

- **Spectrum-based Phase Mapping of Apatite and Zoned Monazite Grains Using PCA**

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# Phosphate Mineralogy 101

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- Apatite ( $\text{Ca}_5[\text{PO}_4]_3[\text{F}, \text{Cl}, \text{OH}]$ )
  - Mineral identified in terrestrial, lunar, martian, and asteroidal rocks (also in bones)
  - Can contain trace concentrations of REE, Th, and U



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  - Can contain trace concentrations of REE, Th, and U
- Monazite ( $[\text{La},\text{Ce},\text{Pr},\text{Nd},\text{Sm},\text{Th}]\text{PO}_4$ )
  - Rare mineral in terrestrial and lunar rocks
  - Monoclinic counterpart of the tetragonal xenotime ( $[\text{HREE},\text{Th},\text{U}](\text{P},\text{Si})\text{O}_4$ )
  - LREE ore
    - Magnets
    - Hybrid car batteries
  - Th, U, and radiogenic Pb concentrations can be high enough for geochronology by EPMA



# Introduction

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- Considerations associated with EDS and WDS X-ray mapping
  - Minimizing the interaction volume of the electron probe
  - Collecting a statistically meaningful number of counts above background
  - Selecting the appropriate elements for mapping
  - Avoiding sample damage



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  - Selecting the appropriate elements for mapping
  - Avoiding sample damage
- Confusing results may be unavoidable
  - Multiple phases with similar compositions
  - Elements that produce interfering X-ray lines
    - In same phase
    - In different phases in the mapped area



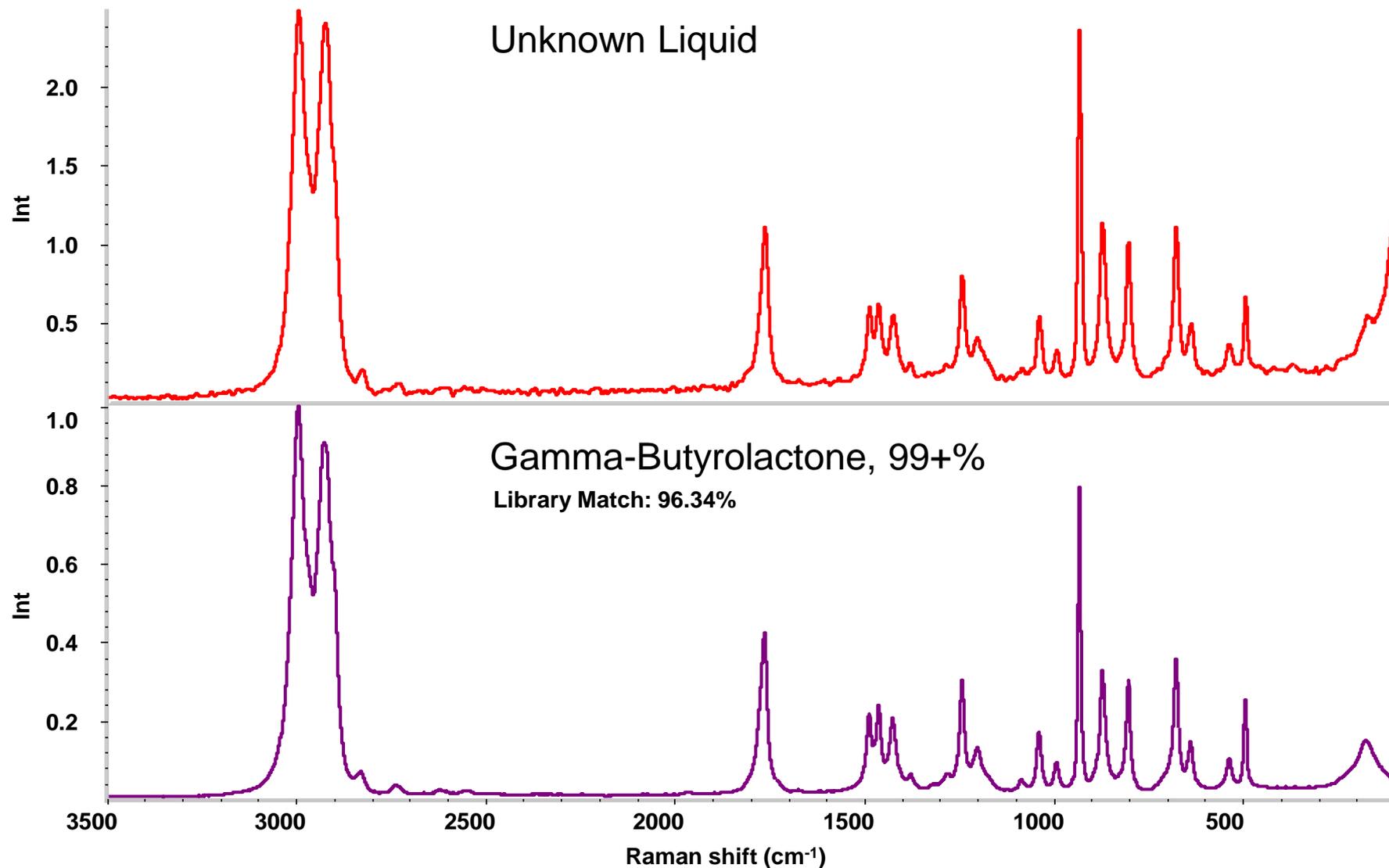
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    - In different phases in the mapped area
- Contrast enhancements and image filtering can help but do not eliminate the confusion





# What about spectrum-based phase mapping?





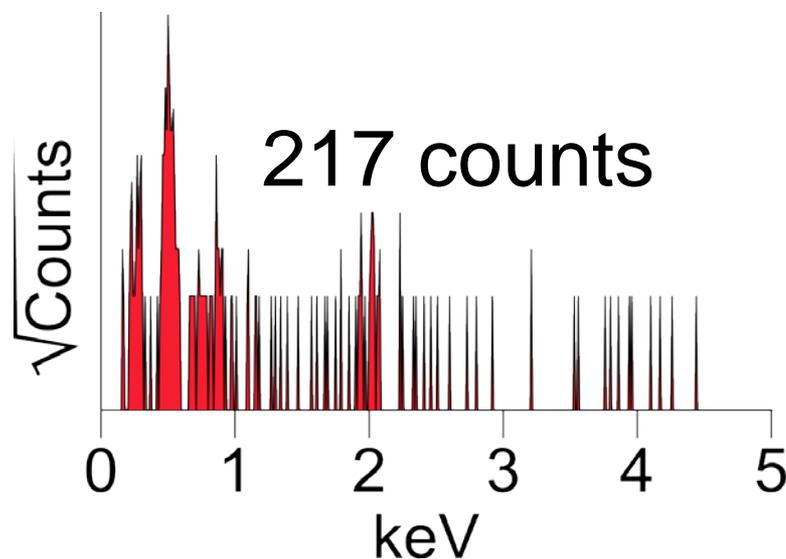
# What about spectrum-based phase mapping?

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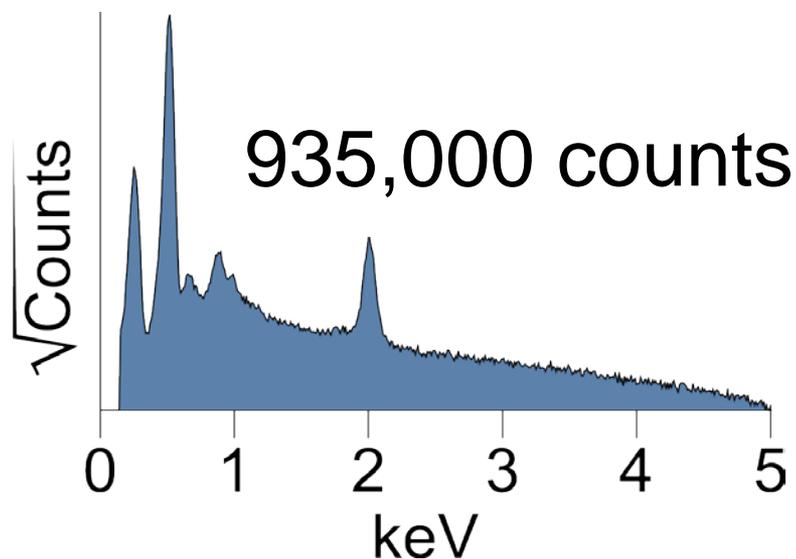
- Software compares a spectrum at each pixel with a spectral library
  - Uses a  $\chi^2$  test to compare spectra
  - Requires a thorough and correct spectral library

# What about spectrum-based phase mapping?

Does

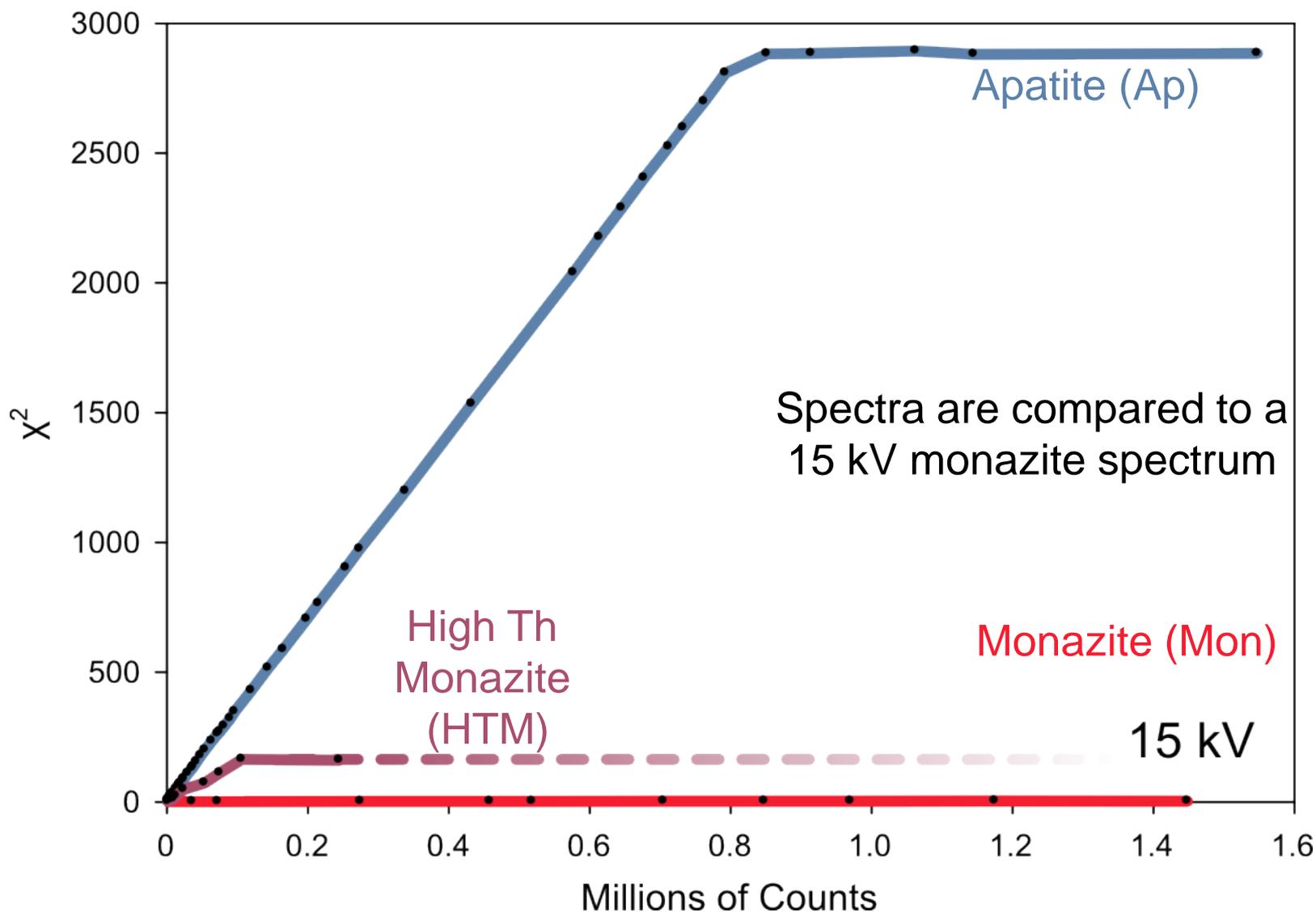


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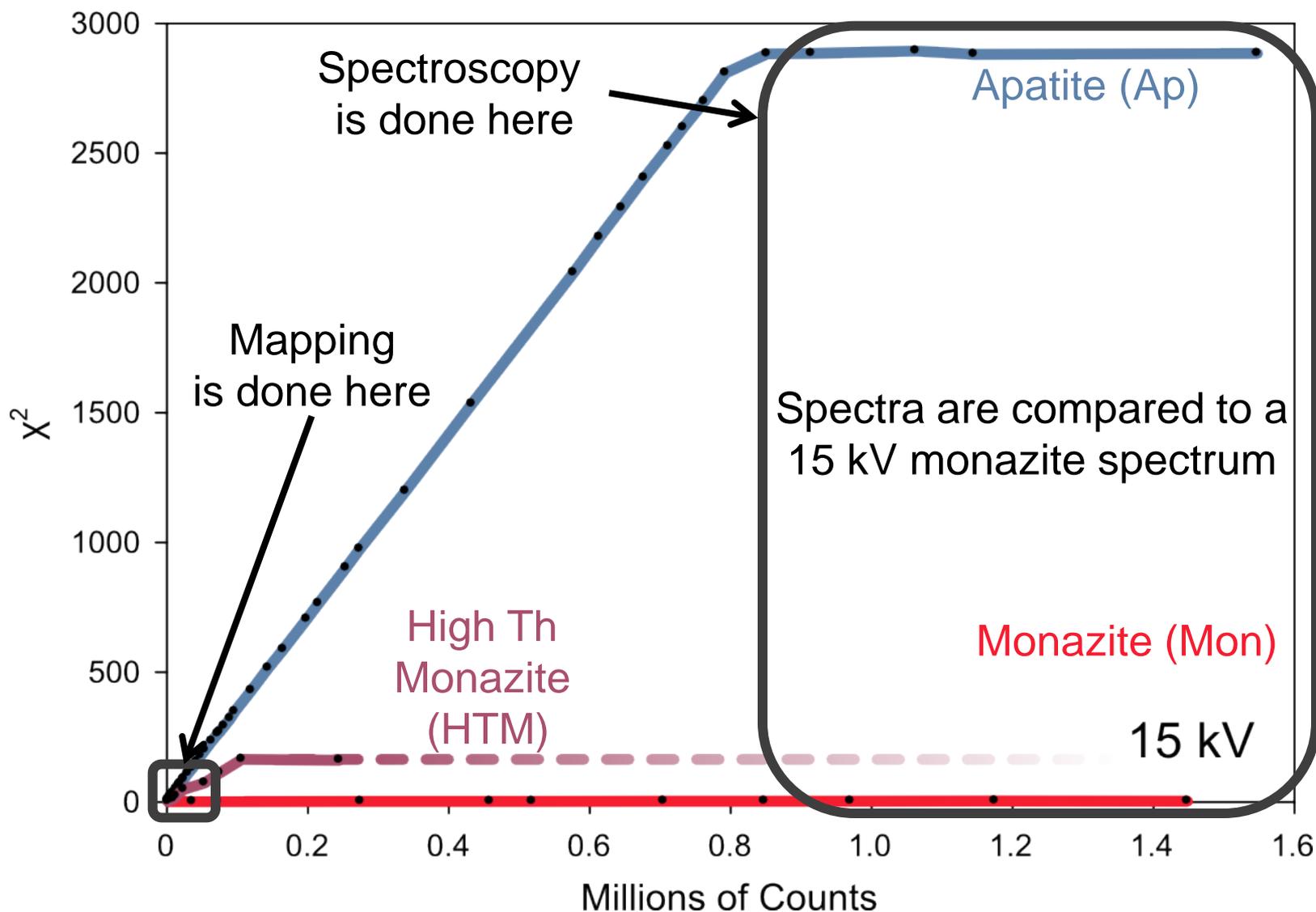


???

# What about spectrum-based phase mapping?

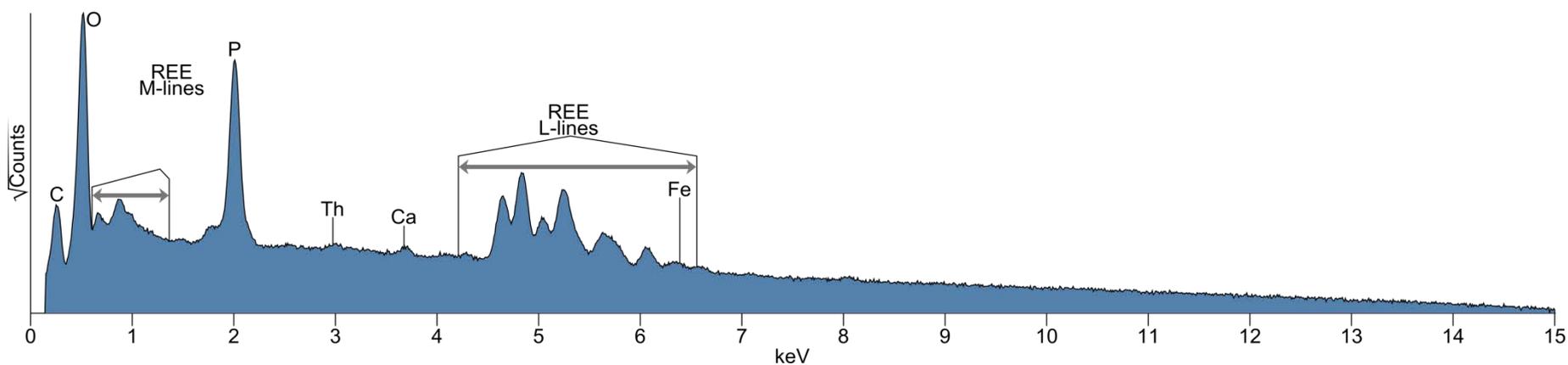
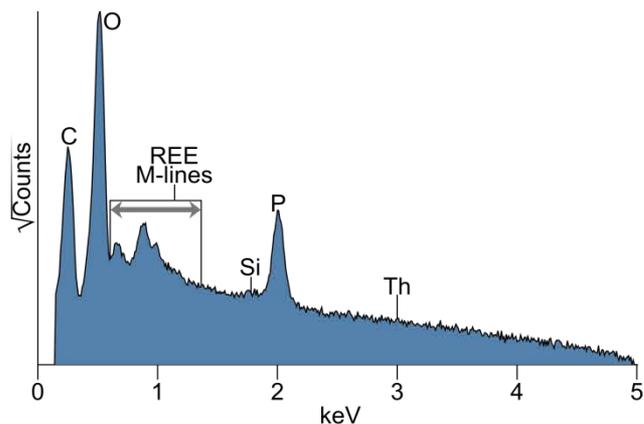


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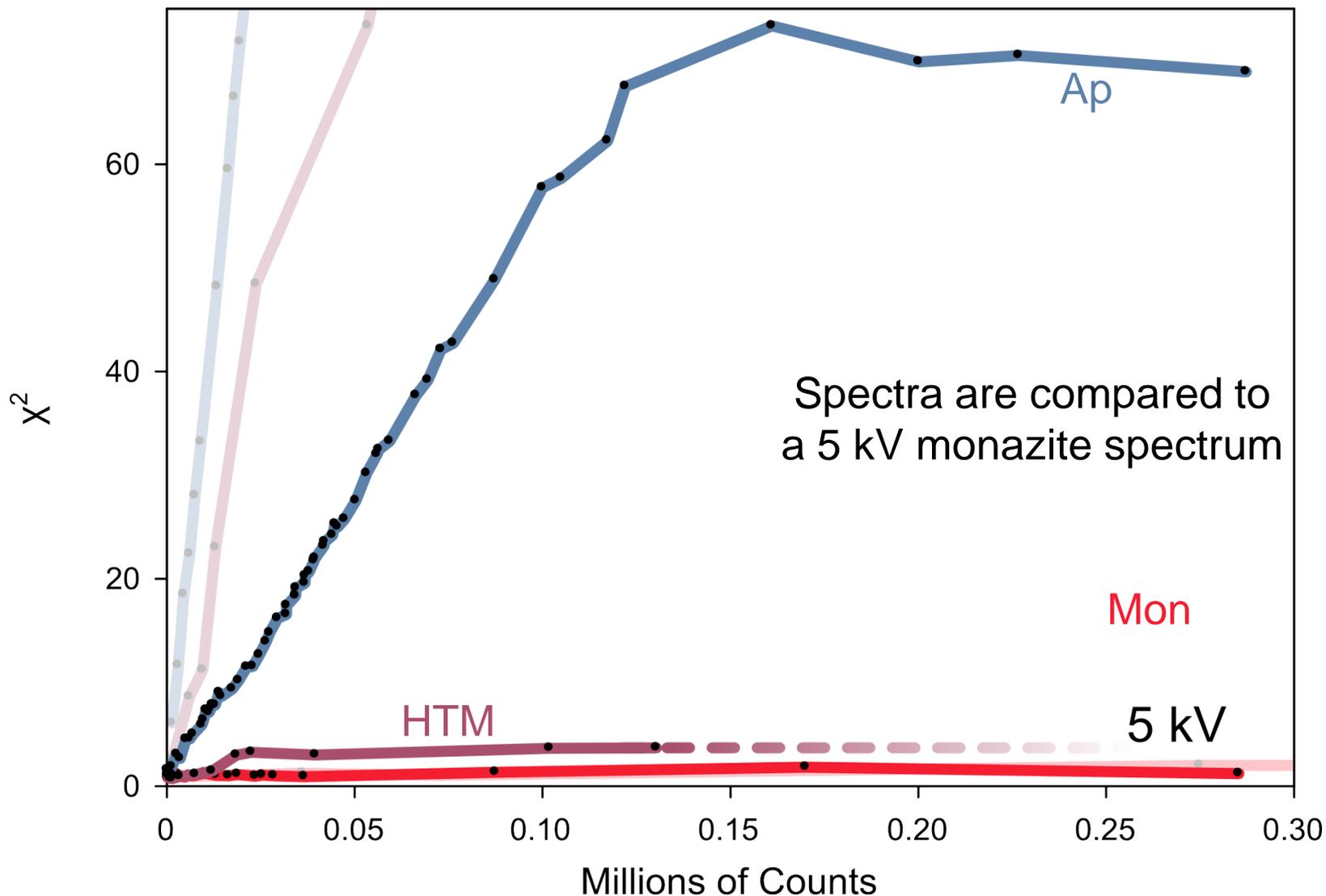


# What about low kV spectrum-based phase mapping?

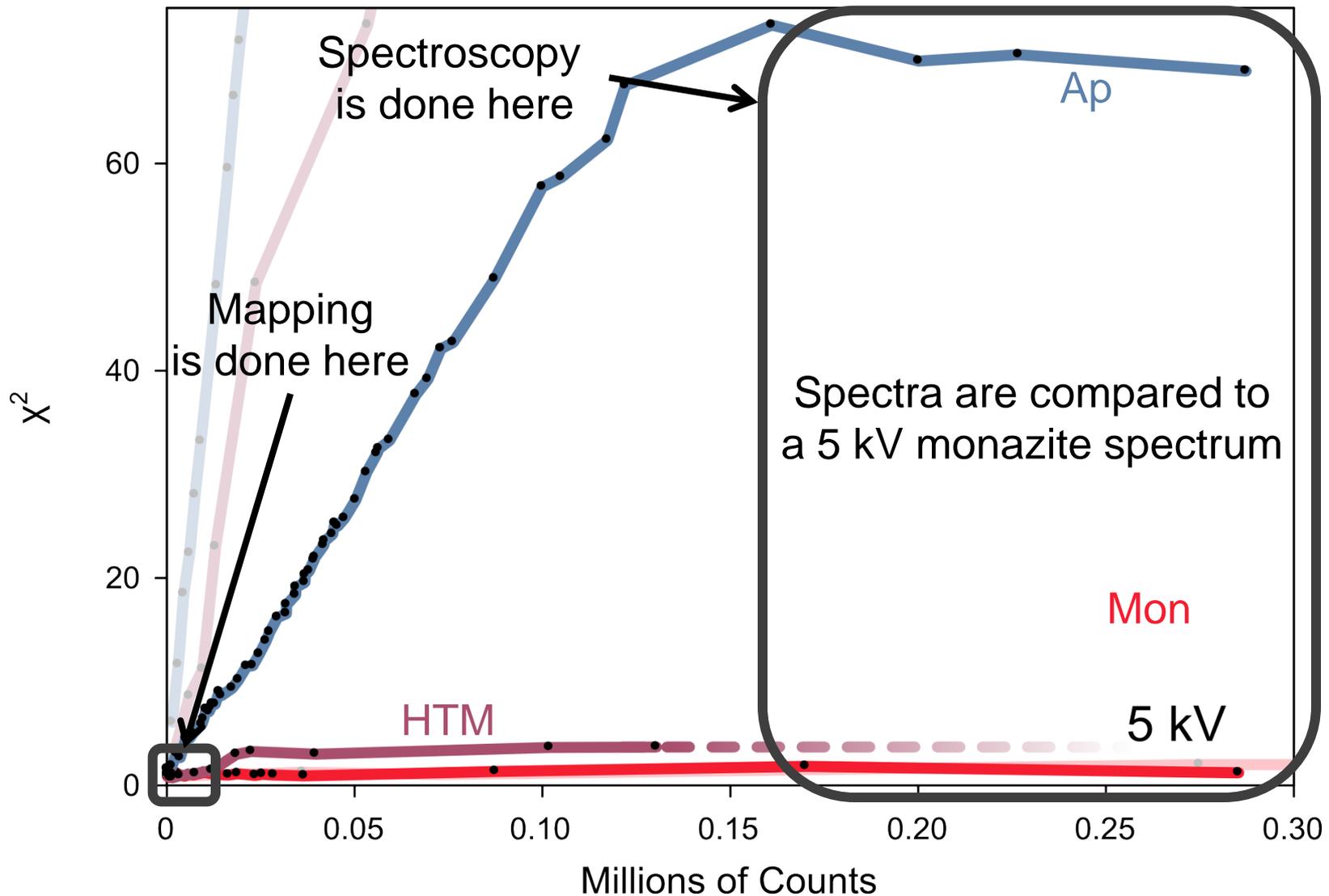
- There is less spectrum for comparison...



# What about low kV spectrum-based phase mapping?



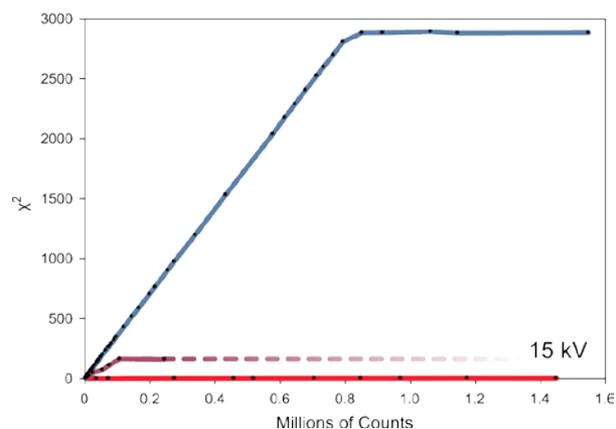
# What about low kV spectrum-based phase mapping?



# What about spectrum-based phase mapping?

## Thought Experiment:

- How many counts to distinguish Apatite and HTM from Monazite?
  - At 15 kV?
    - Compared to itself,  $\chi^2_{\text{Mon}} = \sim 2.5$  for all counts
    - To be distinguishable from monazite,  $\chi^2_{\text{Phase}} > \chi^2_{\text{Mon}}$
    - $\chi^2_{\text{Ap}} \approx 0.00354 \times \text{Counts}_{\text{Ap}}$
    - $\chi^2_{\text{HTM}} \approx 0.0015 \times \text{Counts}_{\text{HTM}} + 1.138$
    - For  $\chi^2 = 2.5$ ,  $\text{Counts}_{\text{Ap}} \approx \underline{700}$ ;  $\text{Counts}_{\text{HTM}} \approx \underline{900}$





# What about SBPM?

## Thought Experiment:

- How many counts to distinguish Apatite and HTM from Monazite?
  - At 5 kV?
    - Compared to itself,  $\chi^2_{\text{Mon}} = \sim 1$  for all counts
    - To be distinguishable from monazite,  $\chi^2_{\text{Phase}} \geq \chi^2_{\text{Mon}}$
    - $\chi^2_{\text{Ap}} \approx 0.000557 \times \text{Counts}_{\text{Ap}}$
    - $\chi^2_{\text{HTM}} \approx 0.0001 \times \text{Counts}_{\text{HTM}} + 0.75$
    - For  $\chi^2 = 1$ ,  $\text{Counts}_{\text{Ap}} \approx \mathbf{1800}$ ;  $\text{Counts}_{\text{HTM}} \approx \mathbf{2500}$



# What about spectrum-based phase mapping?

## Thought Experiment:

- Generate a  $1024 \times 768$  px map
- 100,000 counts per second
- How long to be able to distinguish
  - At 15 kV?
    - Apatite is distinguished from monazite after **1.5 hours**
    - HTM is distinguished from monazite after **2.0 hours**
  - At 5 kV?
    - Apatite is distinguished from monazite after **4.0 hours**
    - HTM is distinguished from monazite after **5.5 hours**



# A Better Way

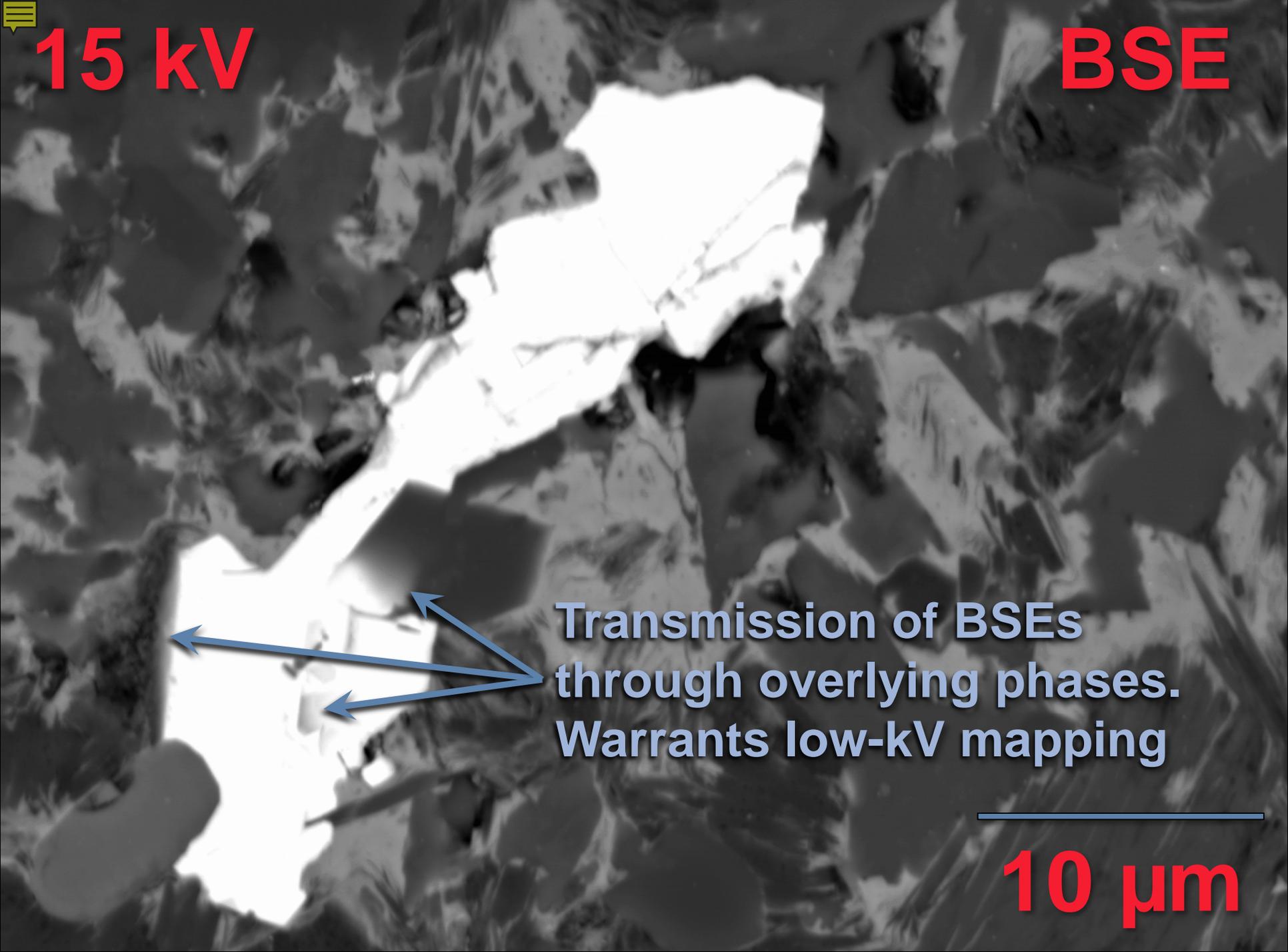
- Elemental mapping can yield messy results
- Spectral matching is SLOW.
- Is there a better way?????
- What does it take to distinguish phases at 25 counts per pixel?
- Principal component analysis to the rescue!
- Let's look at an example...

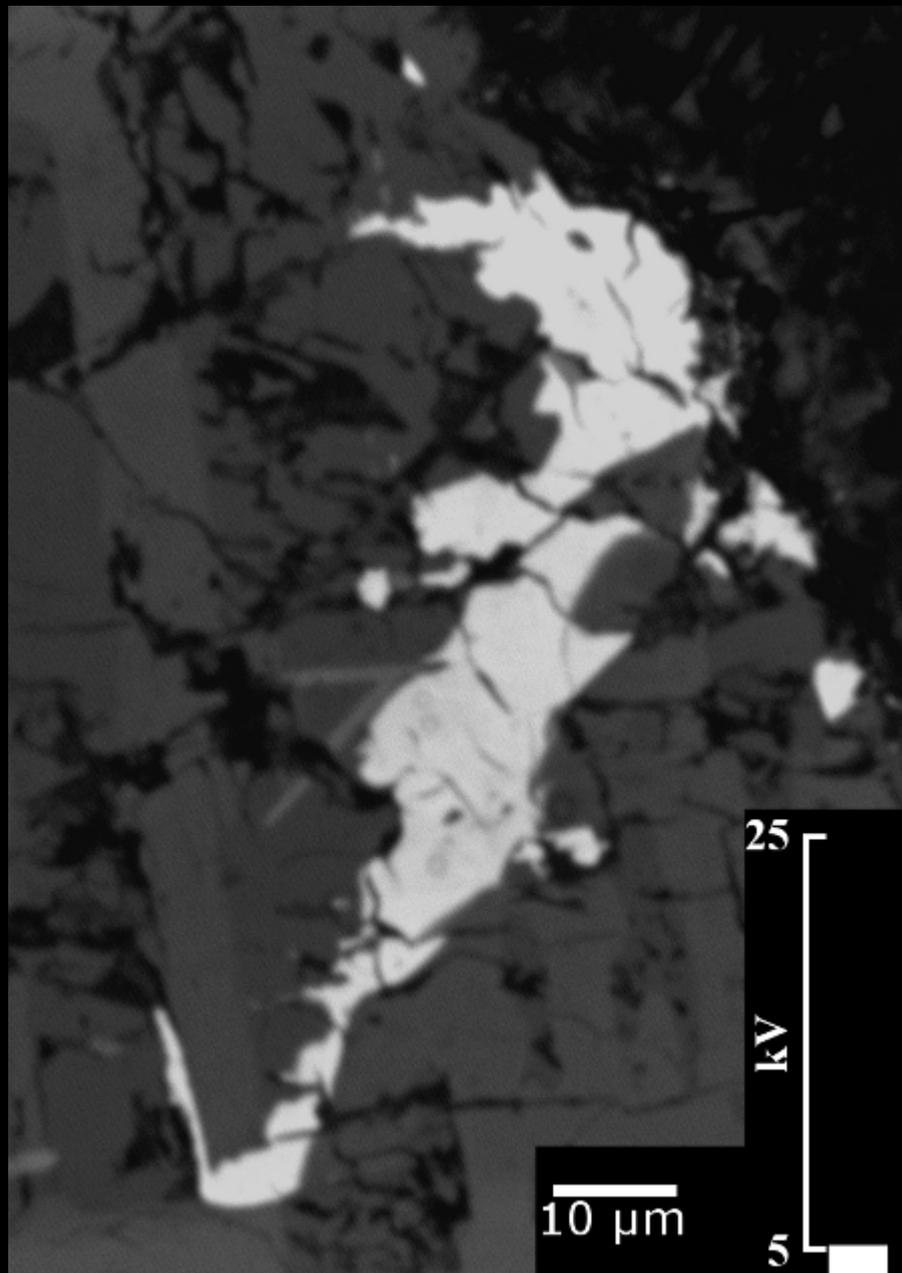
**15 kV**

**BSE**

Transmission of BSEs  
through overlying phases.  
Warrants low-kV mapping

**10  $\mu\text{m}$**





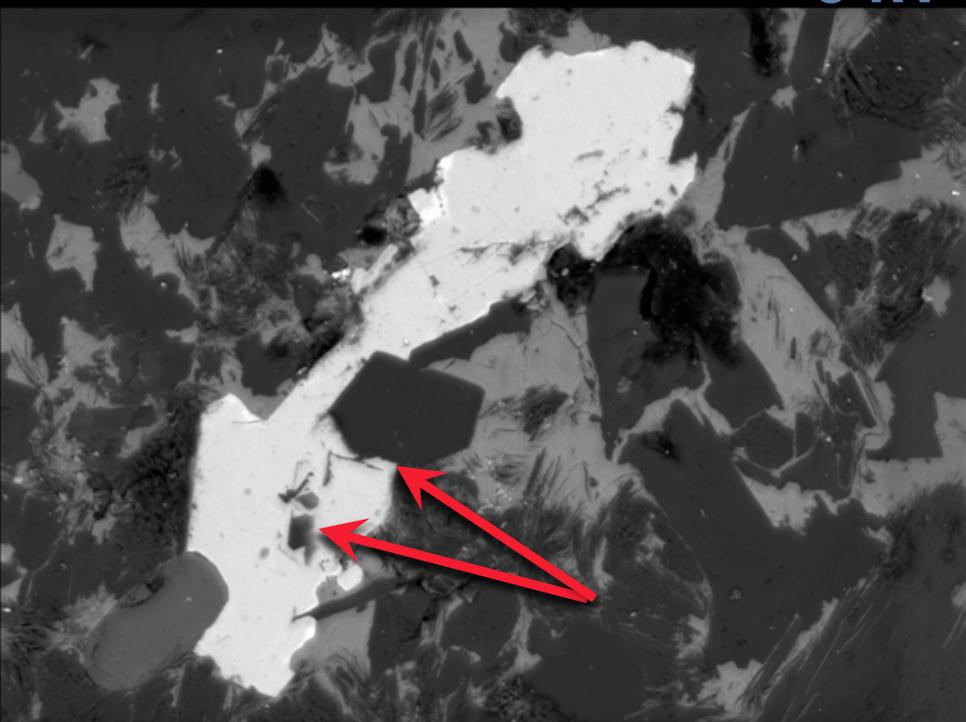
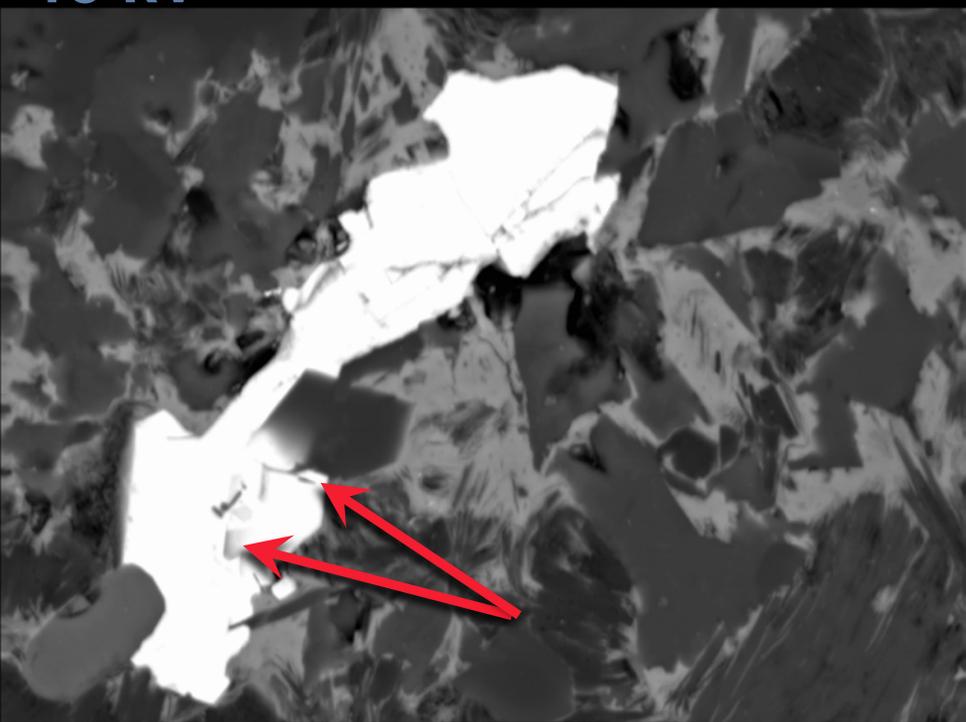
From Seddio et al., 2011



15 kV

BSE

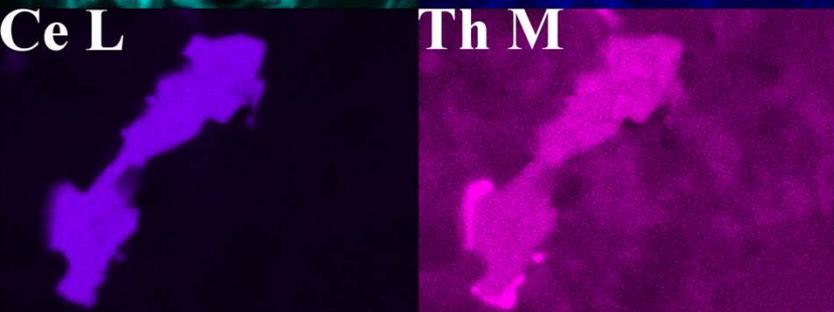
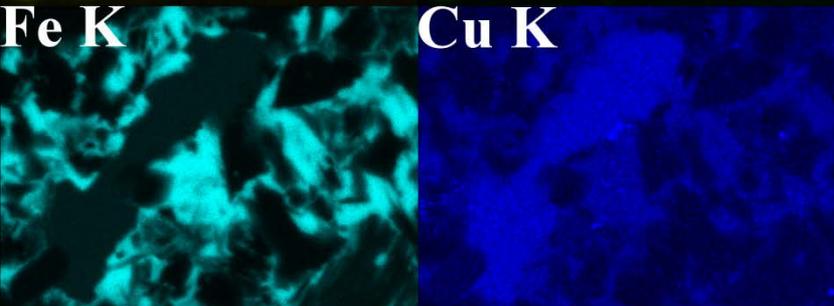
5 kV



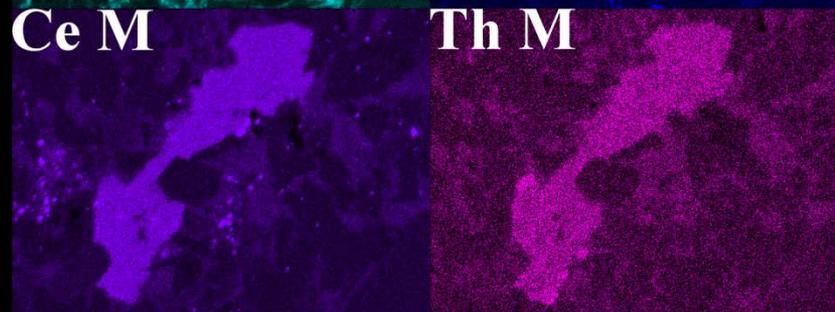
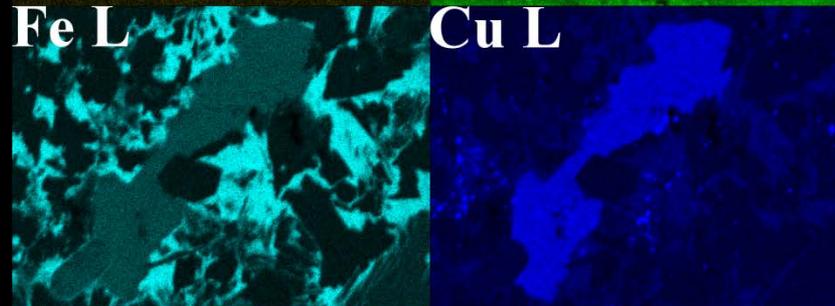
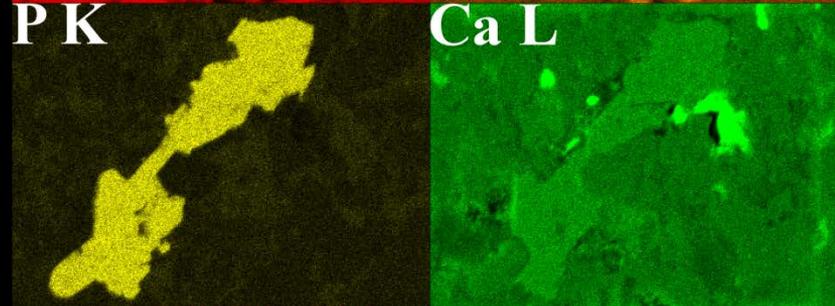
10  $\mu\text{m}$

Both mapping runs were acquired for 2.5 hr

15 kV 1575 counts per px

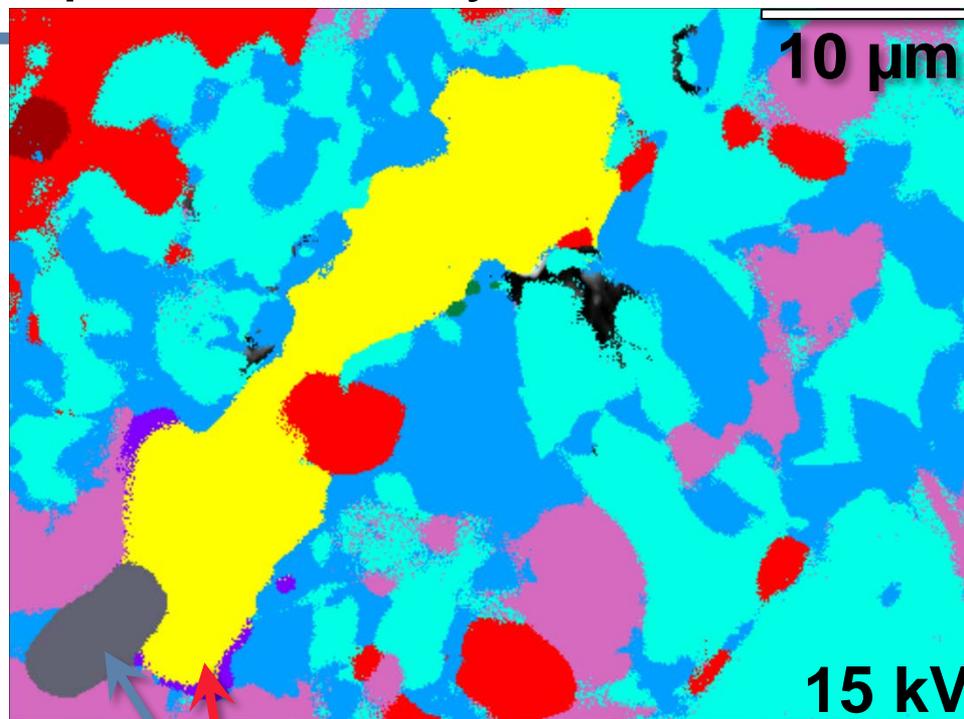


232 counts per px 5 kV

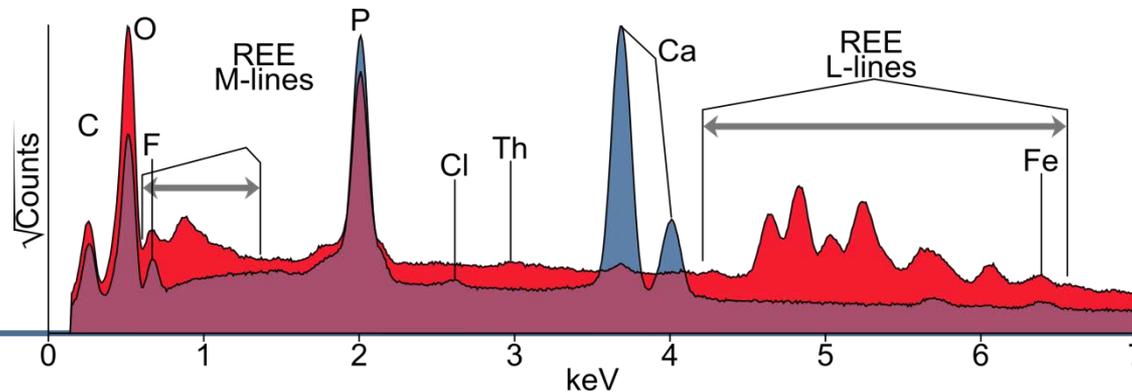


10  $\mu$ m

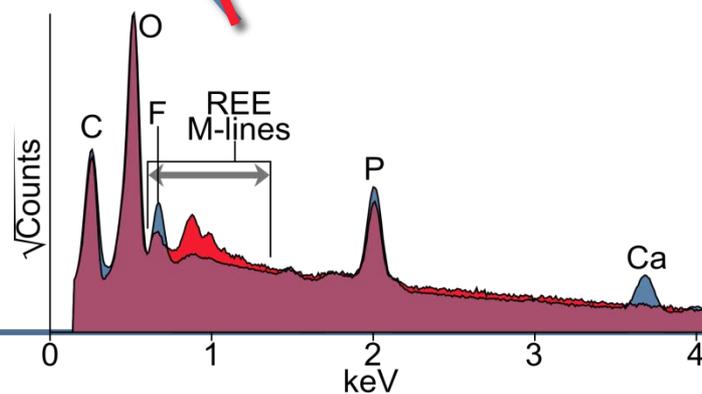
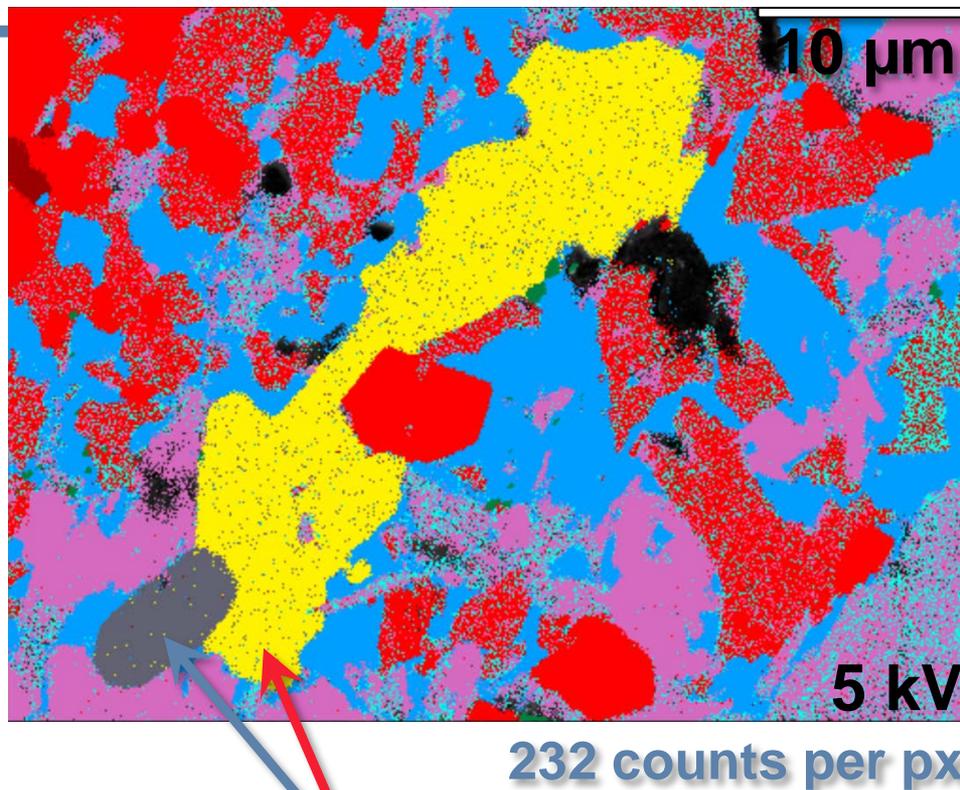
# Principal Component Analysis



1575 counts per px



# Principal Component Analysis

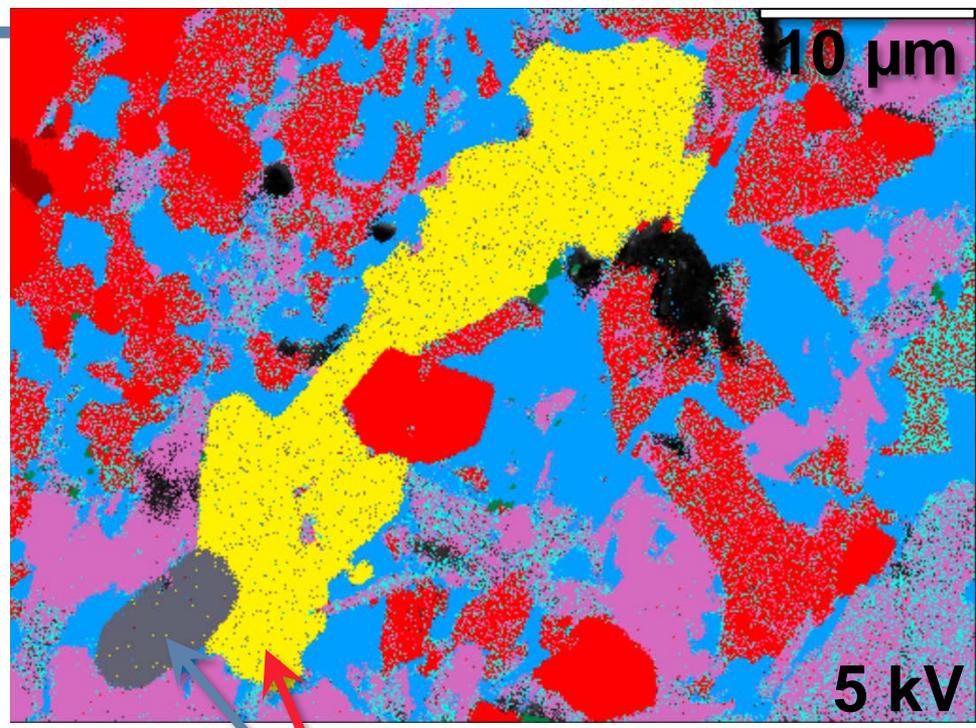




# Principal Component Analysis

**12**

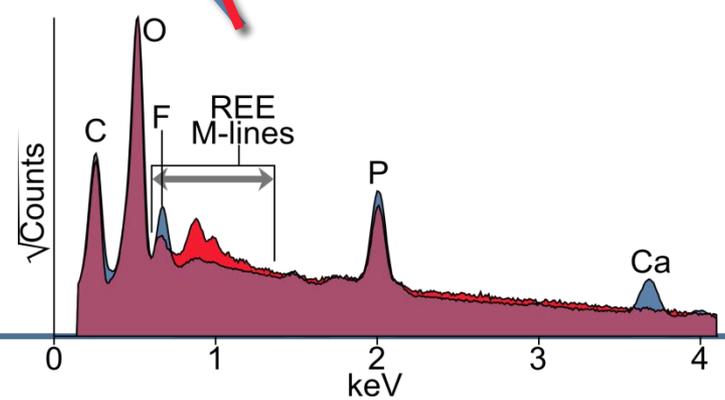
**COUNTS PER  
PIXEL!!!**



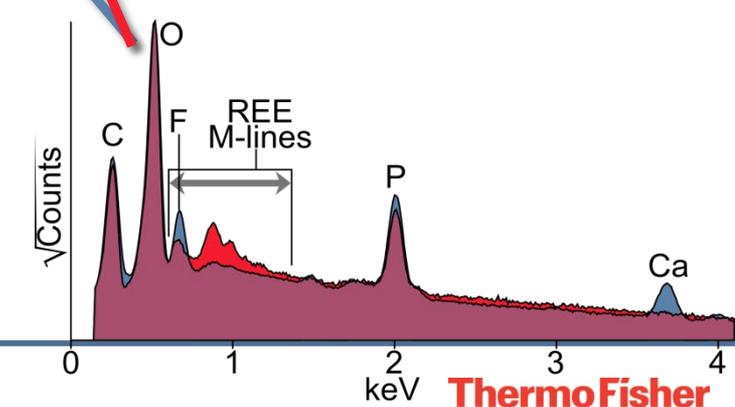
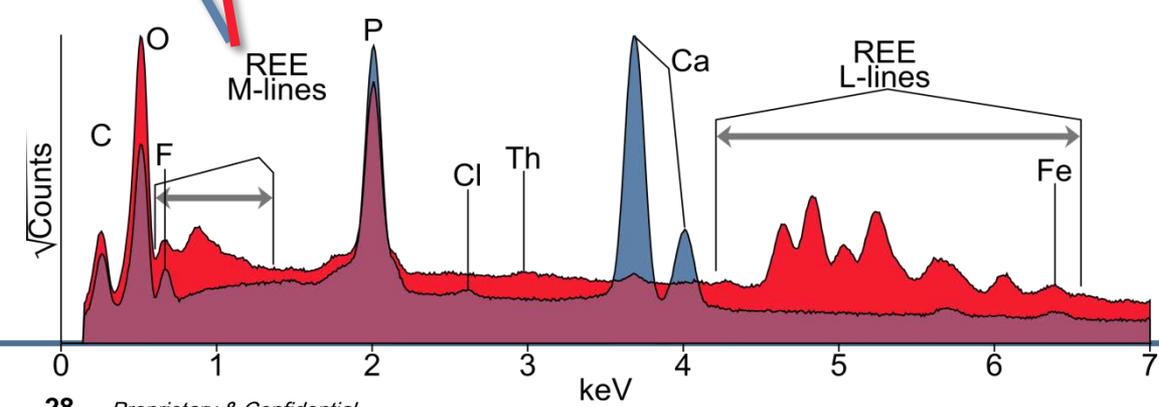
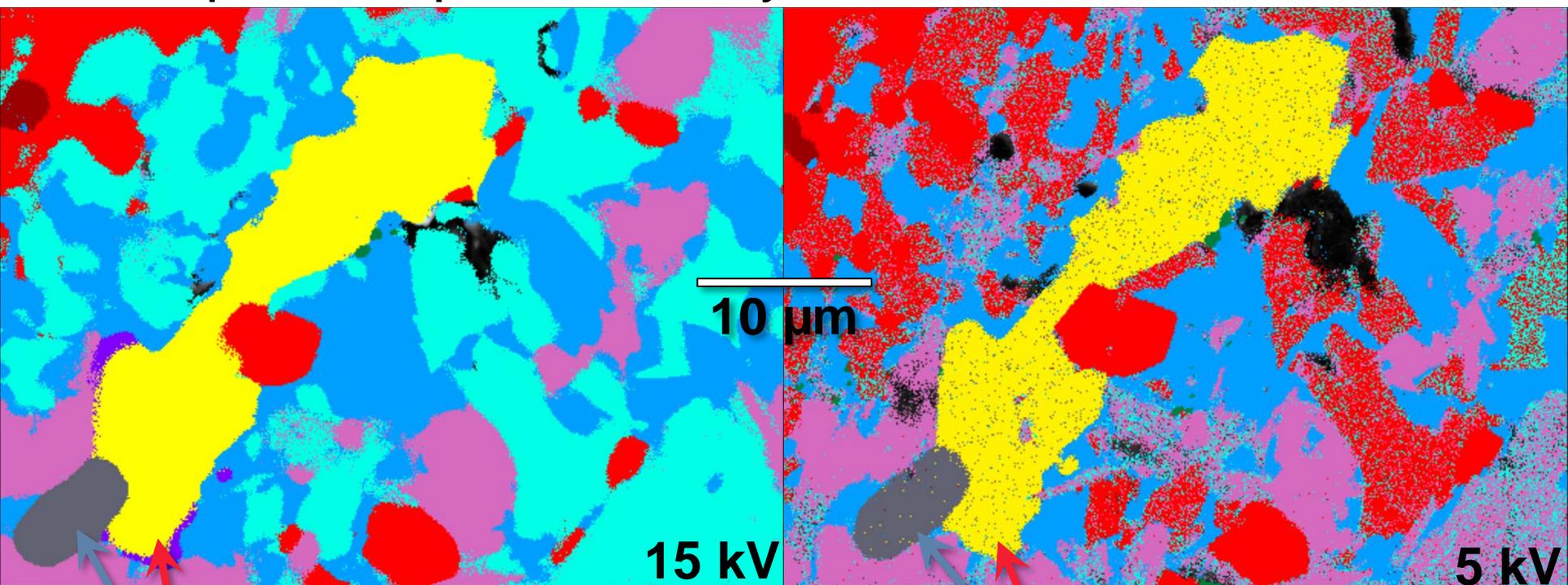
**232 counts per px**

**12**

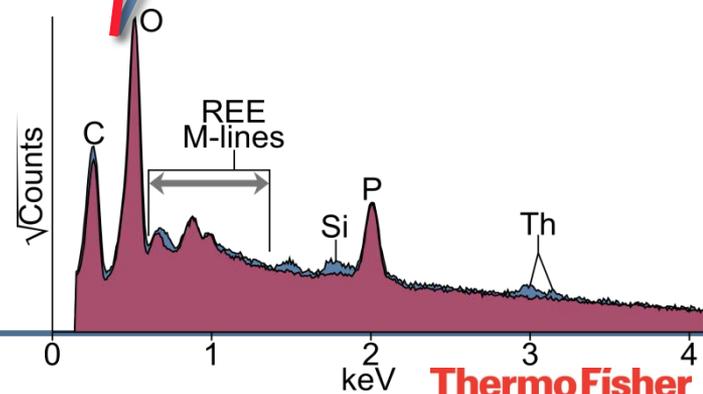
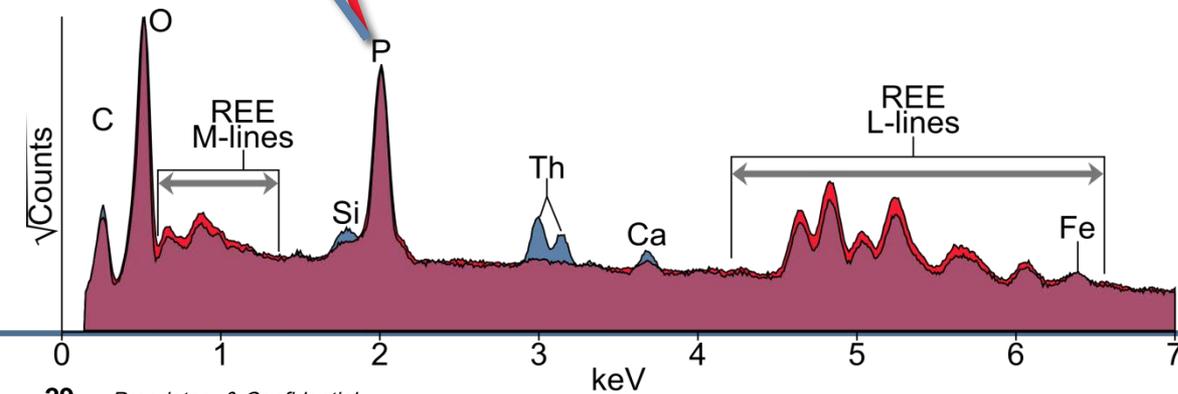
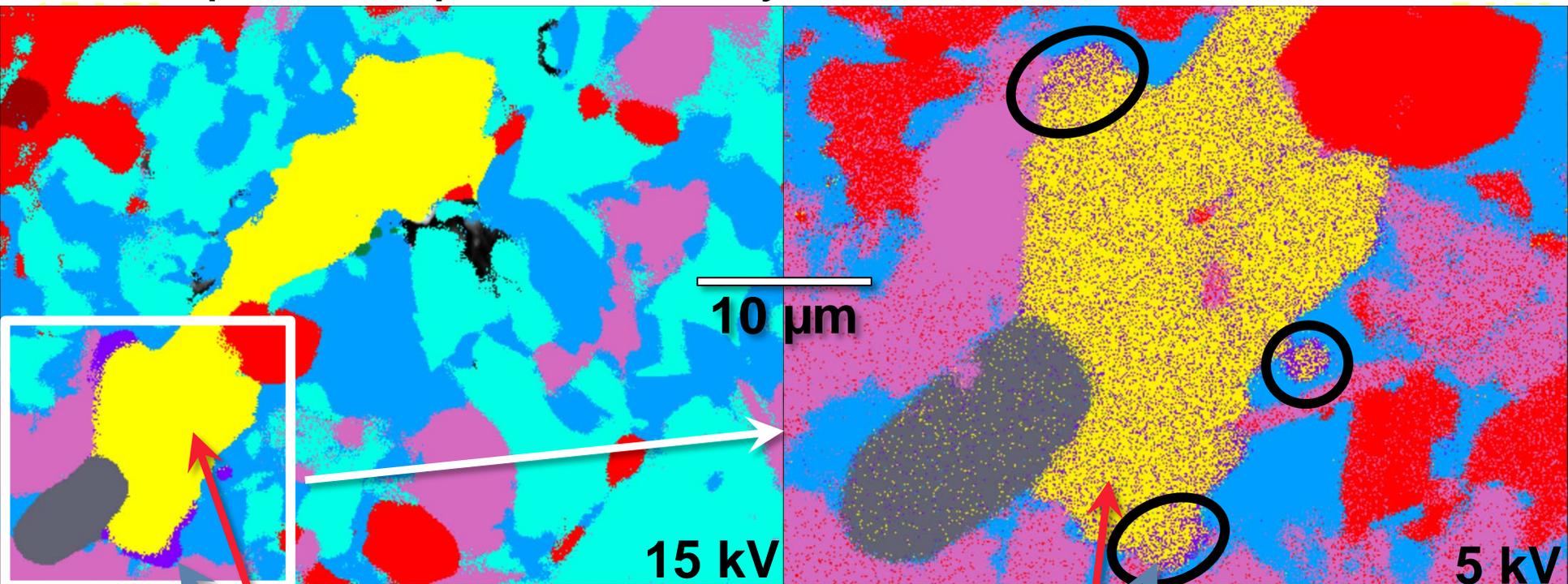
**COUNTS PER  
PIXEL!!!**



# Principal Component Analysis



# Principal Component Analysis



# Conclusions

- Principal component analysis is required for understanding and interpreting otherwise confusing X-ray maps
- It provides identification of phases in a fraction of the time
- Principal component analysis is an accepted technique in ever other industry
  - Delivering packages
  - Scheduling airlines
  - Credit card campaigns
  - Telemarketing
  - Remote sensing

