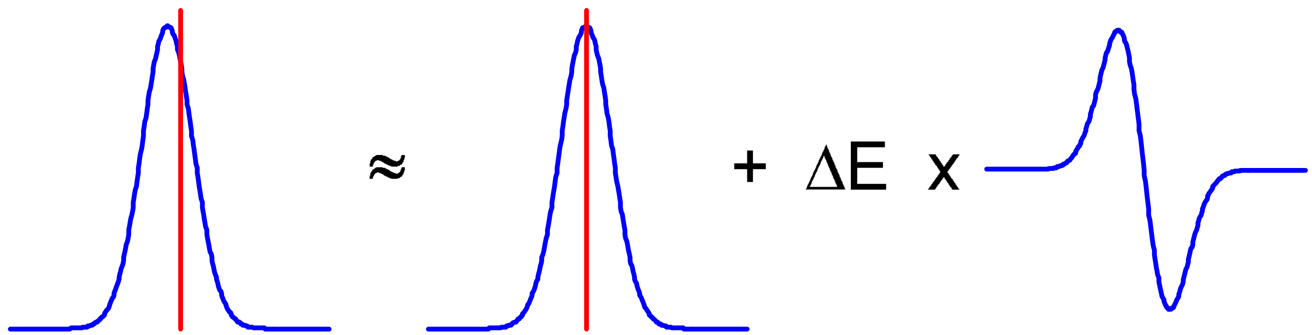
X-axis shift can be accommodated by adding derivatives to the spectral matrix

A shifted peak can be approximated by a Taylor series

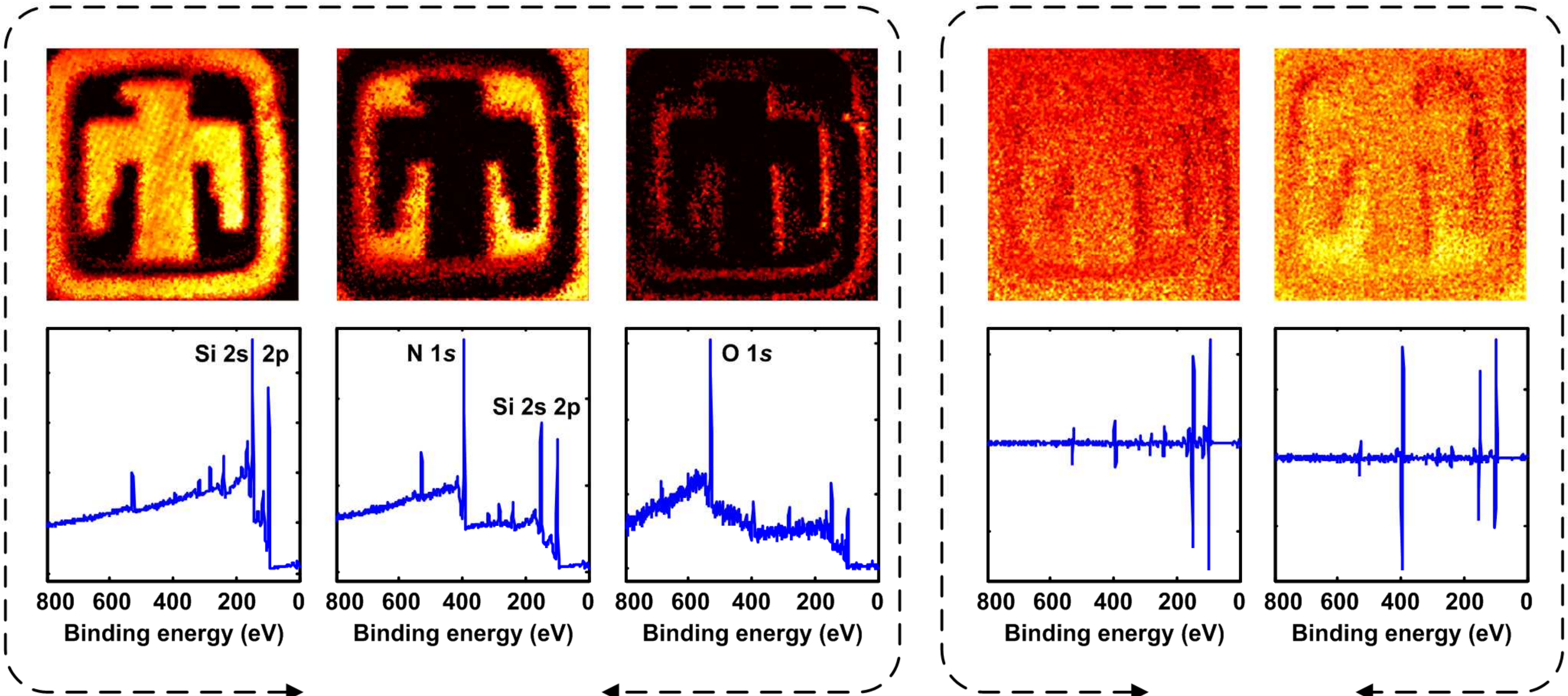


Partition A and S into chemical and shift components

$$\mathbf{A} = \begin{bmatrix} \mathbf{A}^{C} & \mathbf{A}^{D} \end{bmatrix}, \quad \mathbf{S} = \begin{bmatrix} \mathbf{S}^{C} & \mathbf{S}^{D} \end{bmatrix}$$

Incorporate derivatives by using equality constraints

MCR-ALS with simplicity and derivative-equality constraints yields excellent results



3 chemical components

2 artifact components

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Often, it is the small, unexpected things that will bite you

Addressing significant characterization problems of the future will rely upon …

- Ever greater spectroscopic sensitivity
- Ever increasing spectral and spatial resolution
- Combining data from multiple techniques
- Incorporating new dimensions, e.g. time

Spectral imaging hardware has advanced rapidly; image analysis software has lagged

The goals of future software development include:

- **Enabling routine use of spectral imaging techniques**
  Develop numerically efficient, rigorous and robust spectral image analysis algorithms suitable for day-to-day use.

- **Accommodating ever larger data sets**
  Develop novel approaches to analyzing extremely large data sets from large-area and multi-dimensional spectral images.

- **Broadening the application of spectral image analysis**
  Exploit additional qualities of spectral data to enable the successful application of methods to new imaging modalities.

Ultimately, develop tools to help us assess the significance of our analytical findings

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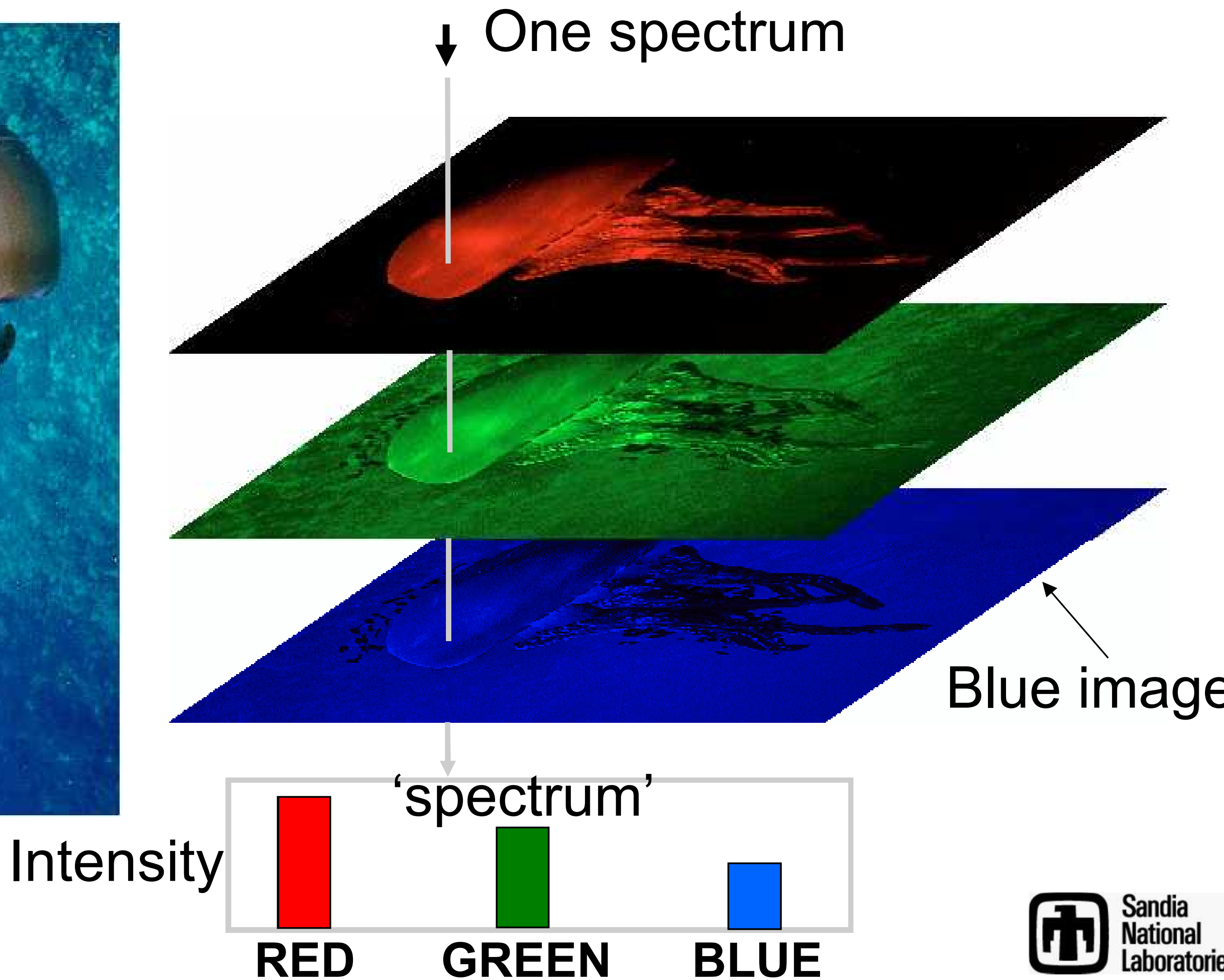
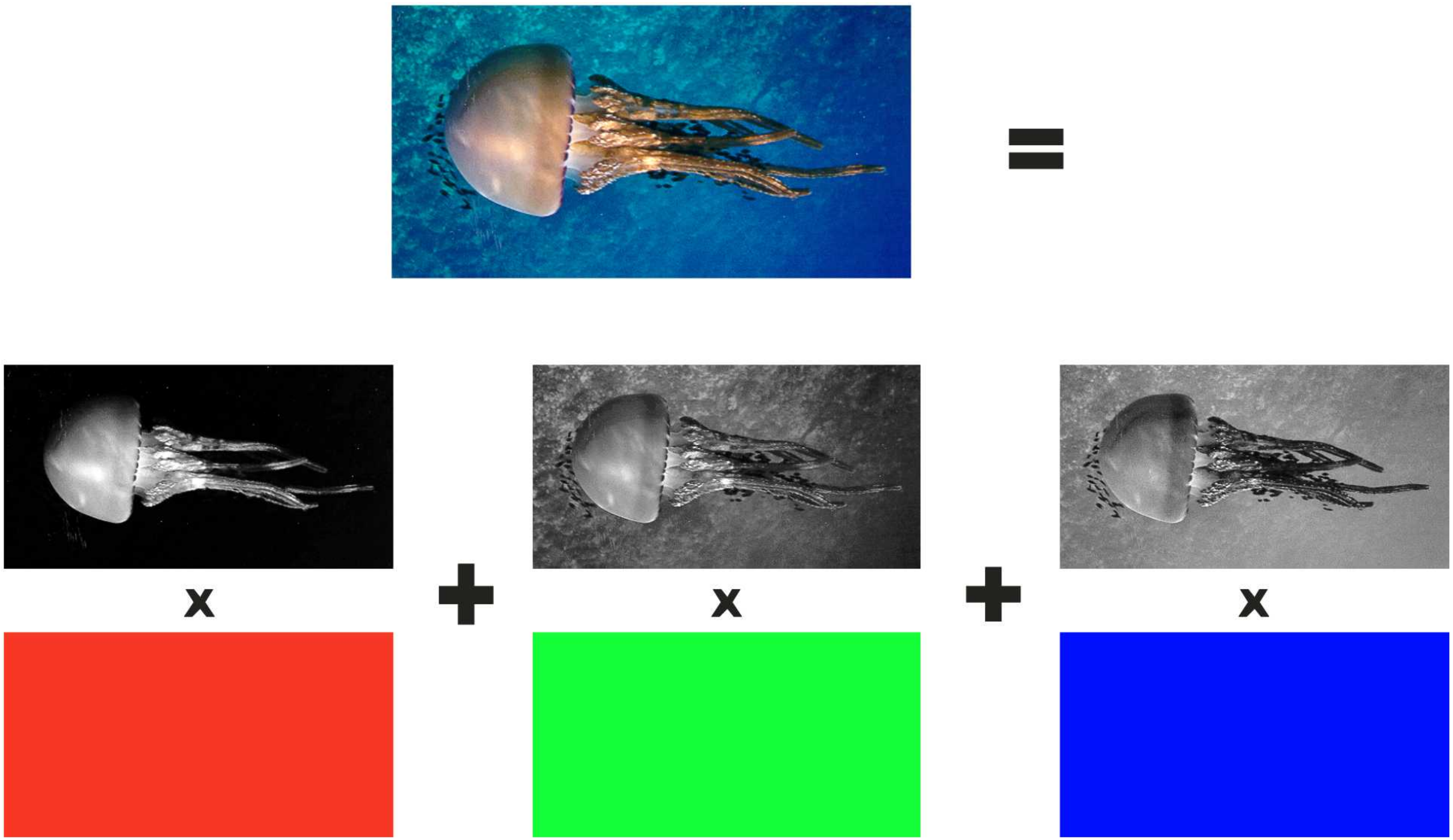
Color picture: a 3-channel spectral image with spectral variables red, green, and blue

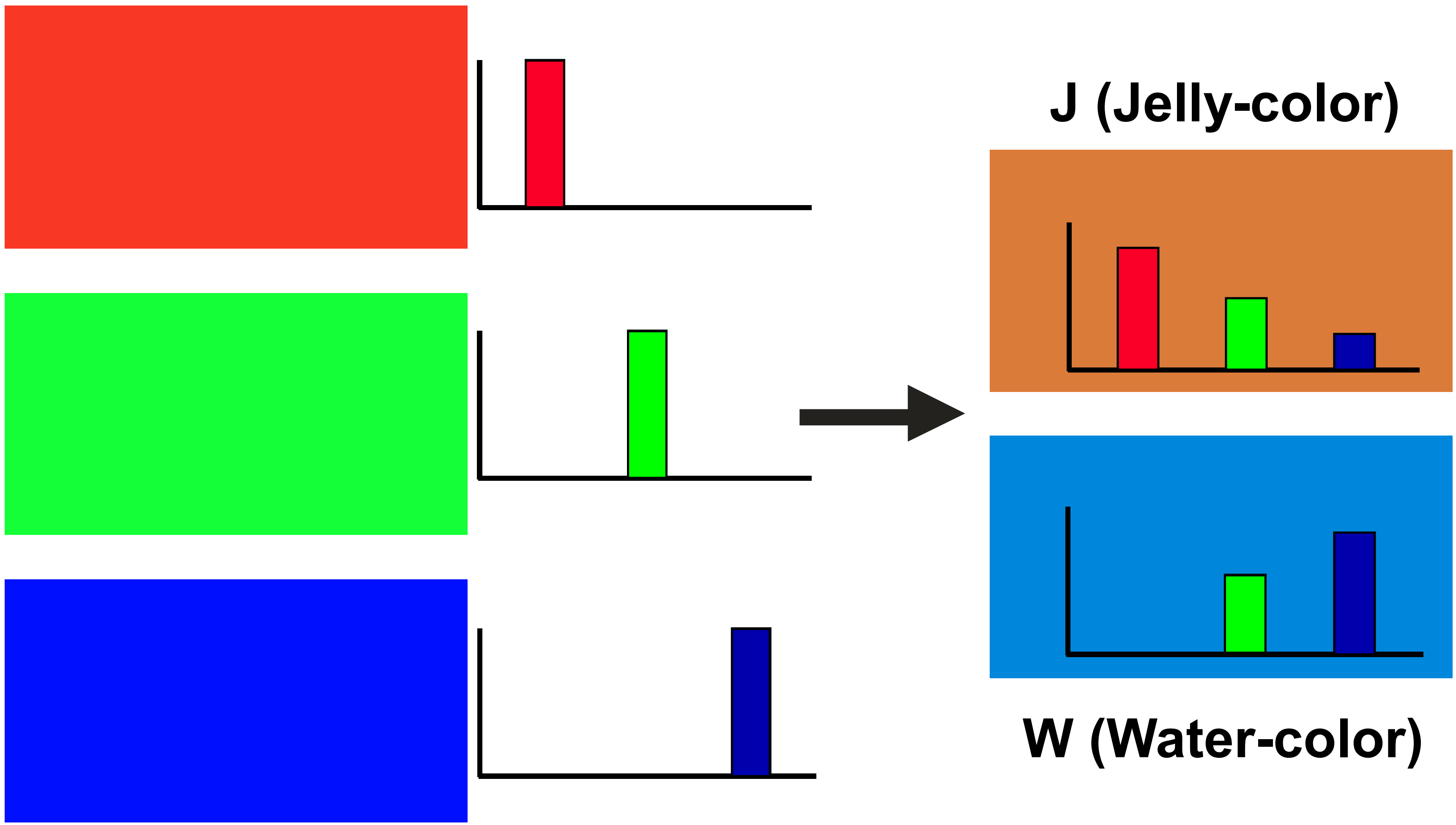


Color Picture = (Intensity) x (Spectral characteristic)^T



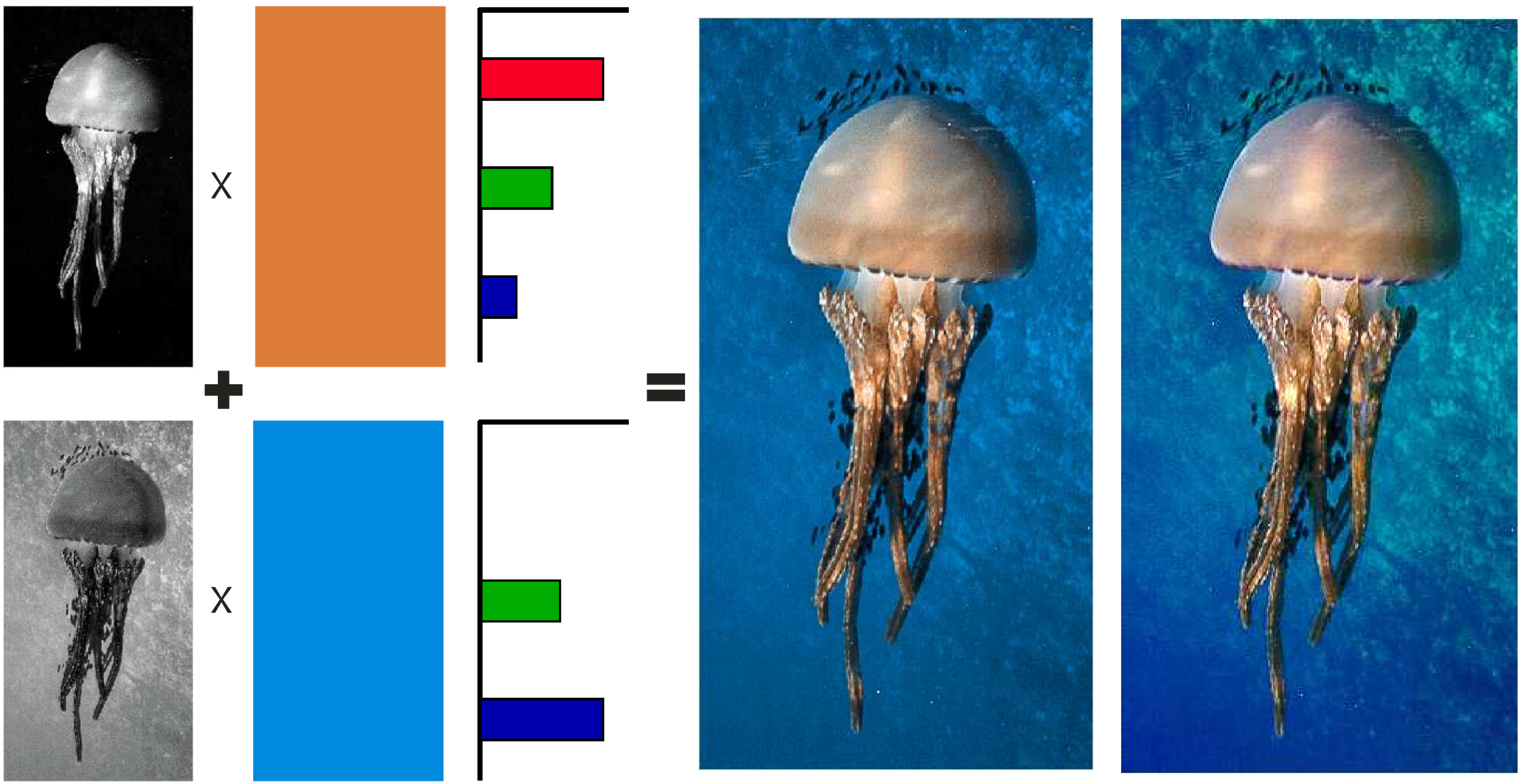
note the linearity assumption

Method transforms RGB into a reduced-dimension color space JW



J and W are linear combinations of R, G and B

Jelly-color and water-color are the “pure components” in the JW color space



2-component reconstruction

Original image

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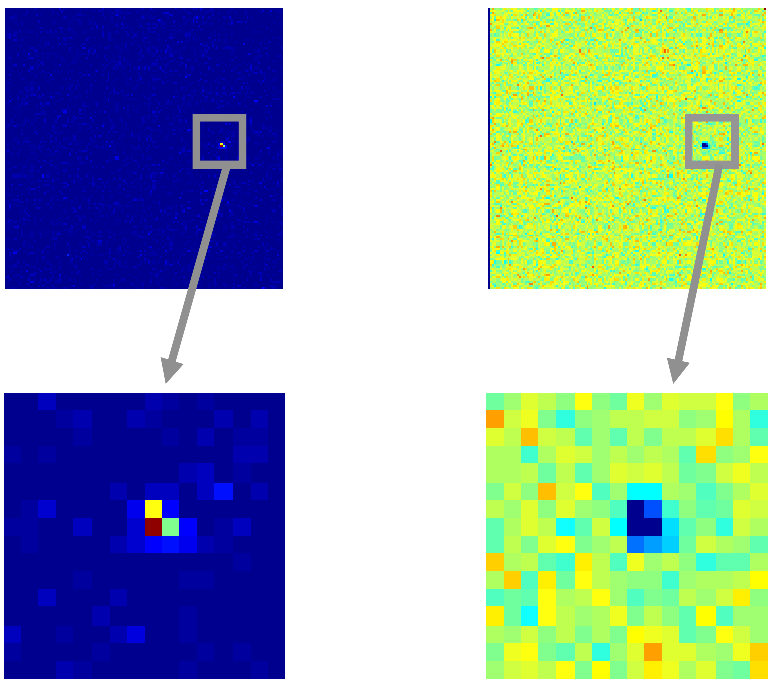
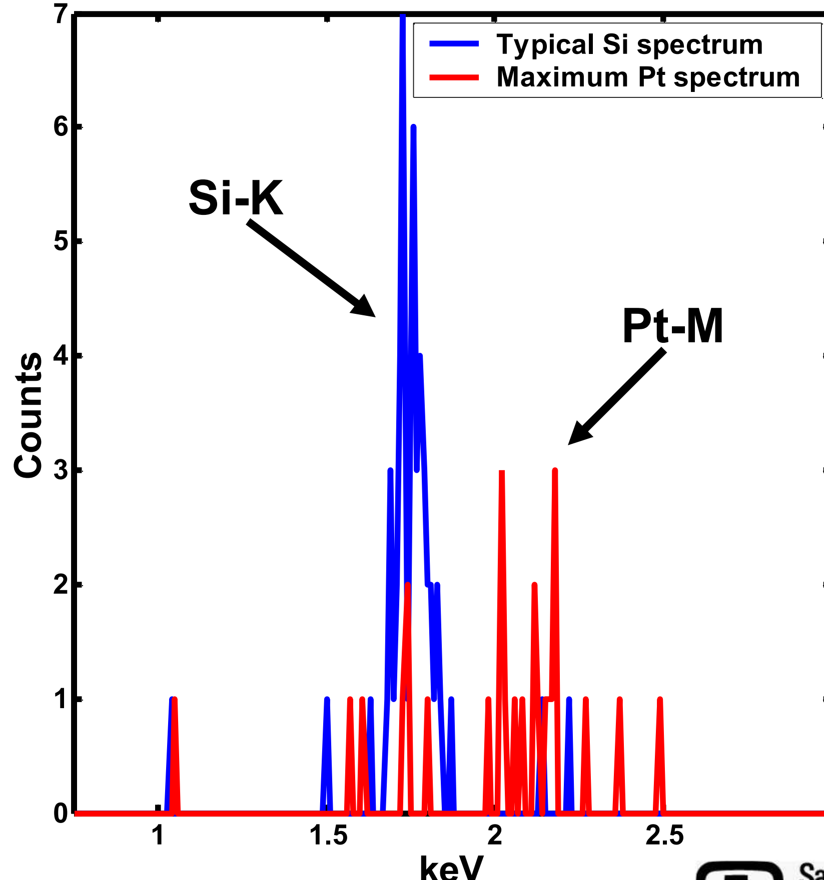
Single-pixel detection is possible, even for low S/N spectrum images

FIB-prepared specimen with 1x1μm by 3 μm deep ‘pixel’ of Pt in Si matrix



Average 55 total counts/pixel



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