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A brief discussion on X-ray spectrum image analysis

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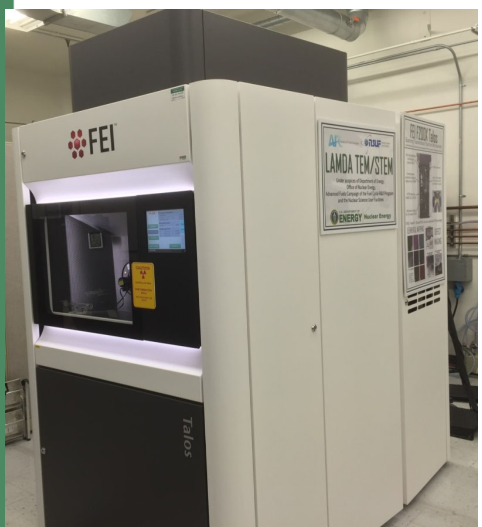
X-rays in electron microscopy: what, why, how

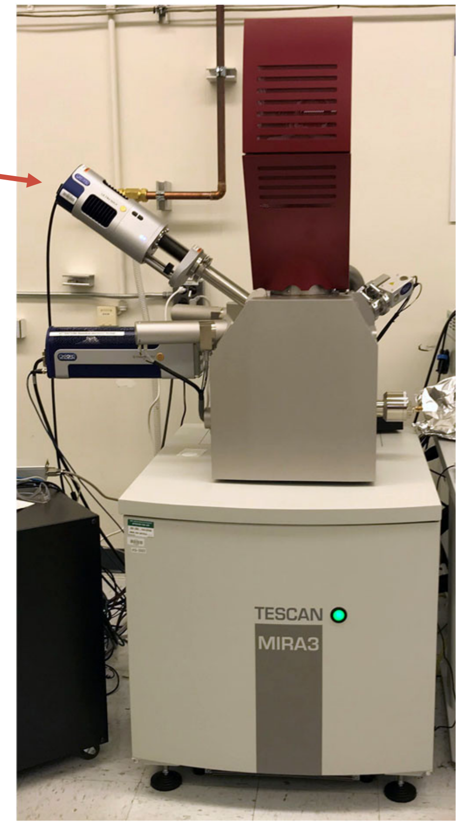
- **Electron microscopy always generates X-rays—might as well put them to work!**

Typical STEM
(Four SDD-EDS, internal)



SDD-EDS: Silicon drift detector energy dispersive X-ray spectrometer

Typical SEM



Equivalent acronyms (interchangeable):

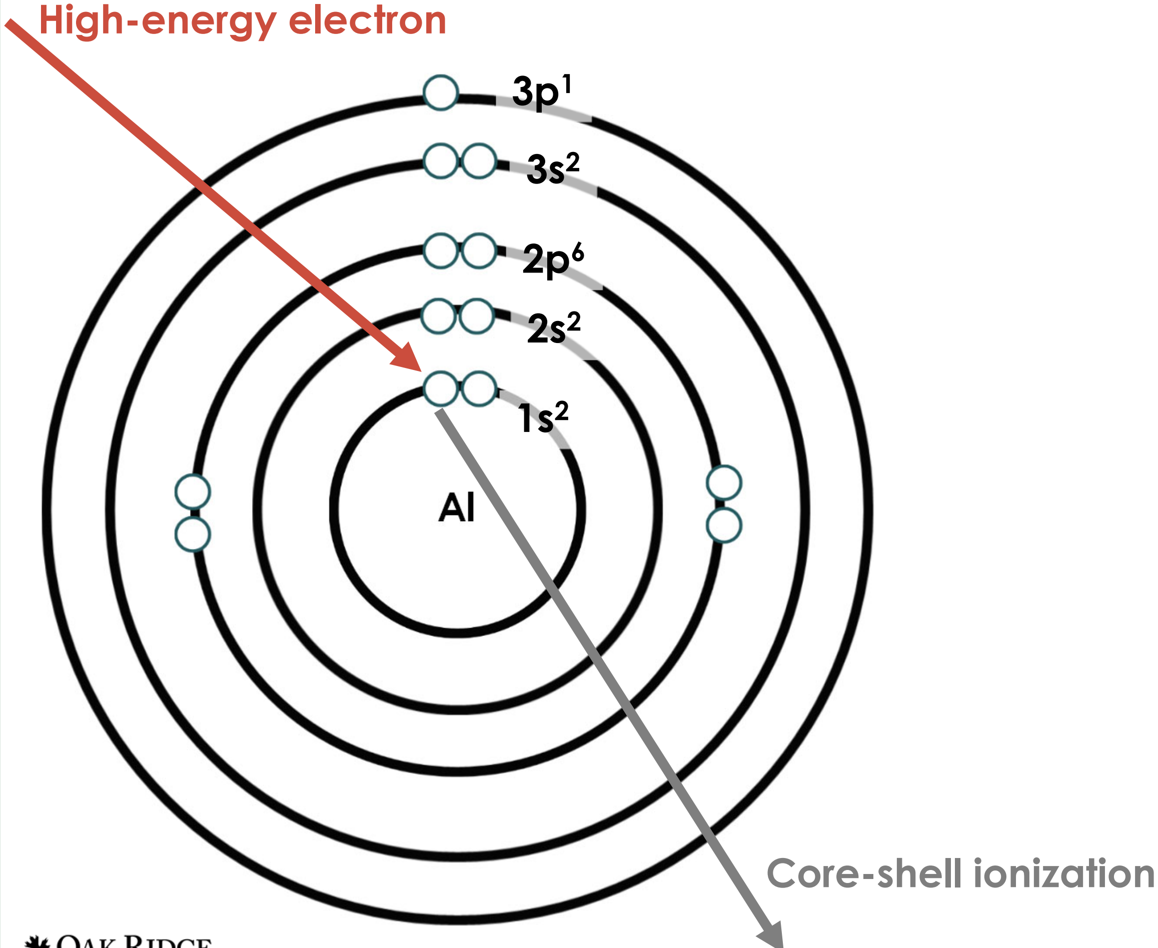
EDS
EDX
EDXS
XEDS

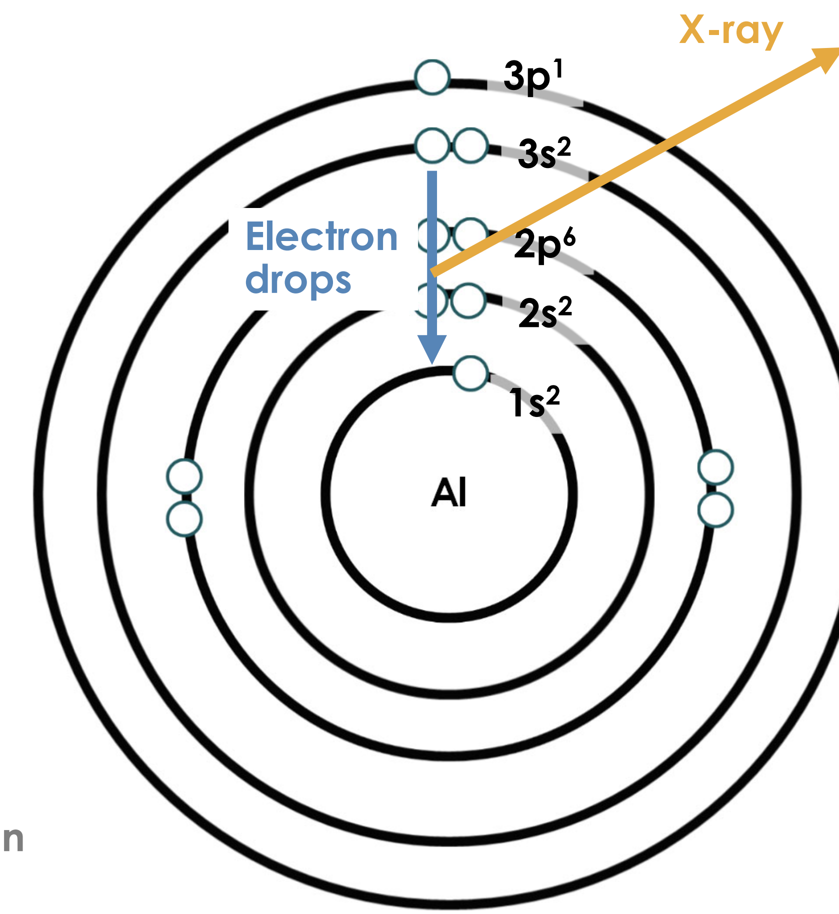
Trade name, <u>not</u> acceptable:

EDAX

(I have seen *all* of these in the literature)

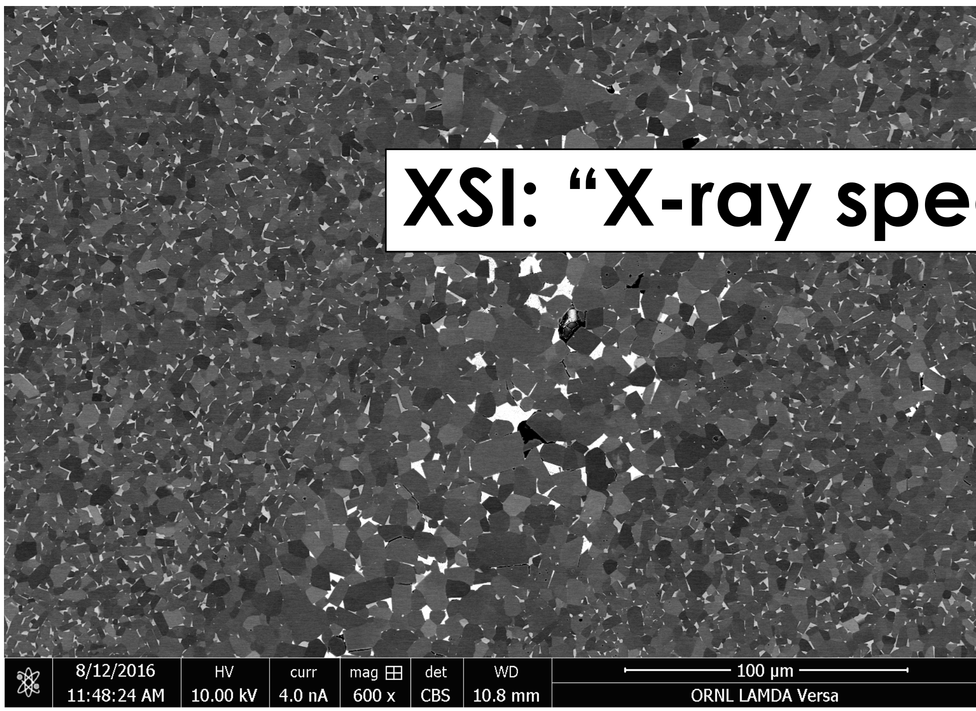
X-rays in electron microscopy: what, why, how



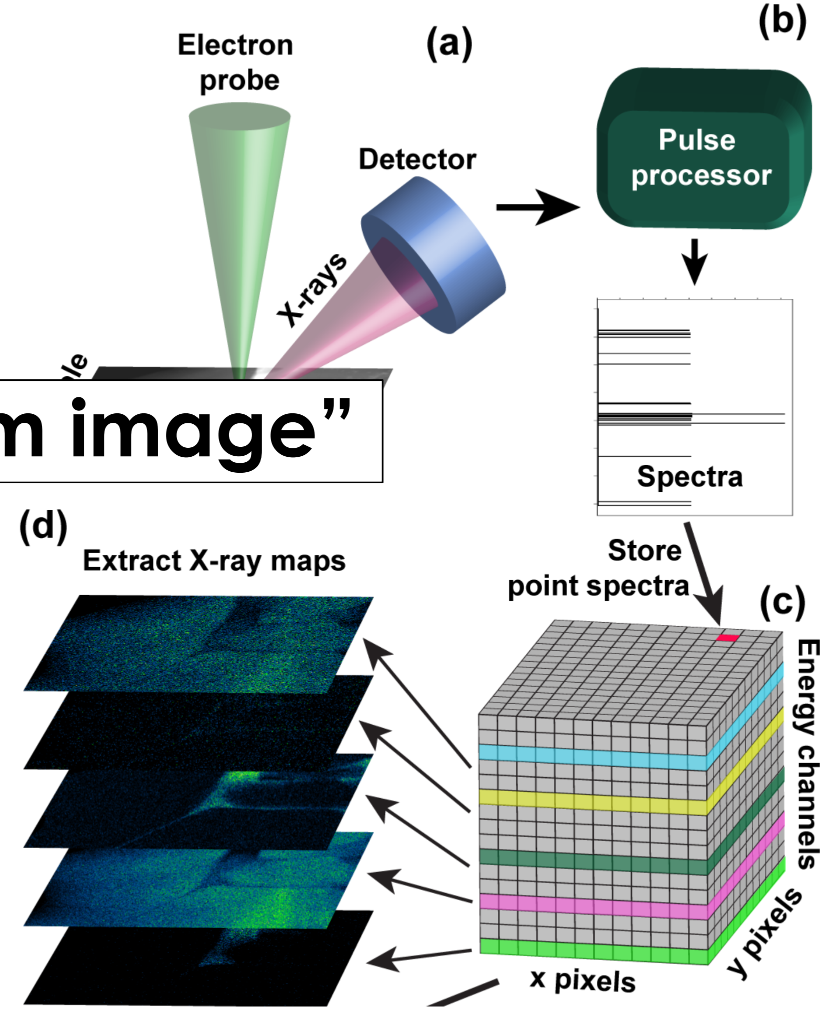


X-rays in electron microscopy: what, why, how

- **Scan a beam across a surface, collect the spatially and energy-resolved X-ray**



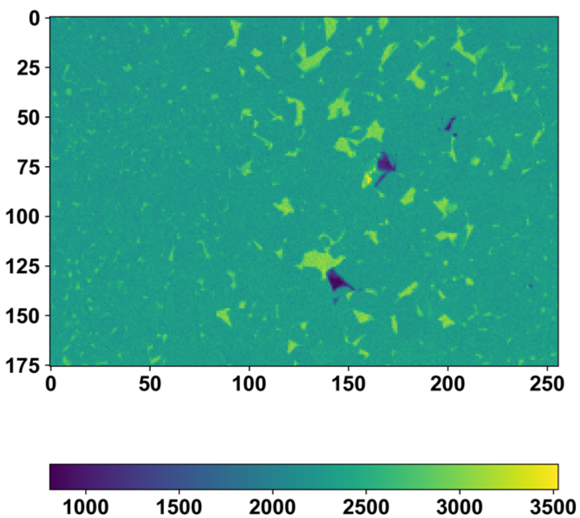
XSI: “X-ray spectrum image”

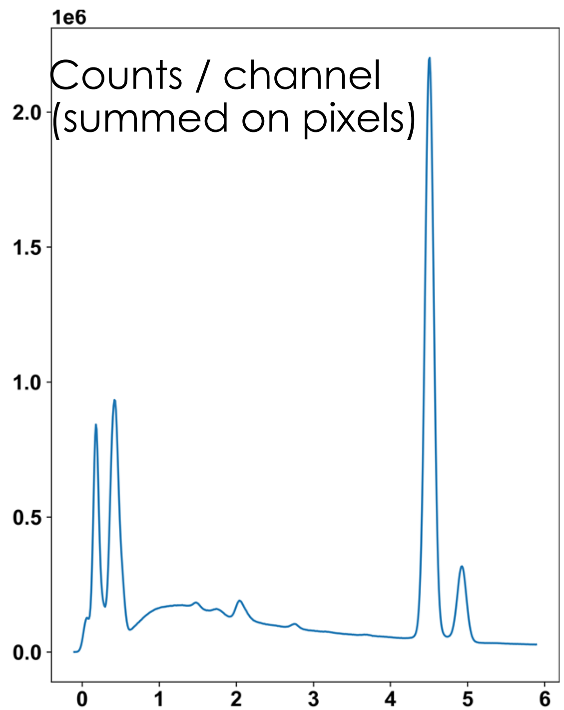


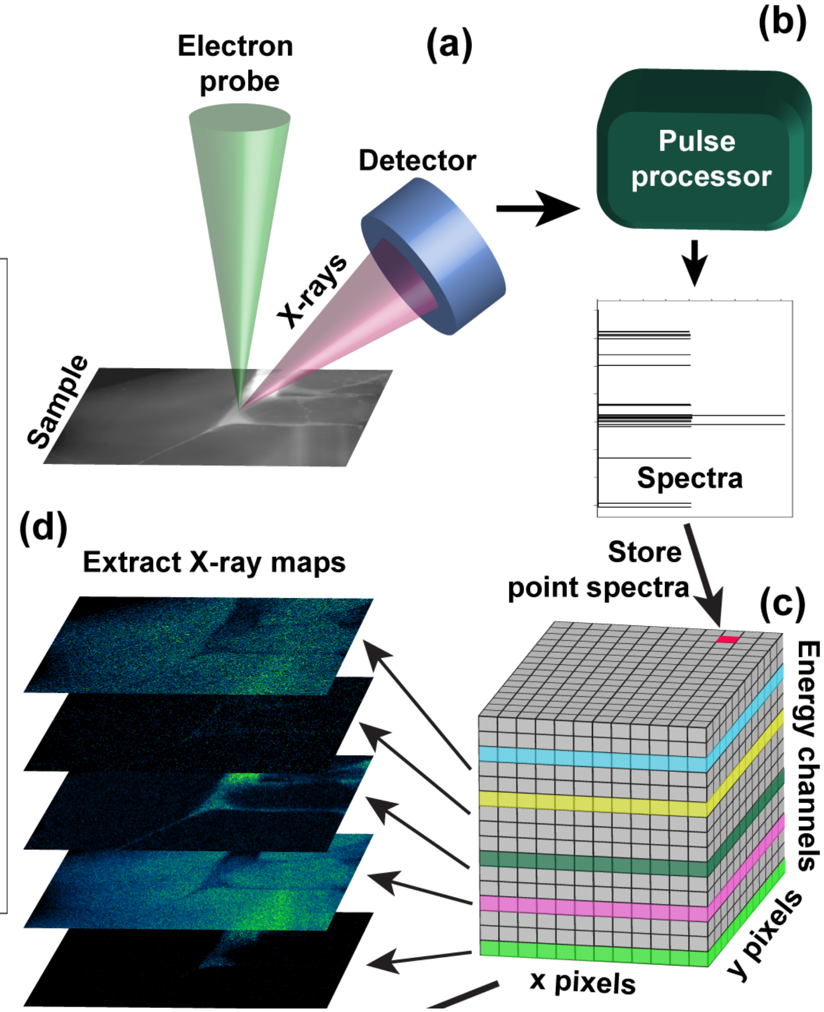
X-rays in electron microscopy: what, why, how

- **Scan a beam across a surface, collect the spatially and energy-resolved X-ray**

Counts / pixel
(summed on energy)

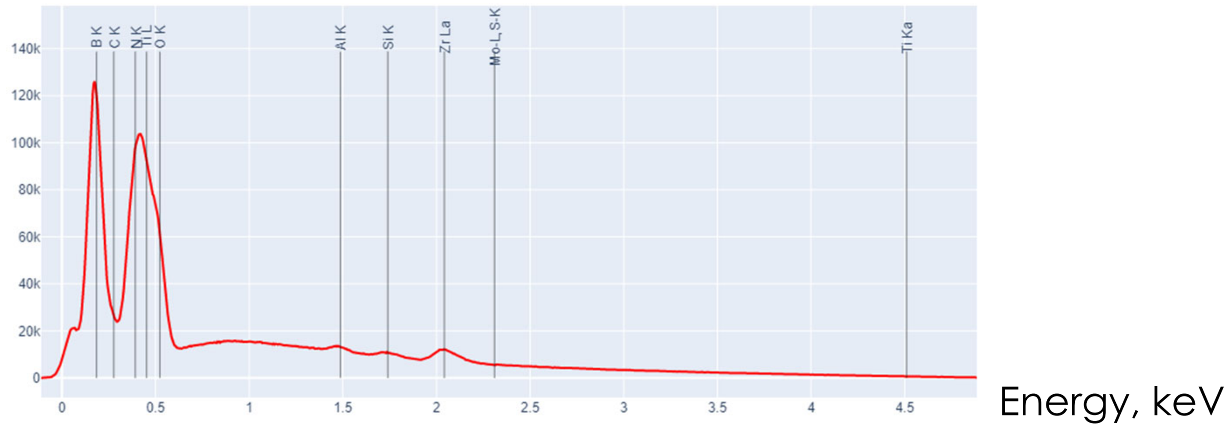






X-rays in electron microscopy: what, why, how

- ***Characteristic*** **and** ***background*** **(Bremsstrahlung) X-rays are always present**



- **When X-rays are good choices:**
  - **Elements ≥C or so, especially elements ≥Al or so**
  - **Amounts ~1 wt% or more**
- **When X-rays are bad choices:**
  - **Be, Li (modern detector); <Al (old detectors)**
  - **Low (<<1 wt%) amounts**

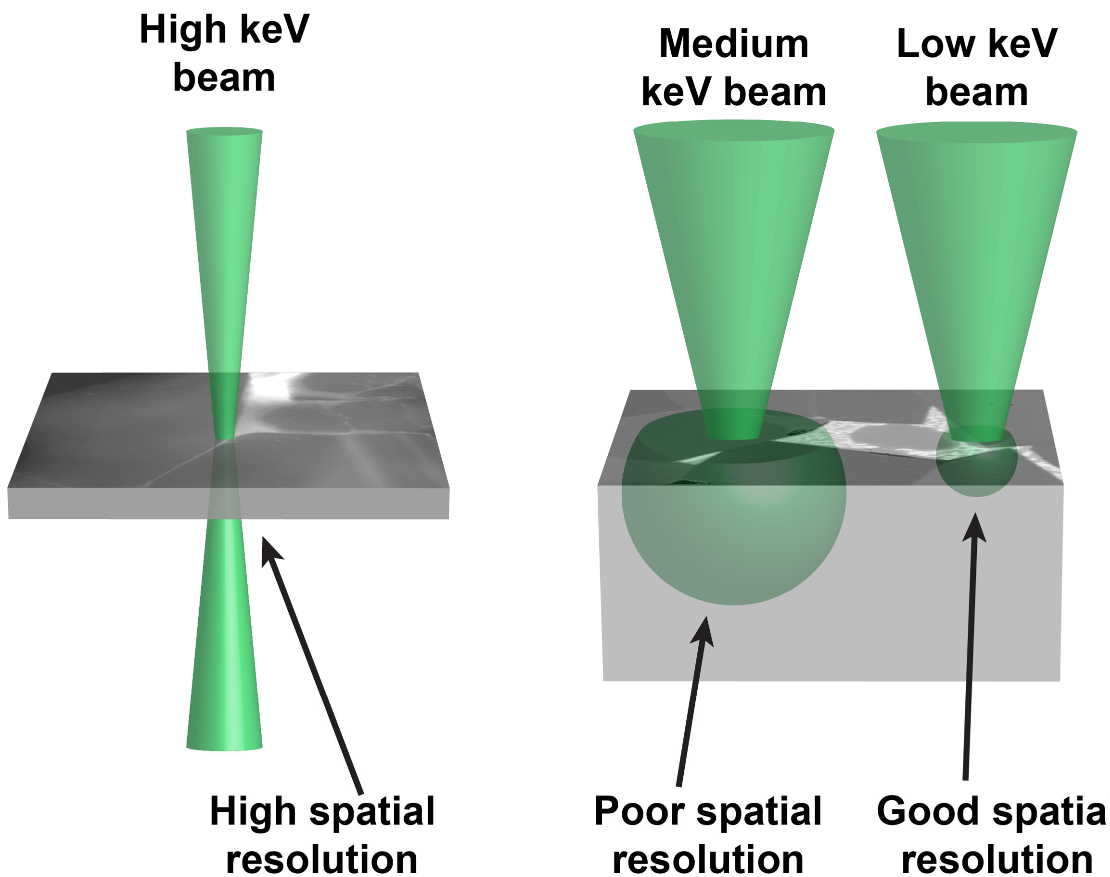
X-rays in electron microscopy: what, why, how

Spatial resolution: three broad cases

High energy:
- Get K or L lines on all elements
- Overlaps usually resolvable

STEM: Thin sample

SEM: Thick sample



Medium energy:
- Get K or L lines on most elements
- Overlaps usually resolvable

Low energy:
- Generally only one set of lines (K, L, or M) for each element
- Overlaps difficult to resolve

Applying ML to X-ray spectrum image data

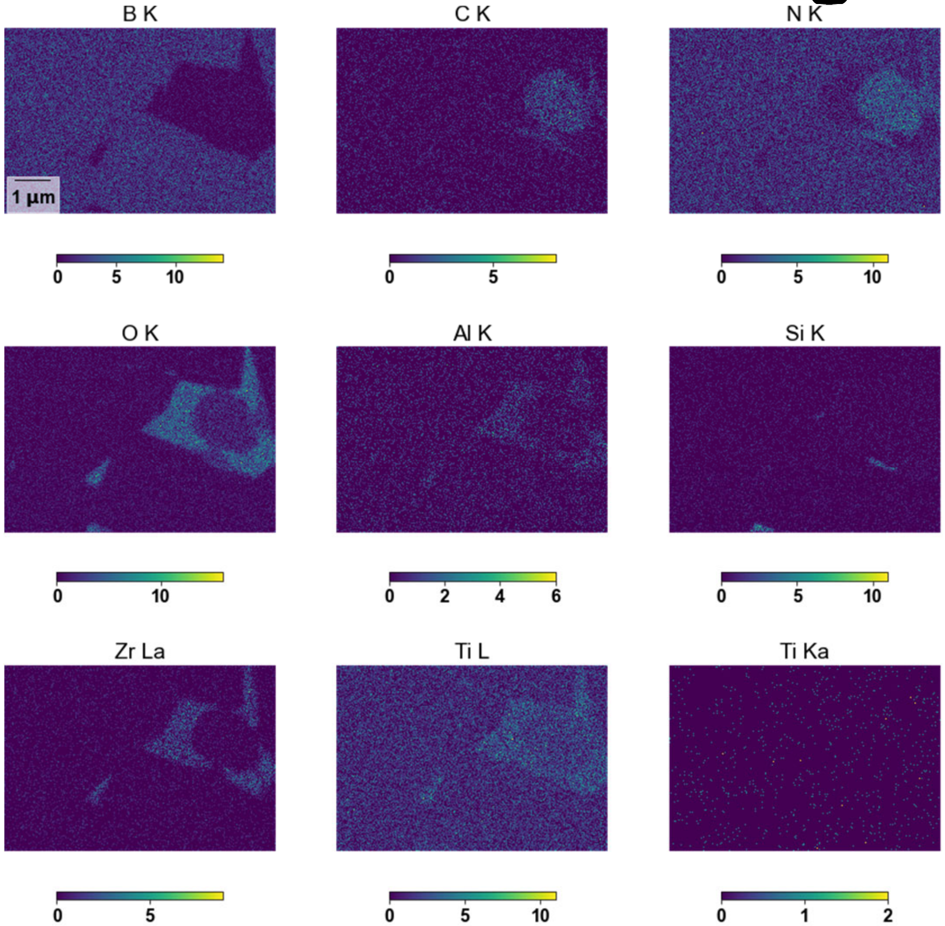
- **Machine learning: PCA, SVD, NMF, K-means, DLNN, SVM, and umpteen bazillion others…**
- **<u>Unsupervised methods</u> generally used:**
  - **Forward models exist, but are not high enough fidelity to populate databases**
  - **We generally want to know *a posteriori* what was in our sample**
  - **X-ray physics is well-approximated by linear combinations of compound/element spectra, so bilinear factor models match the physics wonderfully!**

$$\mathbf{D} \approx \mathbf{A}\mathbf{S}^{\mathrm{T}}$$

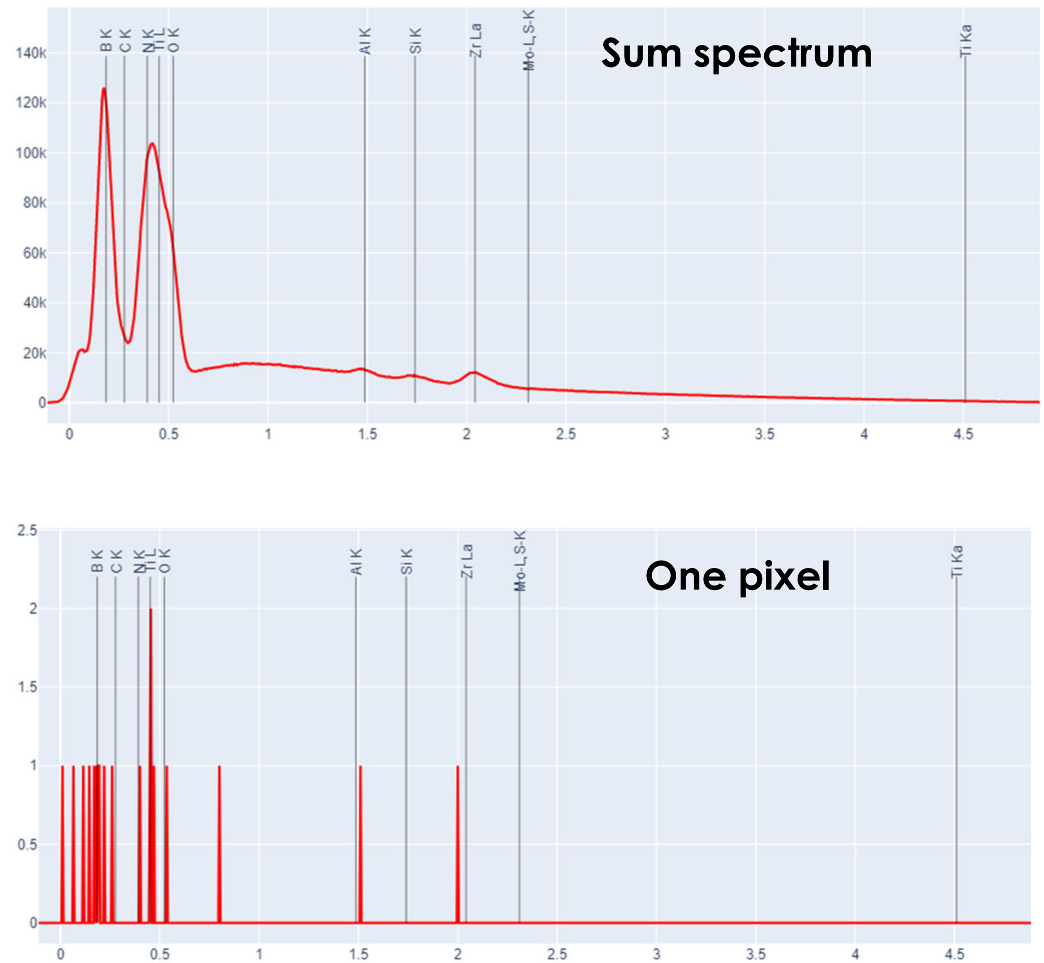
Data ≈ (abundance maps) @ (endmember spectra transpose)

➔*Singular value decomposition-based methods are preferred*

Real XSI data challenges: sparse, large, noisy



TiB_2 sintered ceramic, 5 kV



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Workflow

- We'll go through this step by step

$$I(x, y|E) \to D_{n\times m}$$

$$\hat{D} = GDH$$

$$\hat{D} \approx U\Sigma V^T$$

$$\hat{D} \approx U\Sigma V^T = \hat{A}\hat{S}^T$$

$$\mathbf{S} = \mathbf{H}^{-1}\hat{\mathbf{S}}$$
$$\mathbf{A} = \mathbf{G}^{-1}\hat{\mathbf{A}}$$

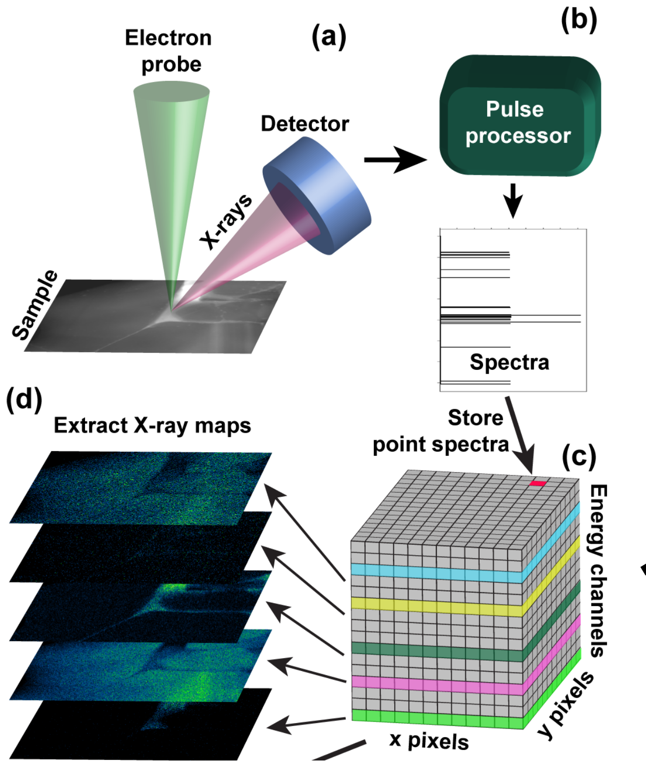
$$D \approx AS^T = TP^T$$

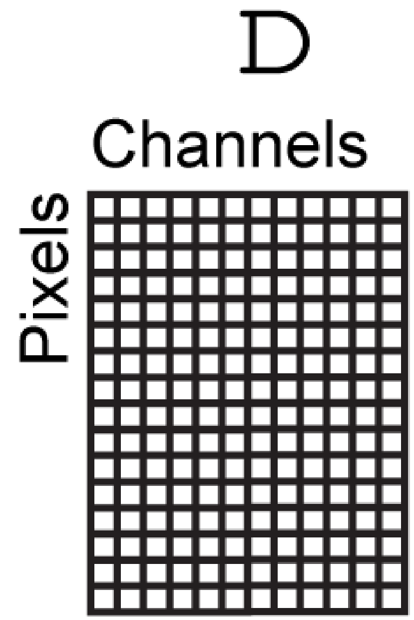
$$D \approx (TR)(R^{-1}P)^T = \tilde{T}\tilde{P}^T$$

Turn raw data into a matrix

$$I(x, y|E) \rightarrow D_{n \times m}$$

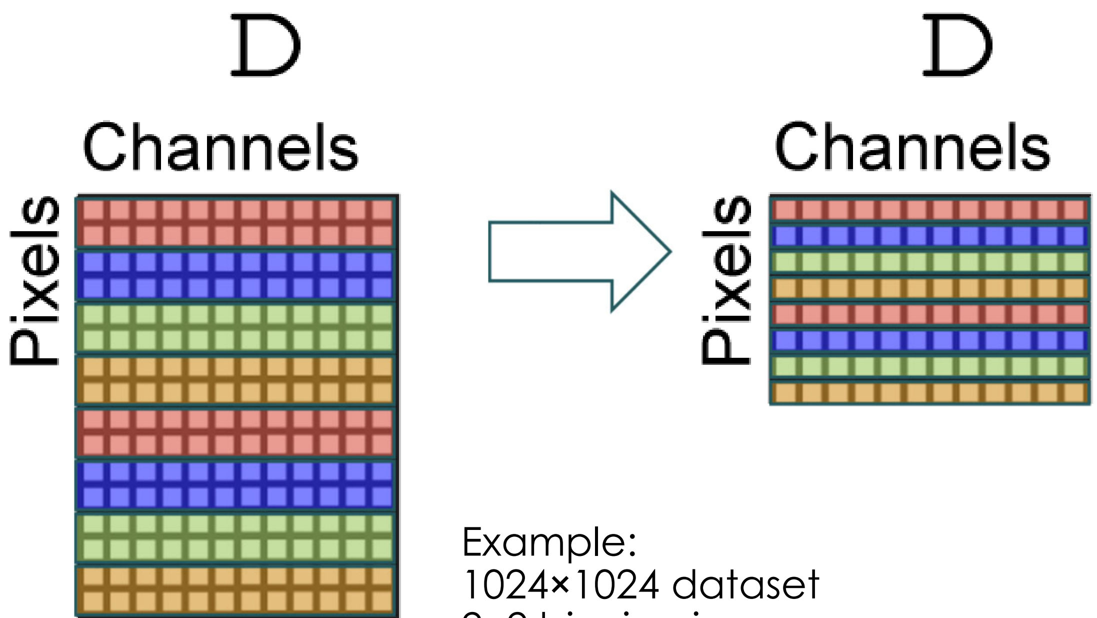
Typically convert datatype to sparse here





Easy enough to reshape back to maps *(x,y)* later

Optional: binning



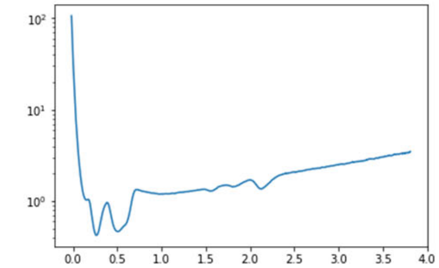
Example:
1024×1024 dataset
2×2 binning in space
➔ 512×512 data, 4× more counts/pixel, 2× degraded spatial resolution

Can also bin on energy (i.e., ×2) to increase counts as loss of energy resolution

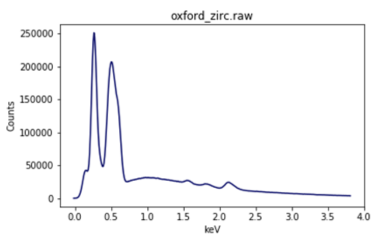
Easy sparse binning: Keenan et al., JVST A, V33(5) 2015, #05E123-1

Need to account for Poisson noise

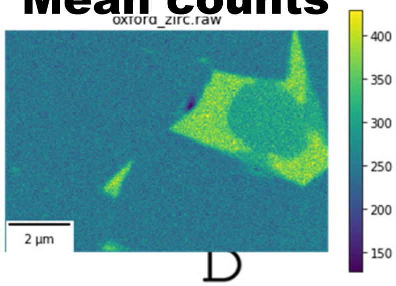
1 / √(mean spectrum)



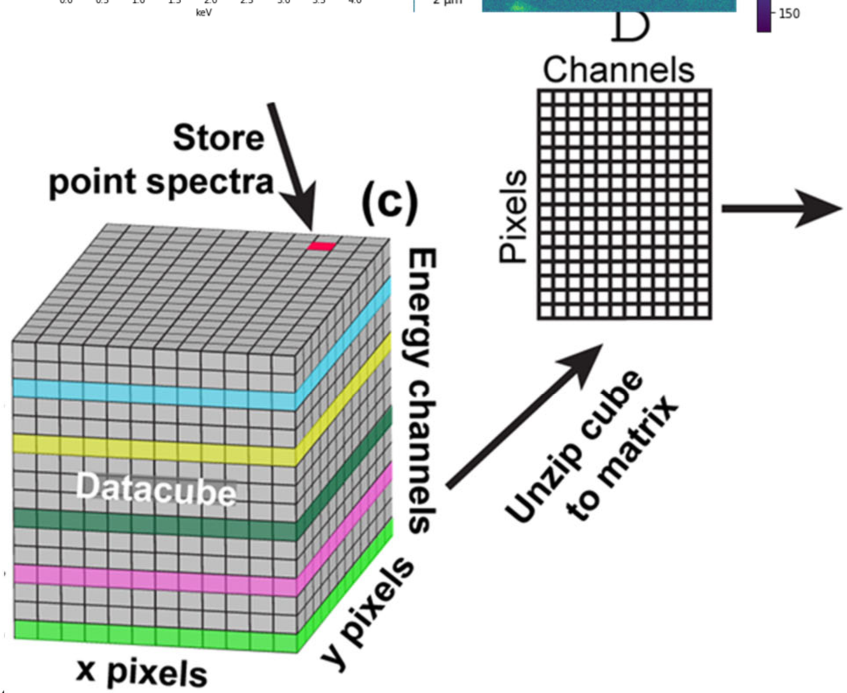
Mean spectrum

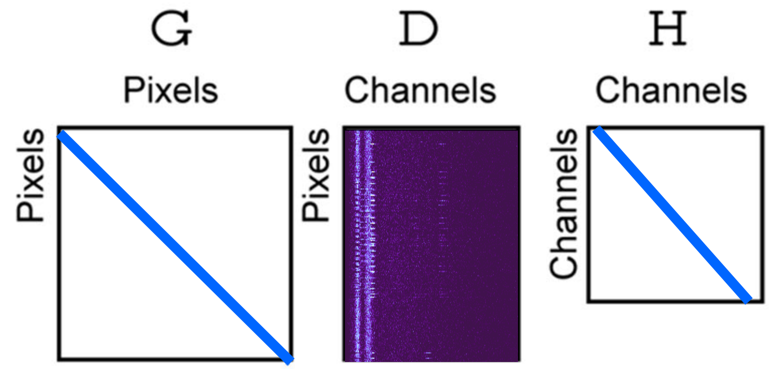


Mean counts



$$\hat{D} = GDH$$

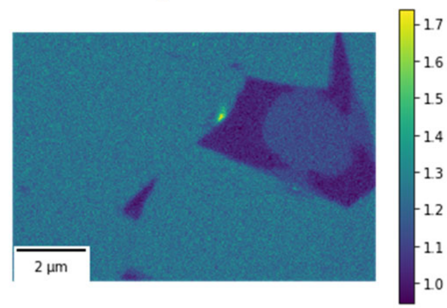




Keenan, Tech and Apps. of Hyperspectral Imaging, Ch. 5, 2007

Keenan & Kotula, Surf. Int. Anal., V36(3) P. 203 (2004)

Etc.

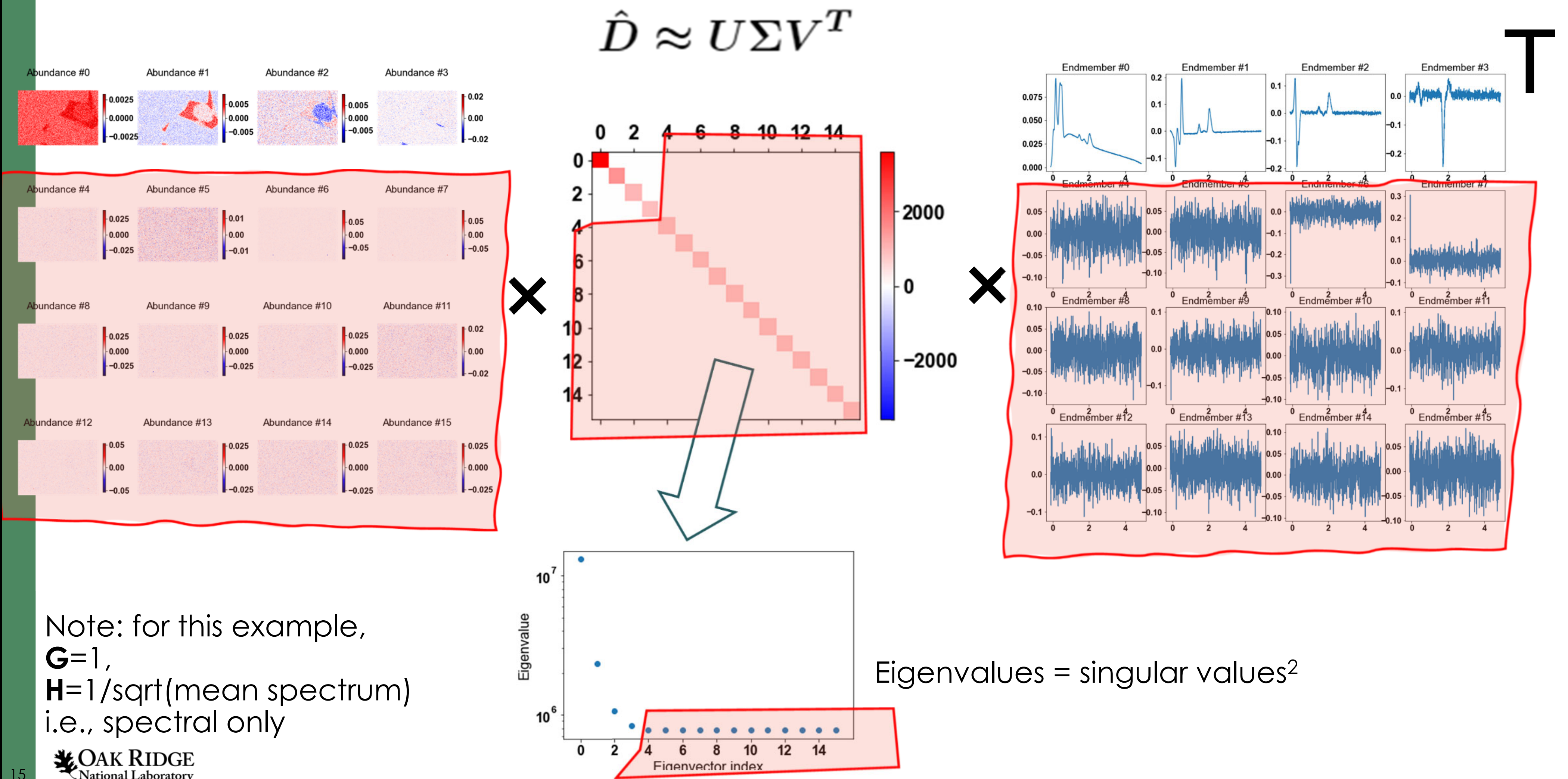


1 / √(mean counts)

Recent insight: For very low count rates (i.e., nanoparticles in STEM), **G=1** (spectral-only binning) may work better. Kotula & Van Benthem (2015). M&M V21(S3): 1423.

Singular Value Decomposition

$$\hat{D} \approx U \Sigma V^T$$



Eigenvalues = singular values^2

Note: for this example,
G=1,
H=1/sqrt(mean spectrum)
i.e., spectral only

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Singular value decomposition ⇔ principal component analysis

$$\hat{D} \approx U\Sigma V^T = \hat{A}\hat{S}^T$$

$$\mathbf{U\Sigma} = \widehat{\mathbf{A}}, \qquad \mathbf{V} = \widehat{\mathbf{S}}$$

Or,

$$\mathbf{U} = \widehat{\mathbf{A}}, \qquad \mathbf{\Sigma V} = \widehat{\mathbf{S}}$$

Then, return from Poisson-scaled space to "real" space:

$$\mathbf{S} = \mathbf{H}^{-1}\hat{\mathbf{S}}$$

$$\mathbf{A} = \mathbf{G}^{-1}\hat{\mathbf{A}}$$

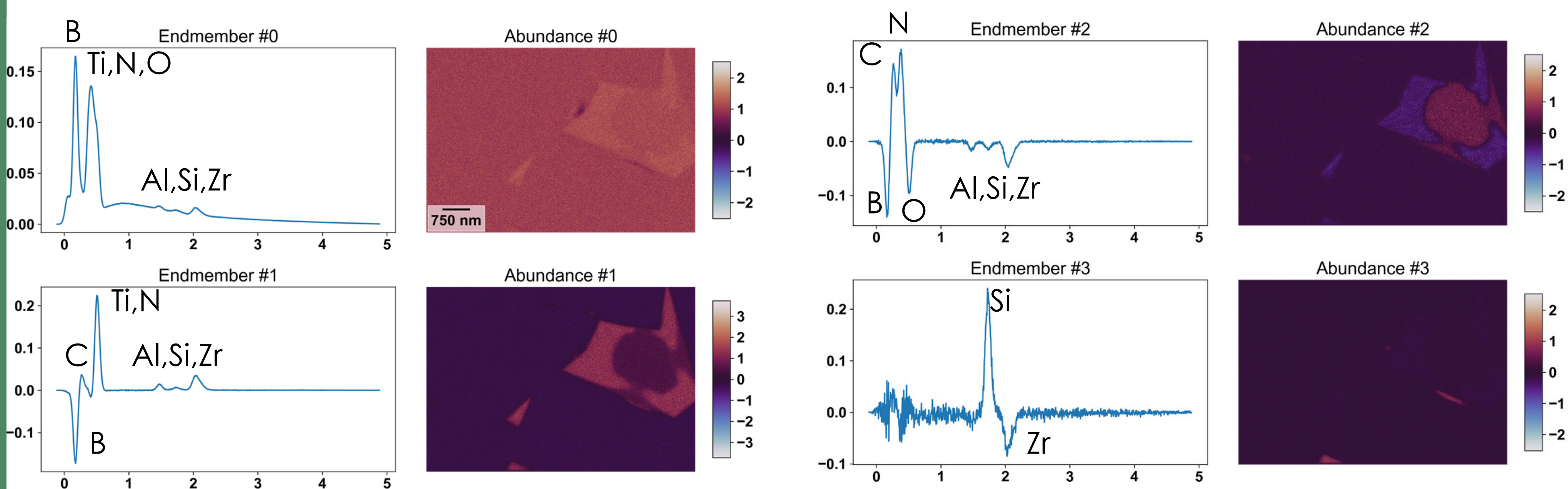
Important point: U, V are orthonormal, therefore A-hat, S-hat are orthonormal or orthogonal. But, the H^{-1}, G^{-1} steps don't preserve this orthogonality, so A, S are not orthogonal; this will be important later. Keenan (2007) shows a simple procedure "fPCA" to make the real-space, PCA-like model orthogonal: **Abundances + endmembers!!!!**

$$D \approx AS^T = TP^T$$

AS^T: arbitrary factor model
TP^T: orthogonal factor model

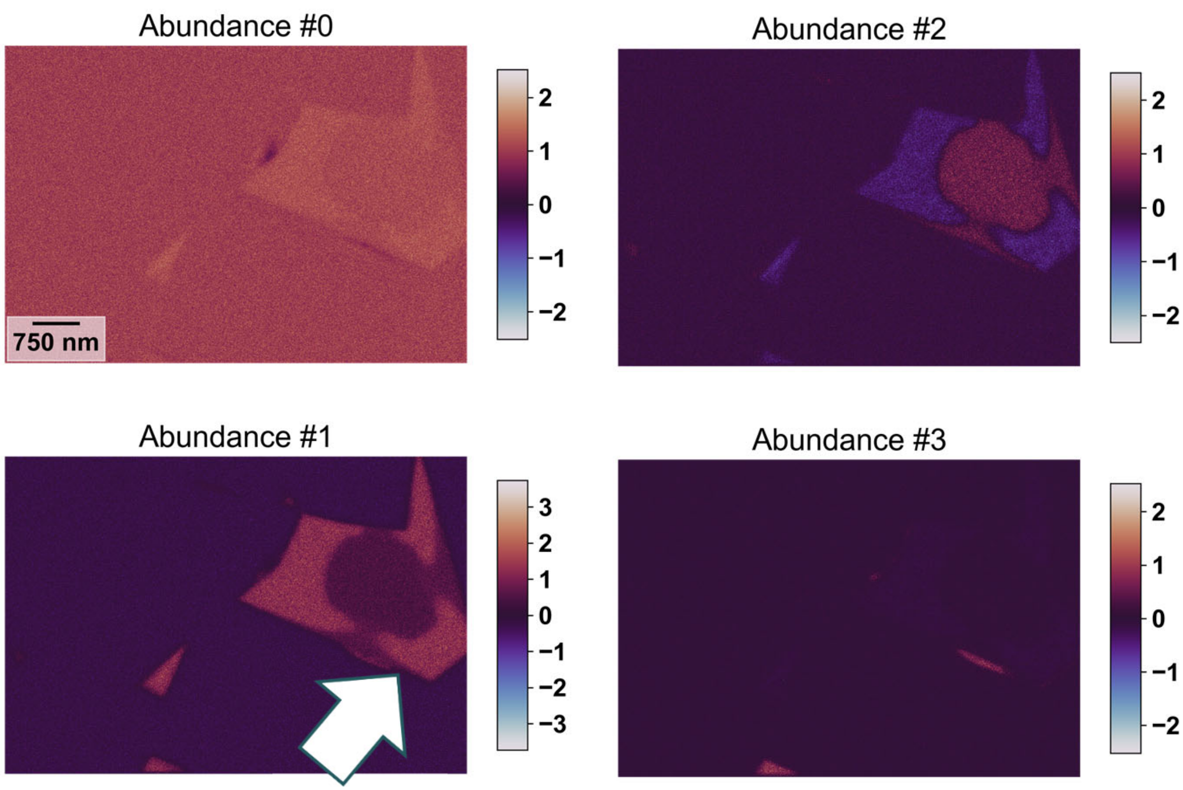
Keenan, M. R. (2007). Techniques and Applications of Hyperspectral Image Analysis. H. F. Grahn and P. Geladi. Chichester, John Wiley & Sons: 89-126.
Keenan, M. R. (2009). Surface and Interface Analysis 41: 79-87.
Keenan, M. R. and P. G. Kotula (2004). Surface and Interface Analysis 36(3): 203-212.

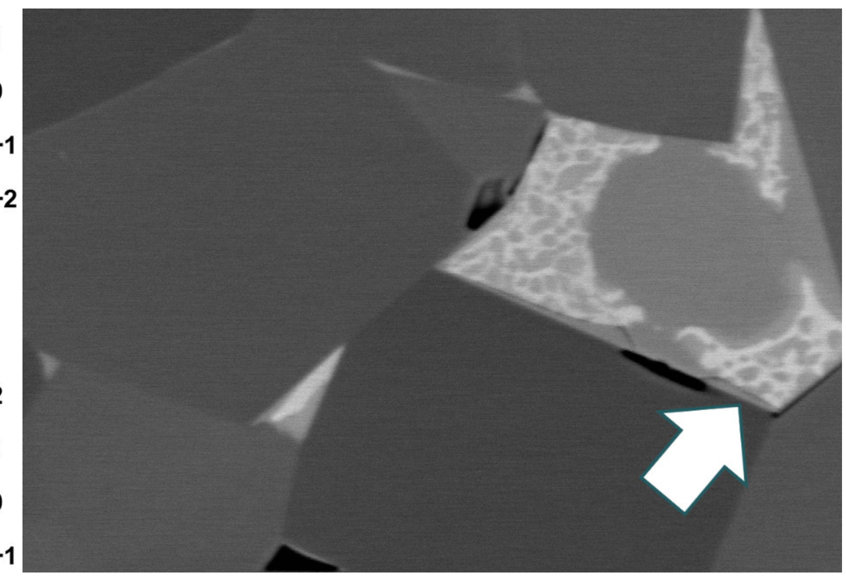
Abundances + endmembers



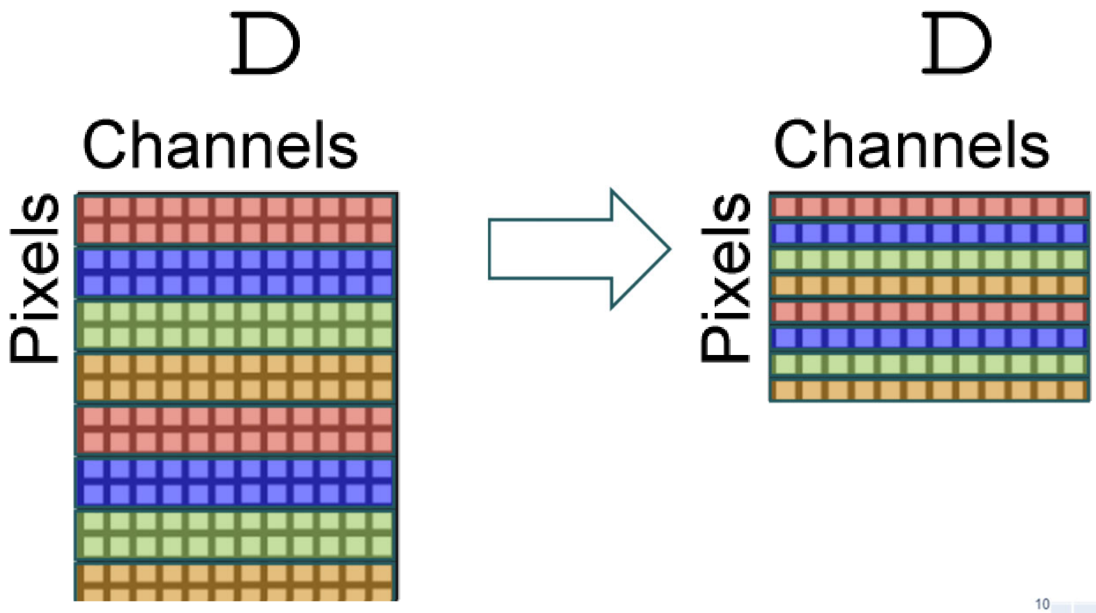
Always ask yourself, "Does this make sense?"

- **Machine learning methods can't help you if you don't bring your domain expertise to bear!**

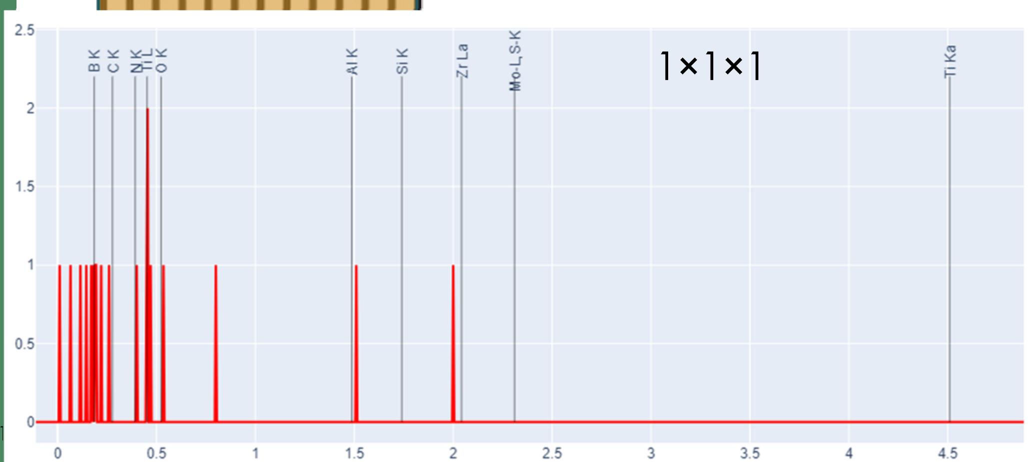


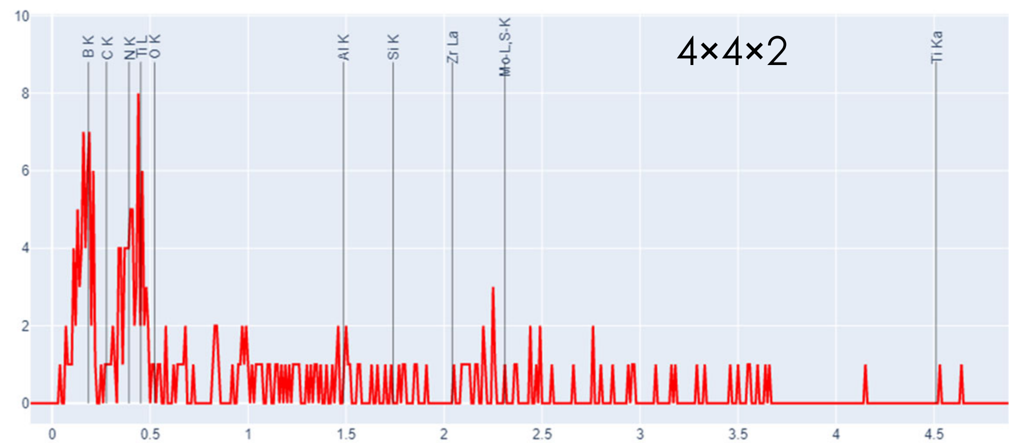


Optional: binning

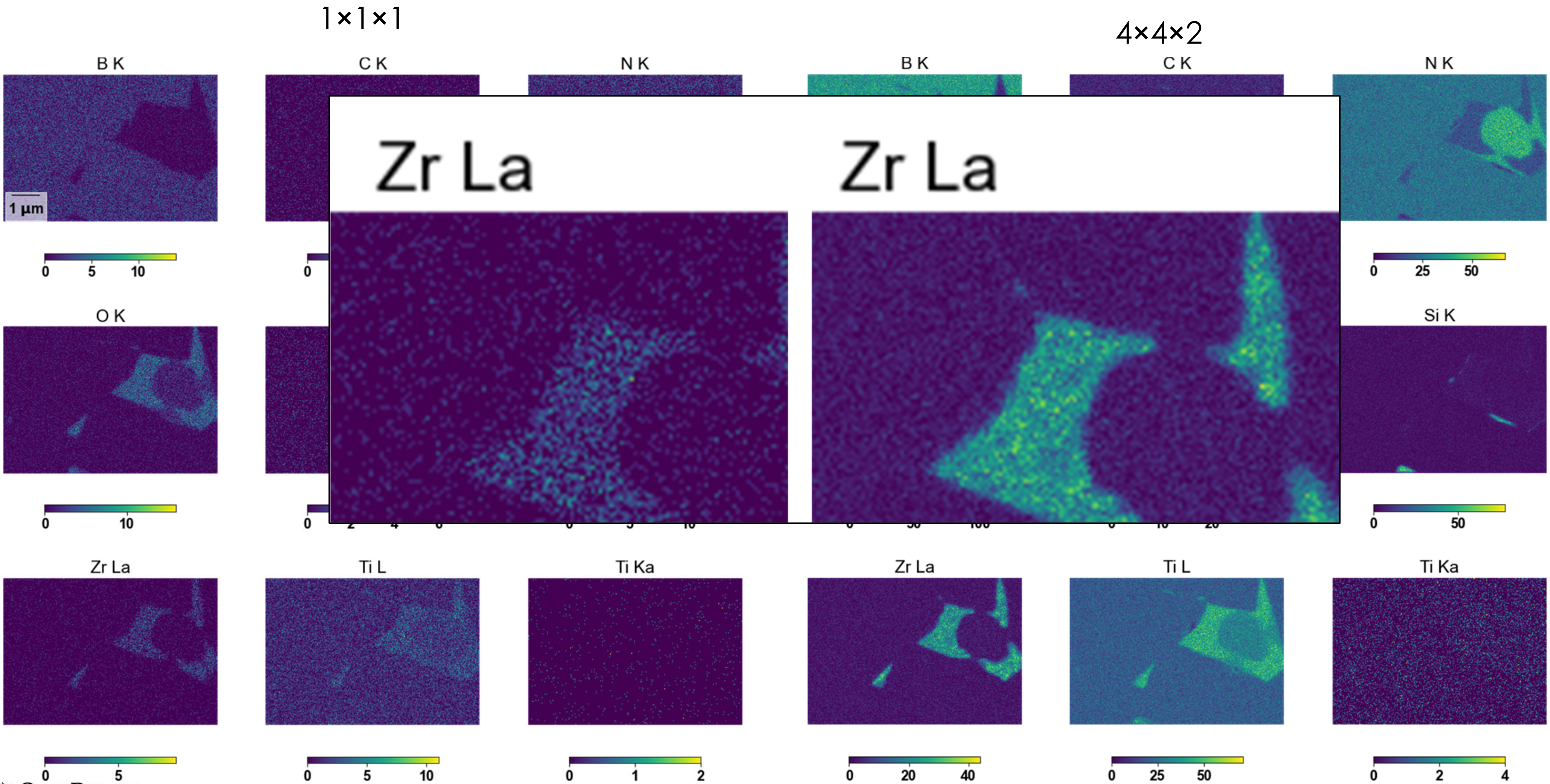


Here: 4×4 space, ×2 spectral
(32× aggregate binning)



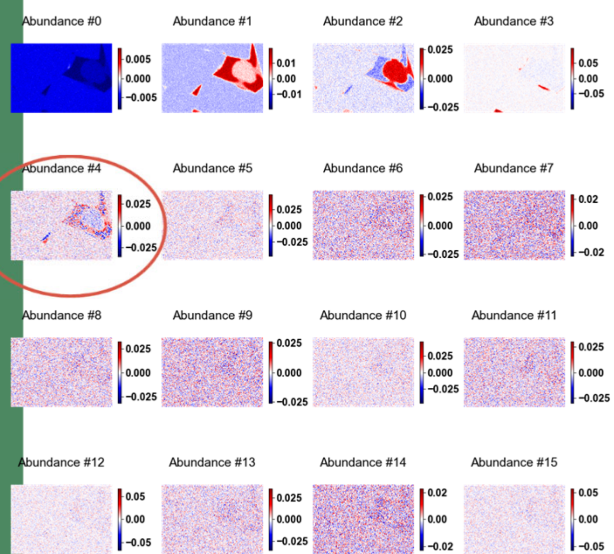


Binning comparison

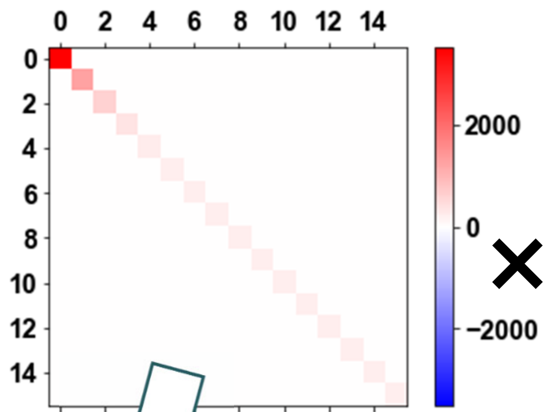


Singular Value Decomposition: binned

$$\hat{D} \approx U \Sigma V^T$$



×



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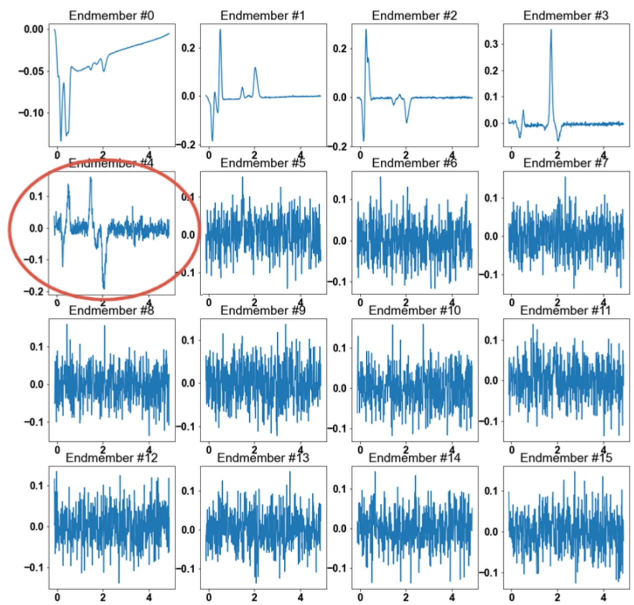

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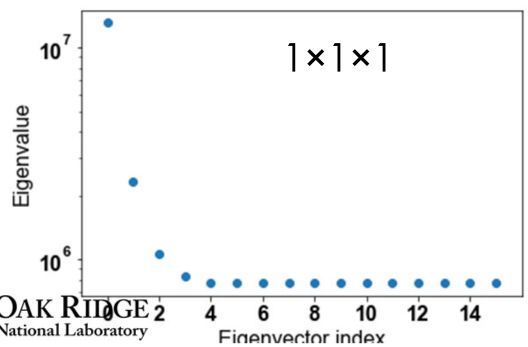
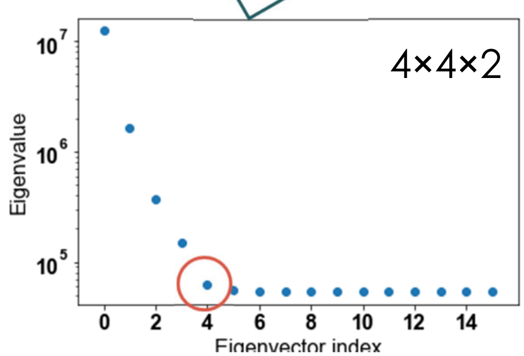
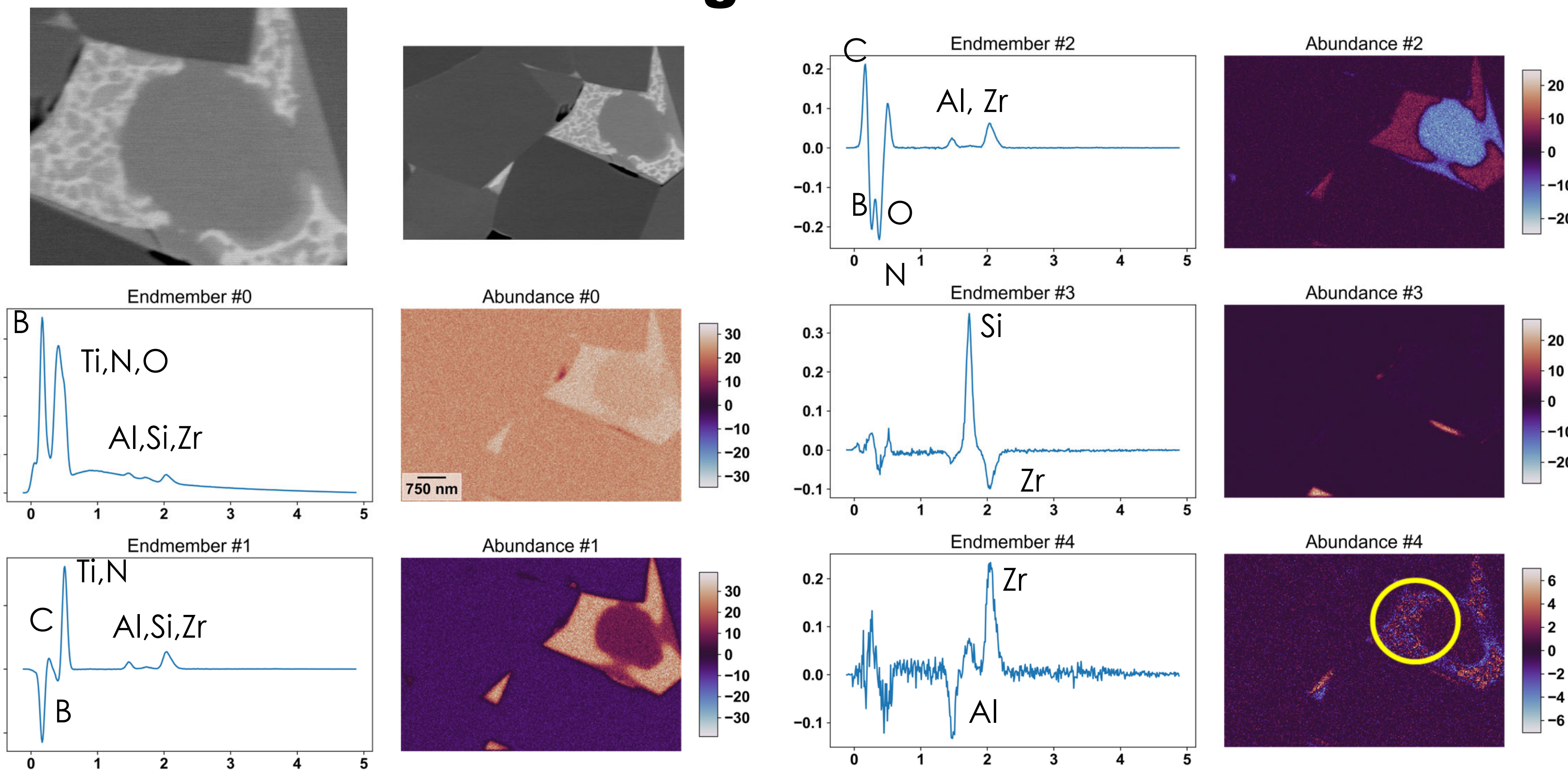




Eigenvalues = singular values^2

Binned: now we’re seeing the features!

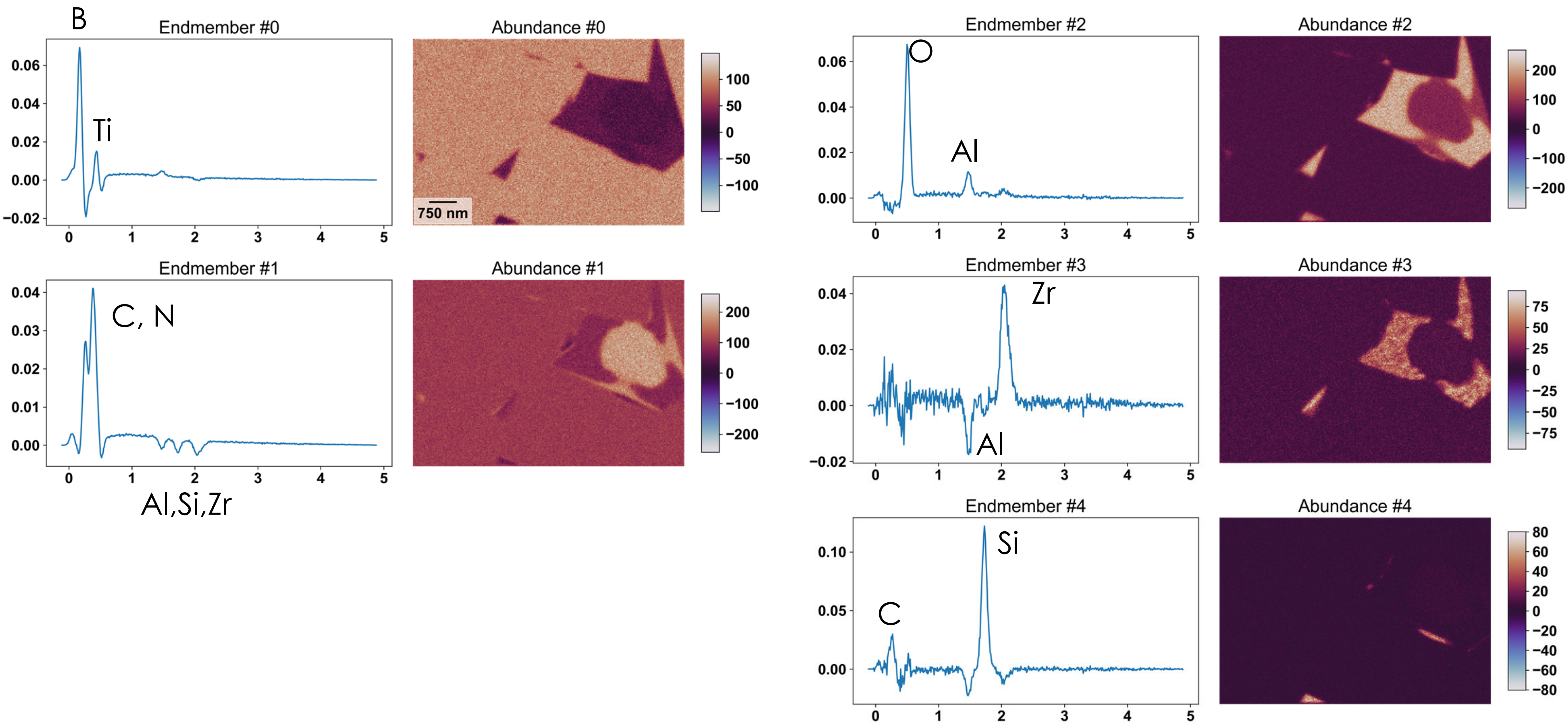


Final step: rotations

$$D \approx (TR)(R^{-1}P)^T = \tilde{T}\tilde{P}^T$$ (Assuming R^{-1} exists)

- **The goal here is to choose an "intelligent" R to make the abundances and endmembers easier to interpret**
- **Literally infinite R exist**
- **Generally choose *orthogonal* rotation, $R^T=R^{-1}$**
- **Most common approach: "varimax criterion"**
- **Rotate to *simplicity*:**
  - **"Simplicity" means, essentially, try to have only one strong value at each pixels or channel**
  - **Make "P" simple → "spectral simplicity"**
  - **Make "T" simple → "spatial simplicity"**
- **Simple concept, but very pedantic in detail:**
  - Smentkowski, V. S., S. G. Ostrowski and M. R. Keenan (2009). Surface and Interface Analysis 41: 88-96.
  - Keenan, M. R. (2007). Techniques and Applications of Hyperspectral Image Analysis. H. F. Grahn and P. Geladi. Chichester, John Wiley & Sons: 89-126.
  - Keenan, M. R. (2009). Surface and Interface Analysis 41: 79-87.

Spectral simplicity: find elements



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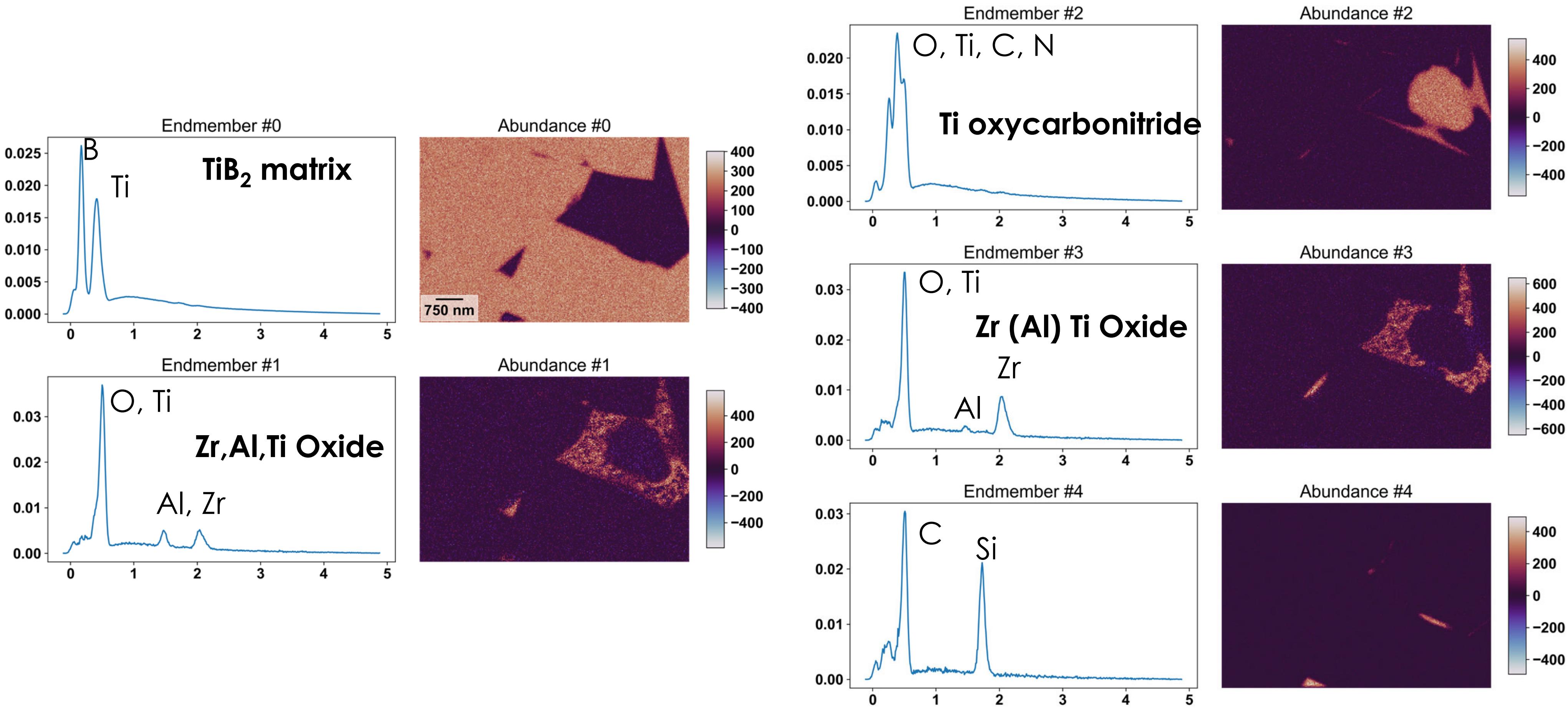
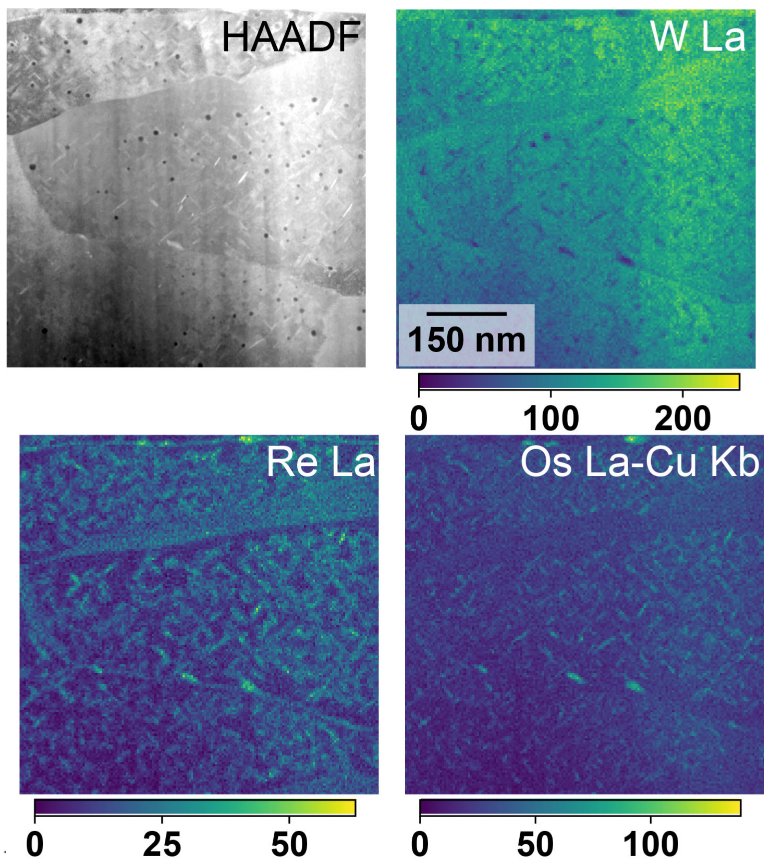
Spectral simplicity: find "phases"

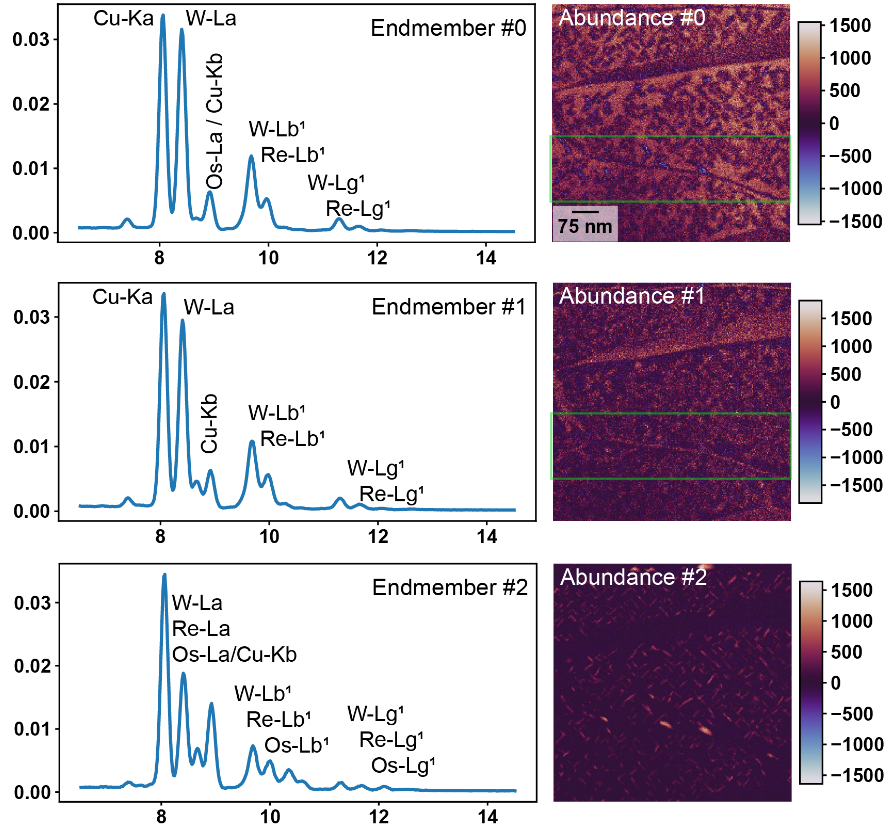


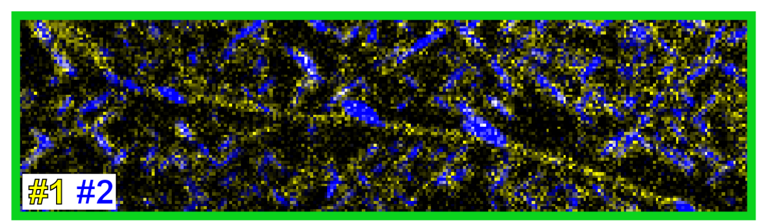
Polishing media (colloidal silica)

Another example: STEM EDS XSI

Neutron-irradiated tungsten, W-Re-Os alloy (Cu TEM holder)







Topics not covered today:

- Cluster analysis (K-means, etc.)
- Choosing analysis energy ranges
- Pros and cons of binning
- Blind source separation / independent component analysis
- Combining with other signals (i.e., EBSD)
- Non-linear effects: absorption, fluorescence

Feel free to contact me offline: parishcm@ornl.gov

Machine Learning of X-ray spectrum images

- S(T)EM-EDS XSIs are large, noisy, and sparse, and therefore ideal for computational attack
- Unsupervised approaches seem most suitable
- The physics are close to linear, so bilinear factor analysis (i.e., PCA/SVD) is supremely suited
- Interpretation of the results requires domain expertise