



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

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Phosphate Mineralogy 101

- 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



Phosphate Mineralogy 101

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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

- 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



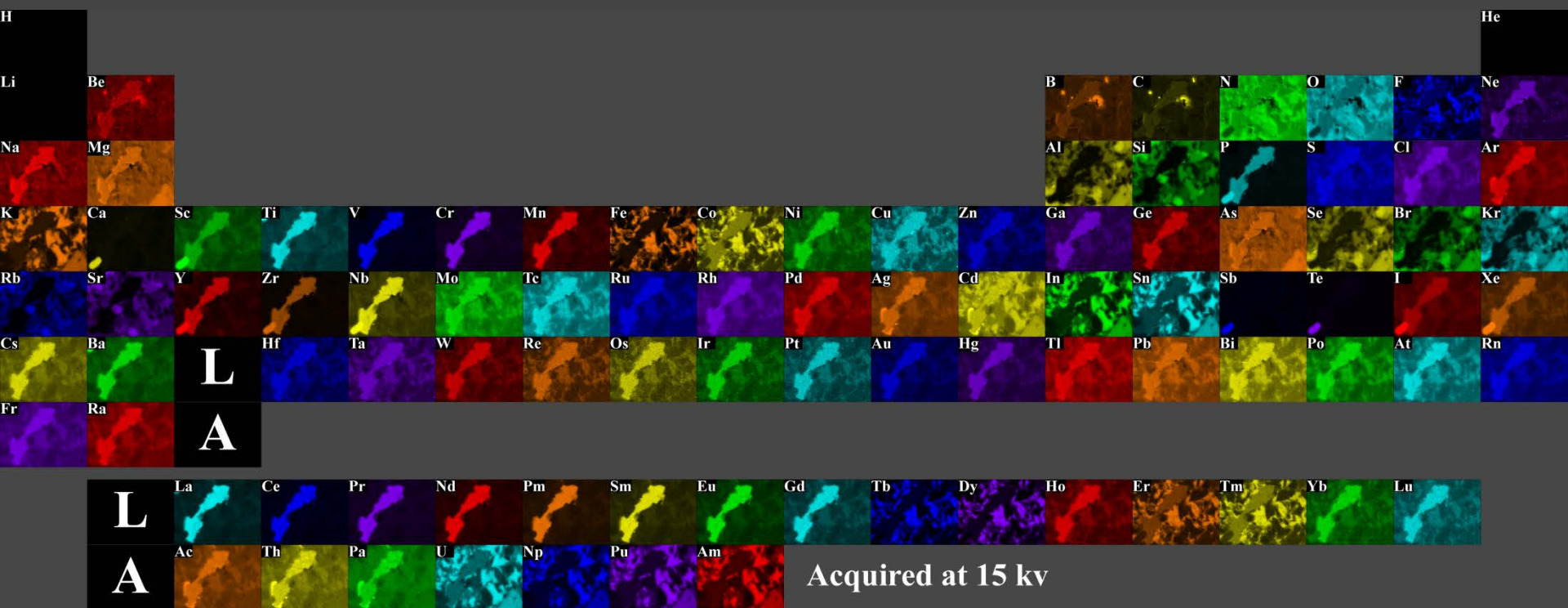
Introduction

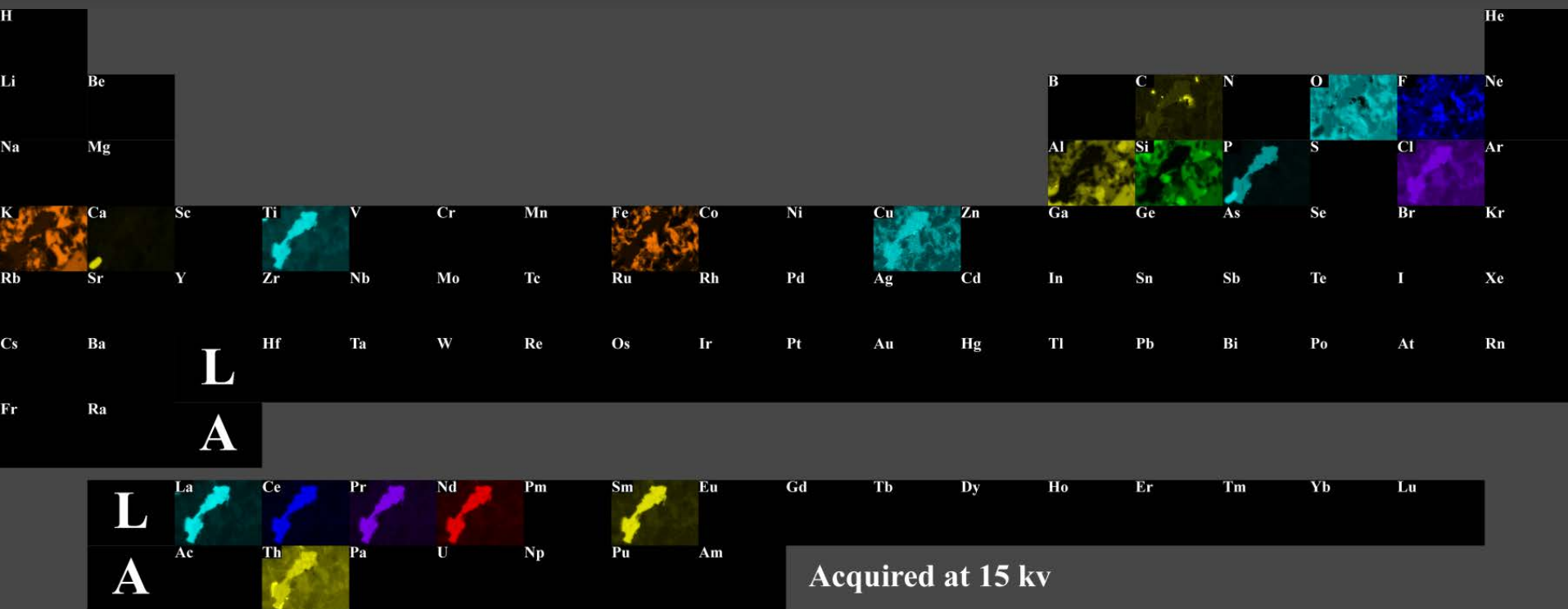
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- Confusing results may be unavoidable
 - Multiple phases with similar compositions
 - Elements that produce interfering X-ray lines
 - In same phase
 - In different phases in the mapped area



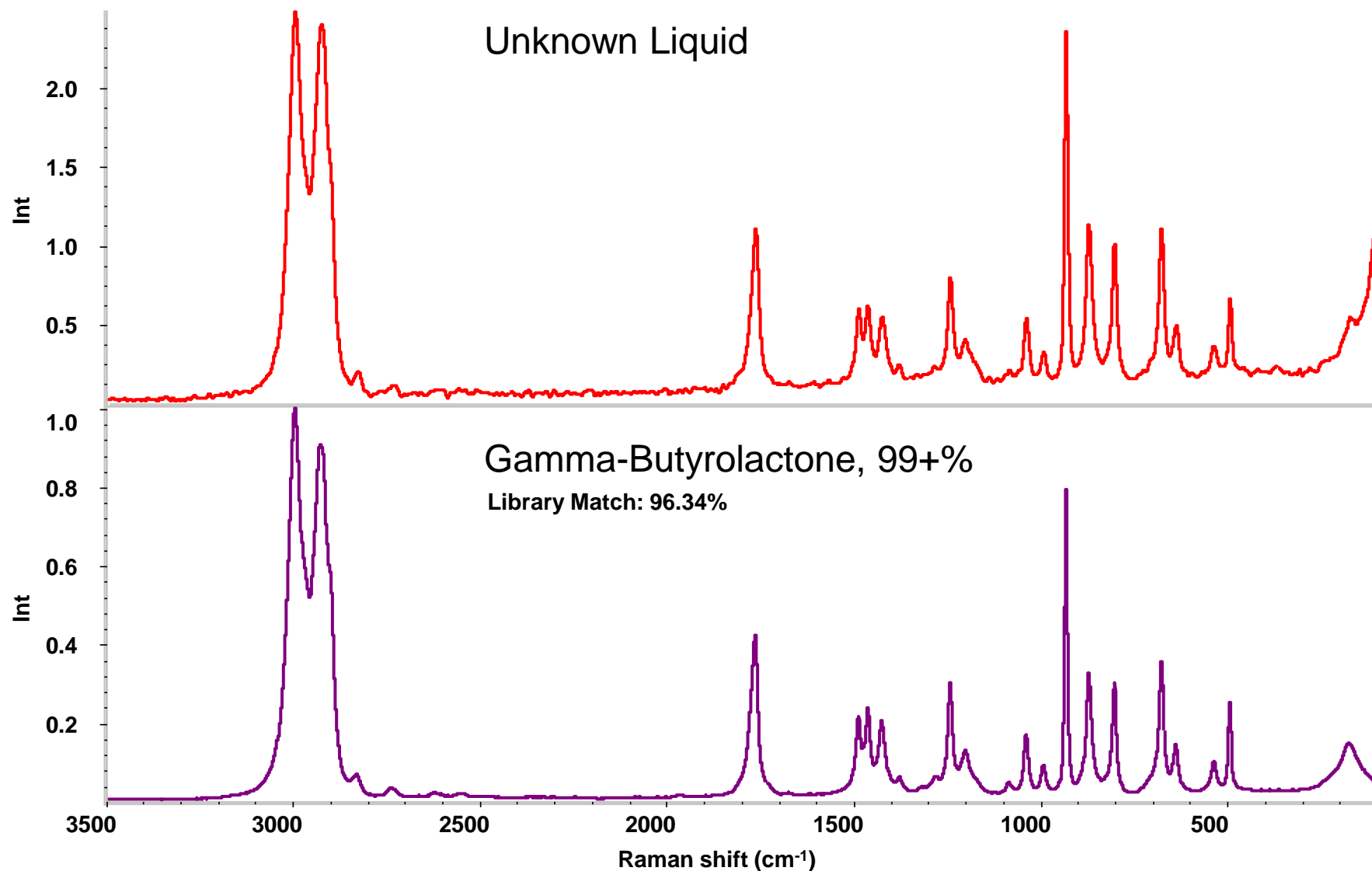
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 - In same phase
 - In different phases in the mapped area
- Contrast enhancements and image filtering can help but do not eliminate the confusion





What about spectrum-based phase mapping?





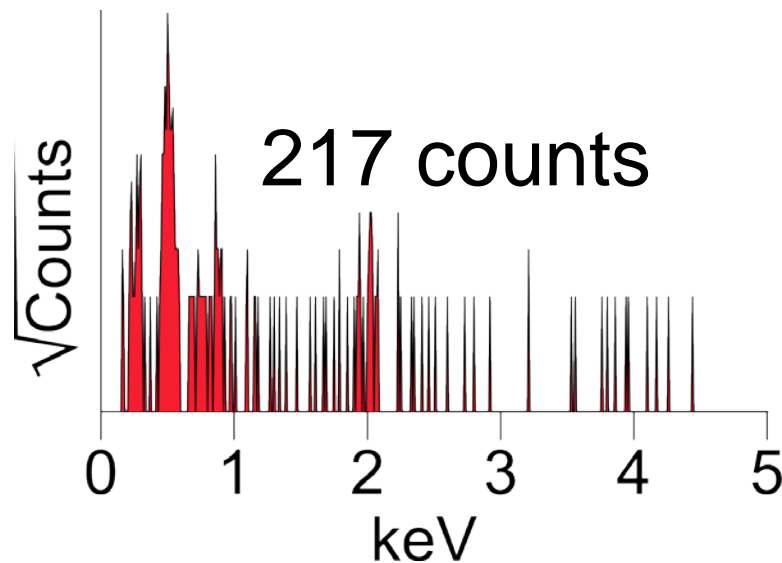
What about spectrum-based phase mapping?

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

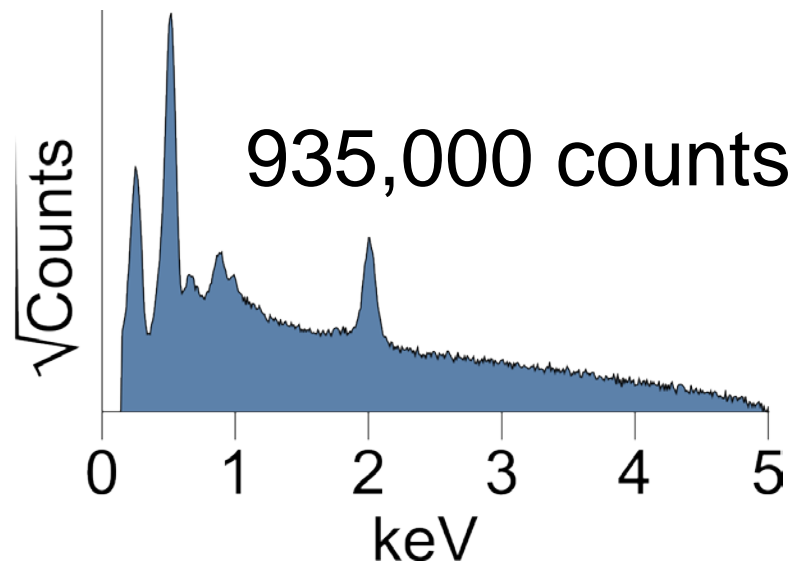


What about spectrum-based phase mapping?

Does

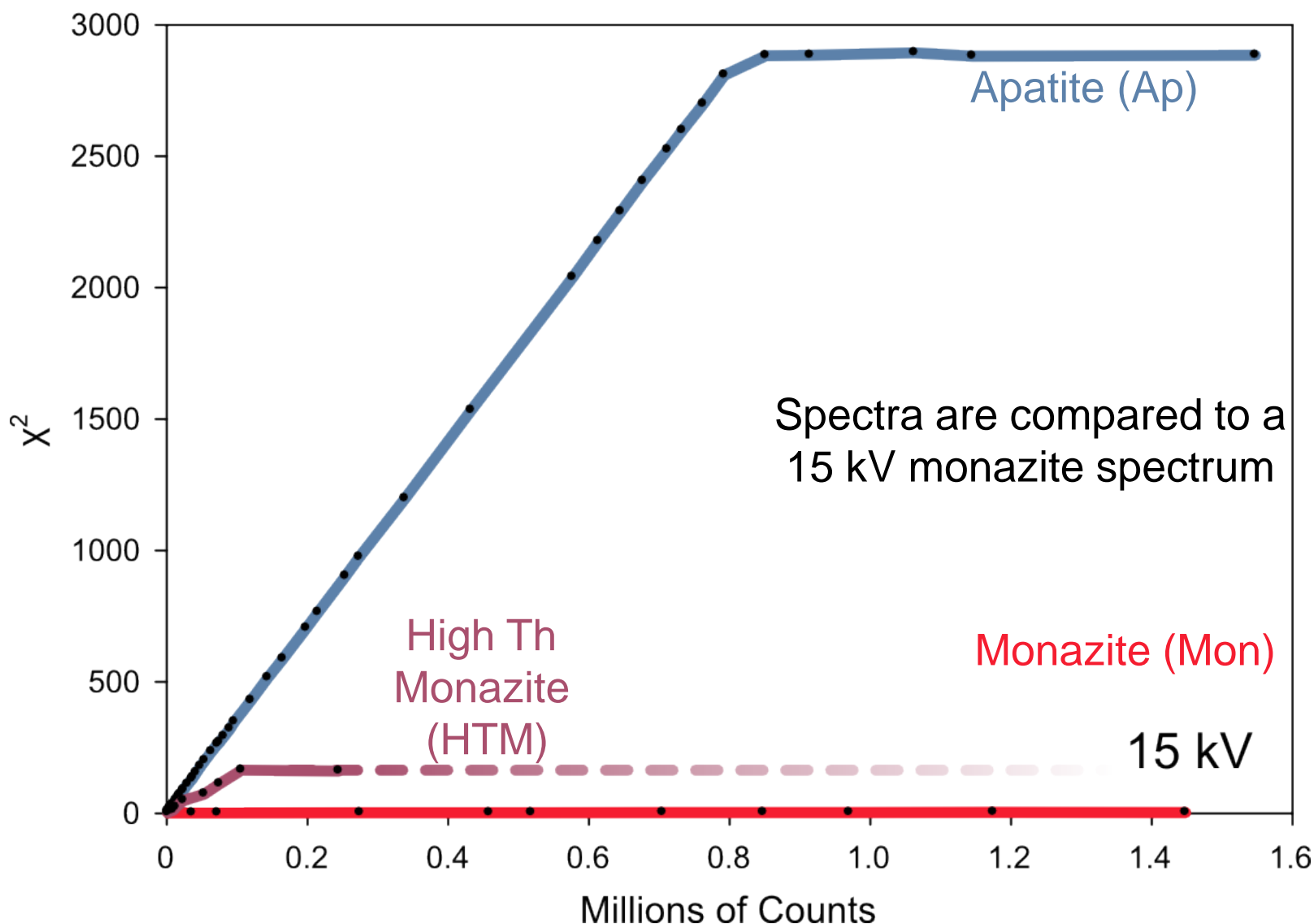


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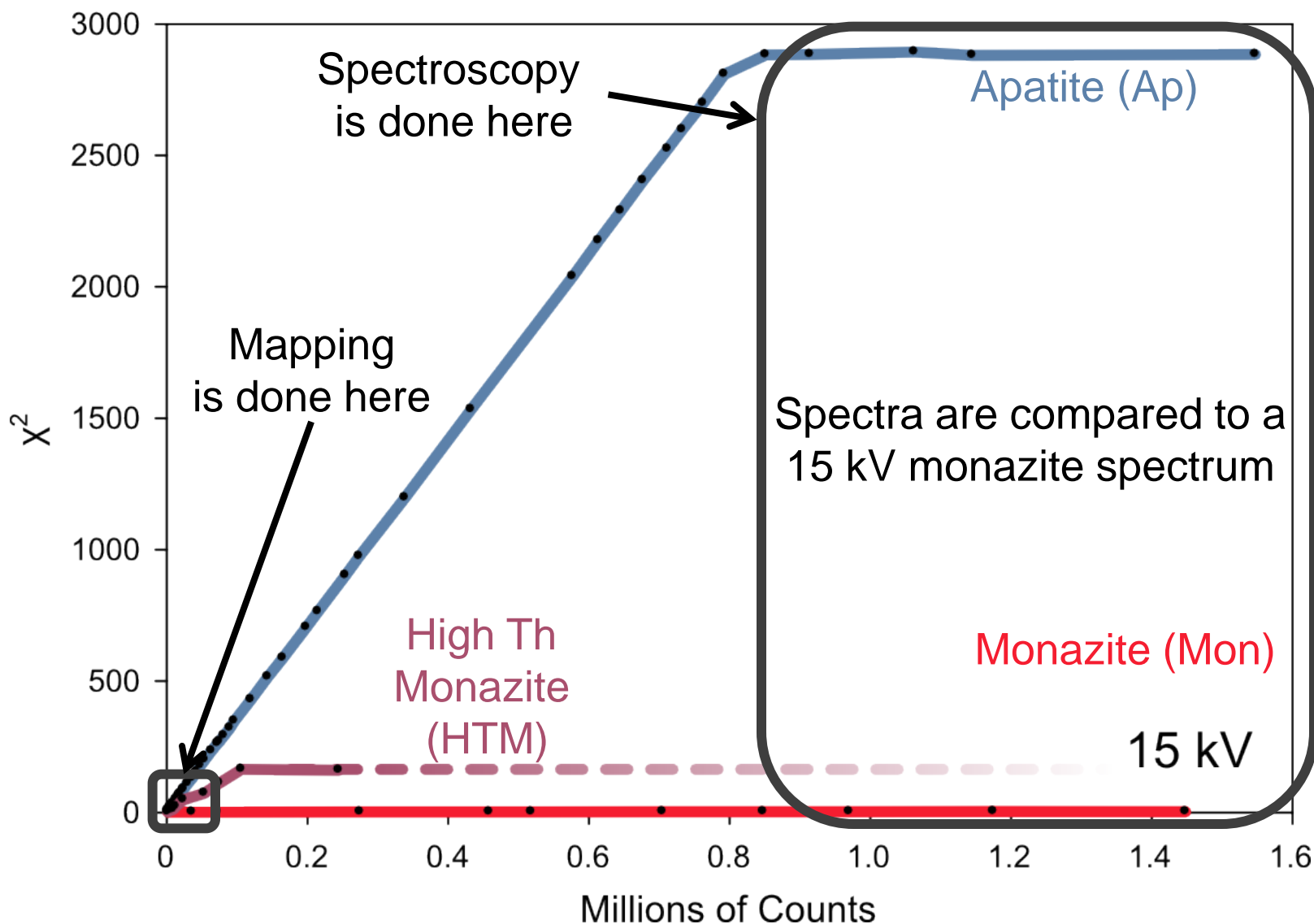


???

What about spectrum-based phase mapping?

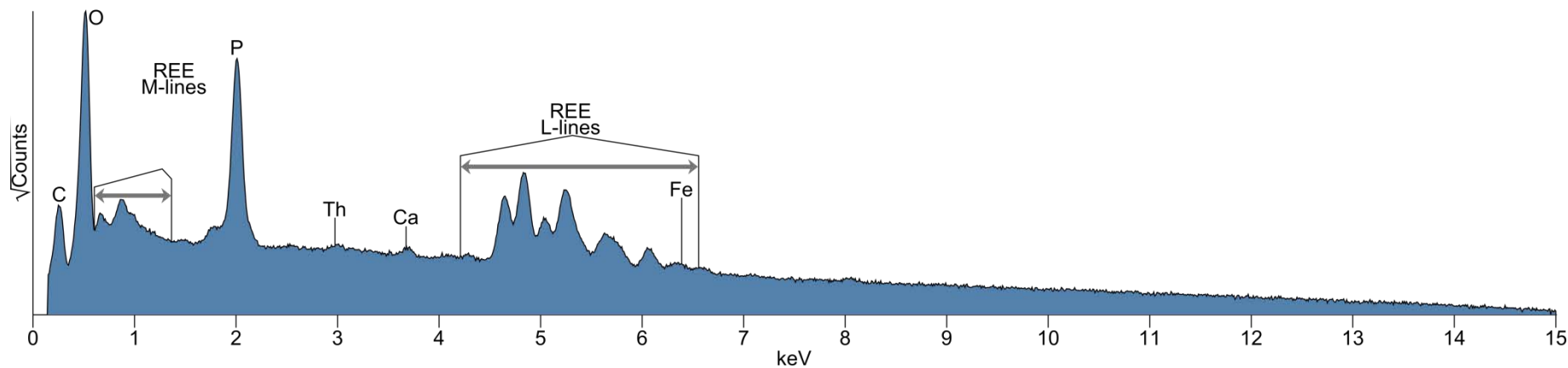
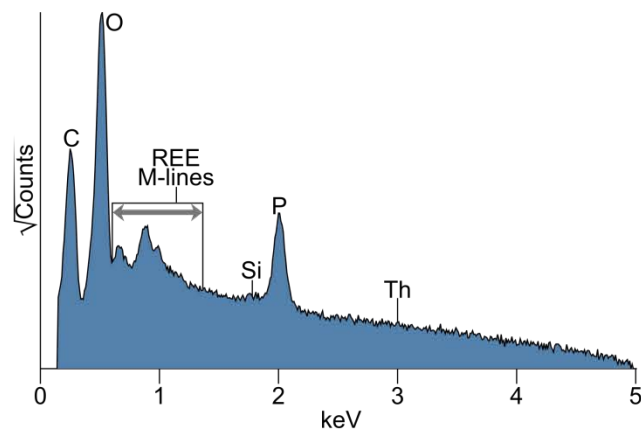


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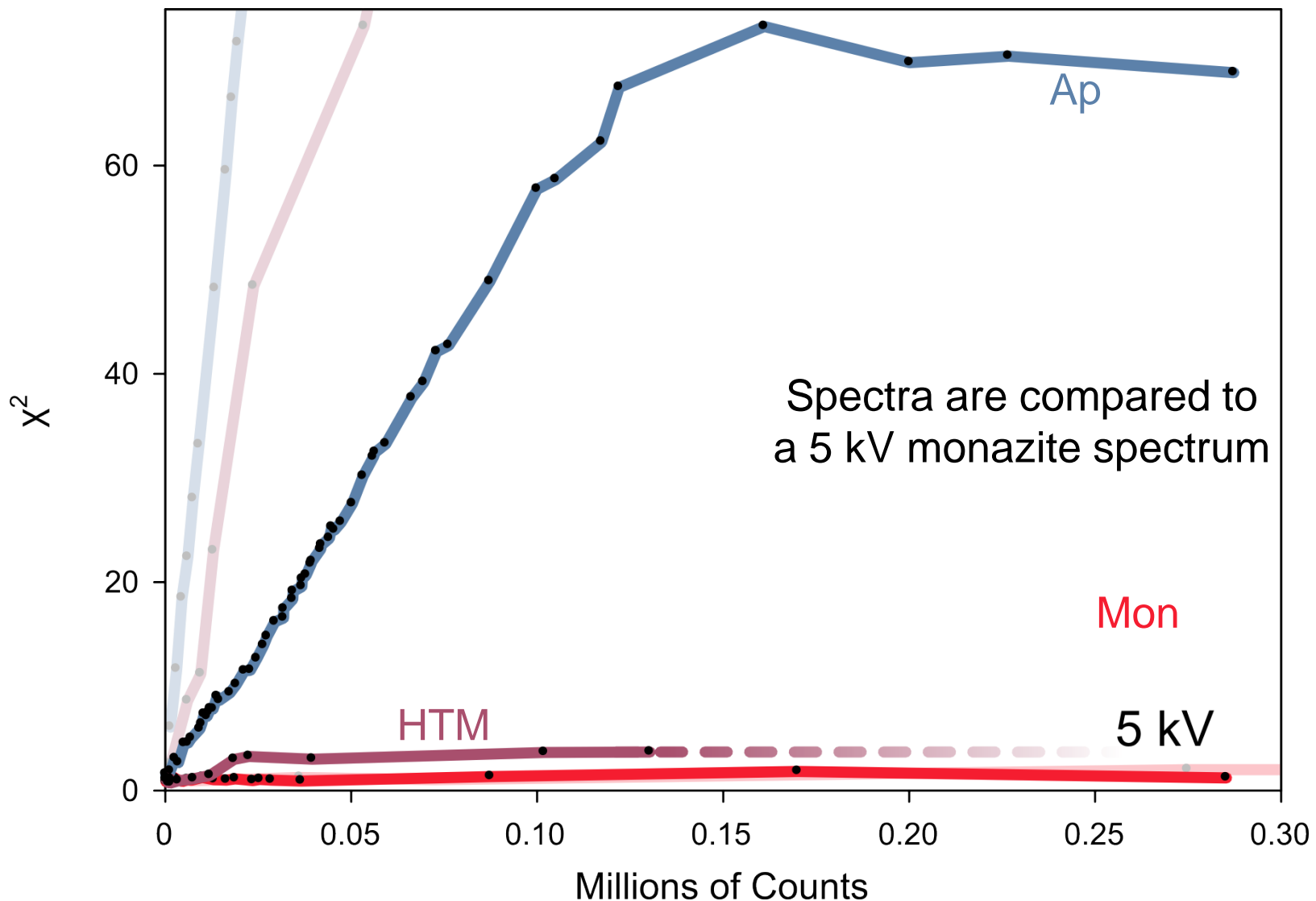


What about low kV spectrum-based phase mapping?

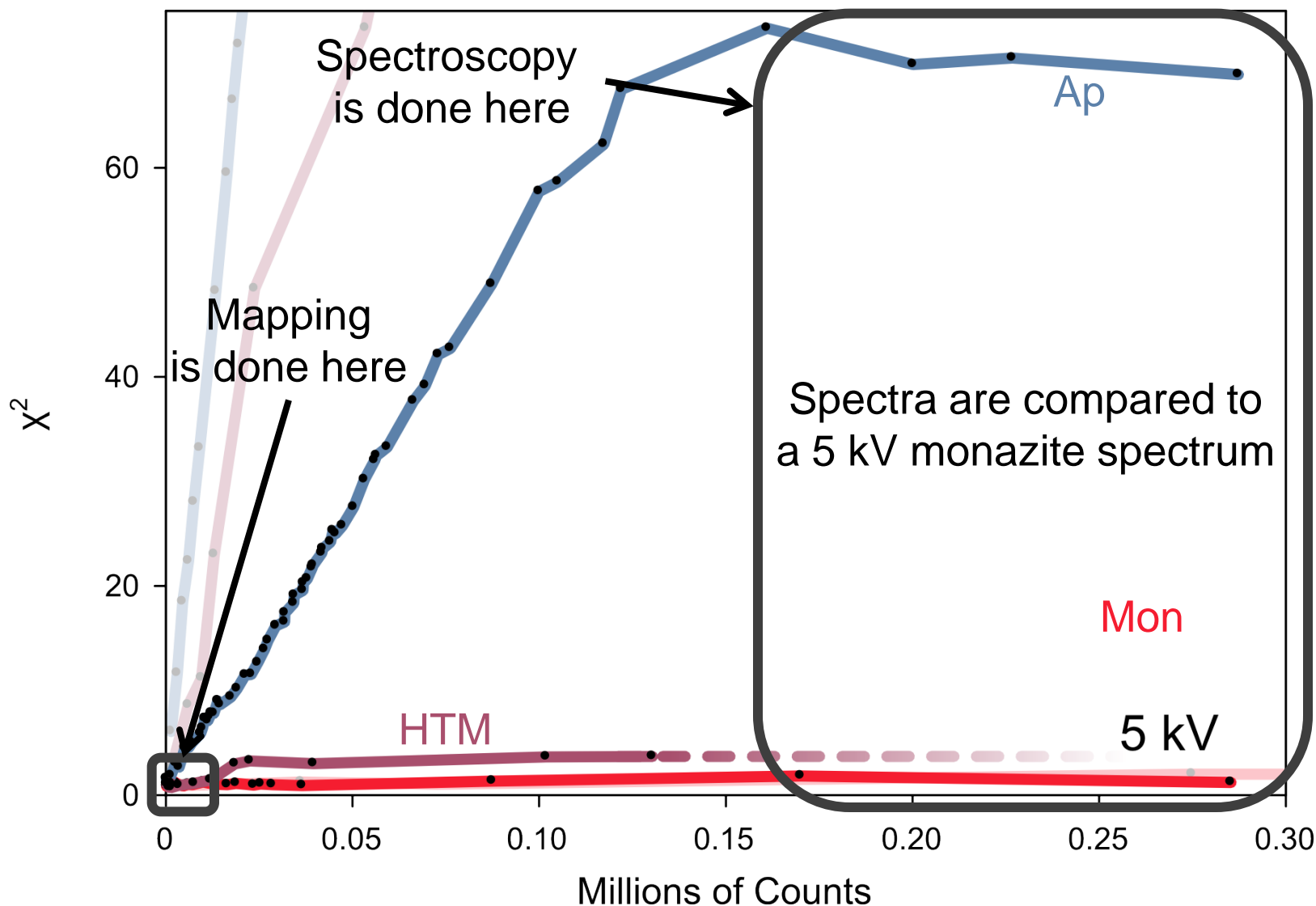
- There is less spectrum for comparison...



What about low kV spectrum-based phase mapping?



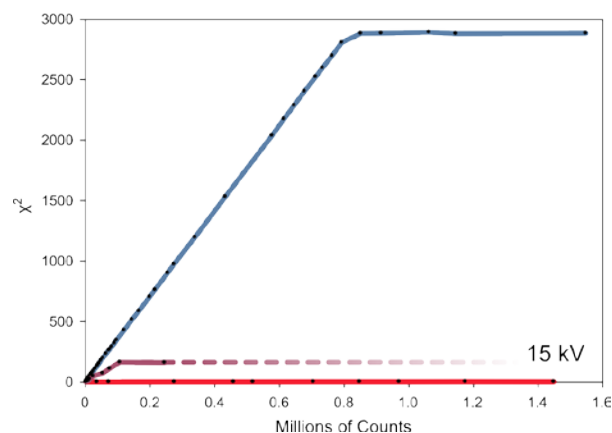
What about low kV spectrum-based phase mapping?



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 $\chi^2 = 1$, $\text{Counts}_{\text{Ap}} \approx \underline{\mathbf{1800}}$; $\text{Counts}_{\text{HTM}} \approx \underline{\mathbf{2500}}$



What about spectrum-based phase mapping?

Thought Experiment:

- Generate a 1024×768 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**



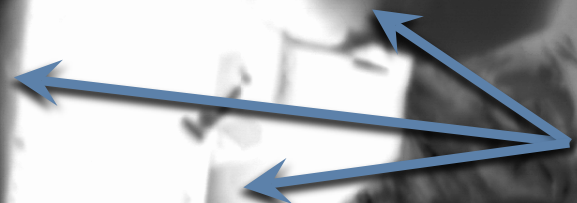
A Better Way

- 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

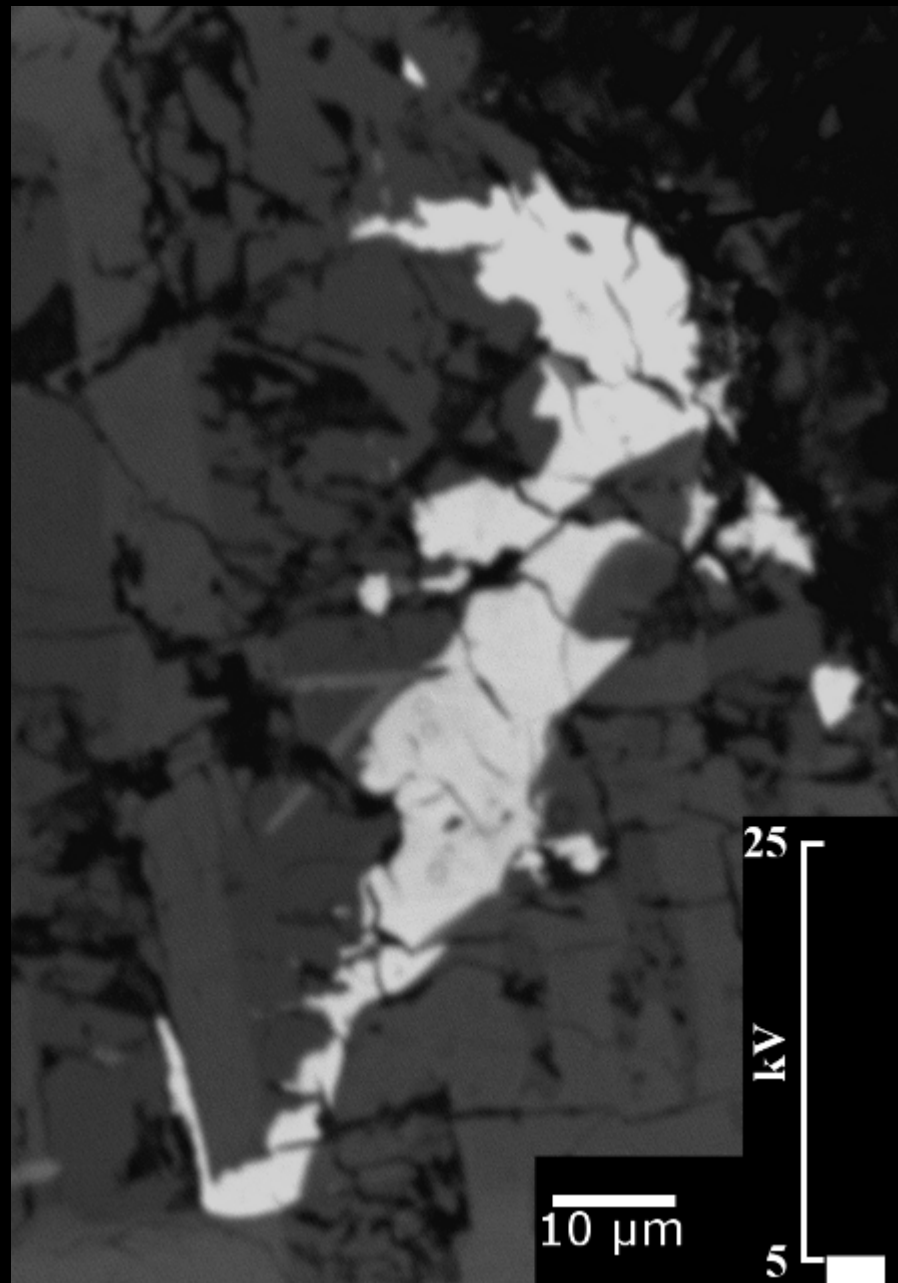
BSE



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



10 μm



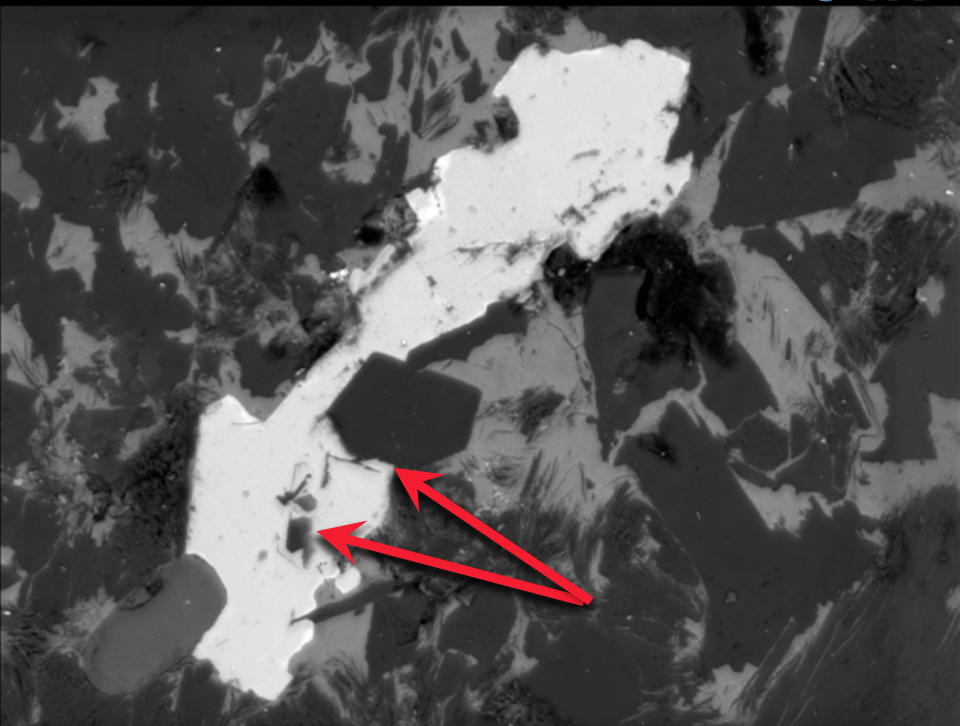
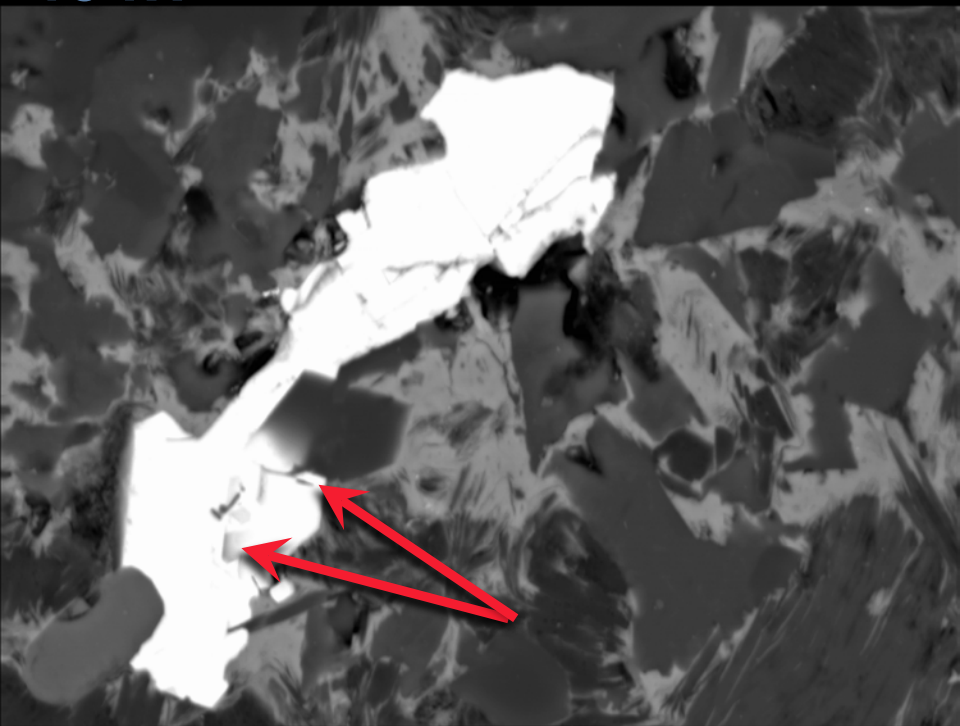
From Seddio et al., 2011



15 kV

BSE

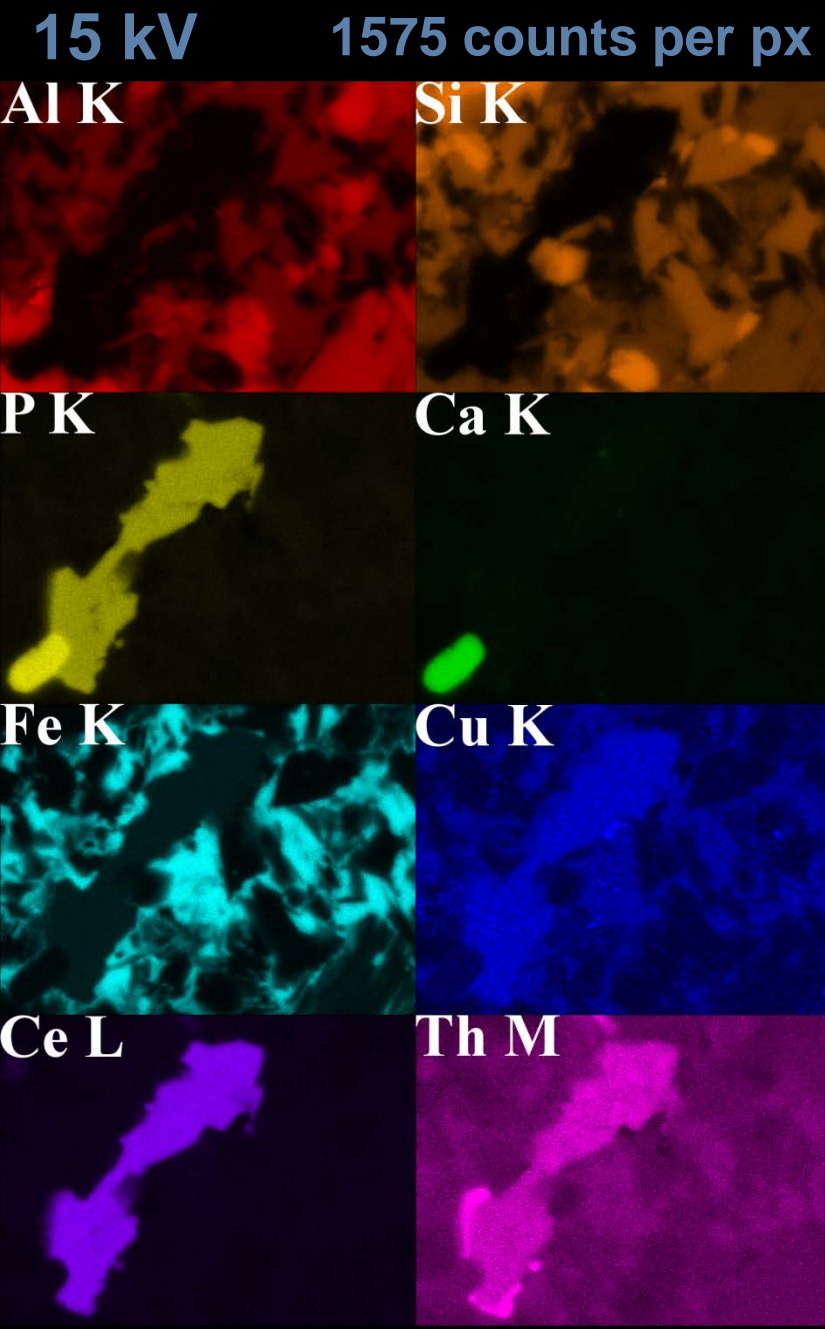
5 kV



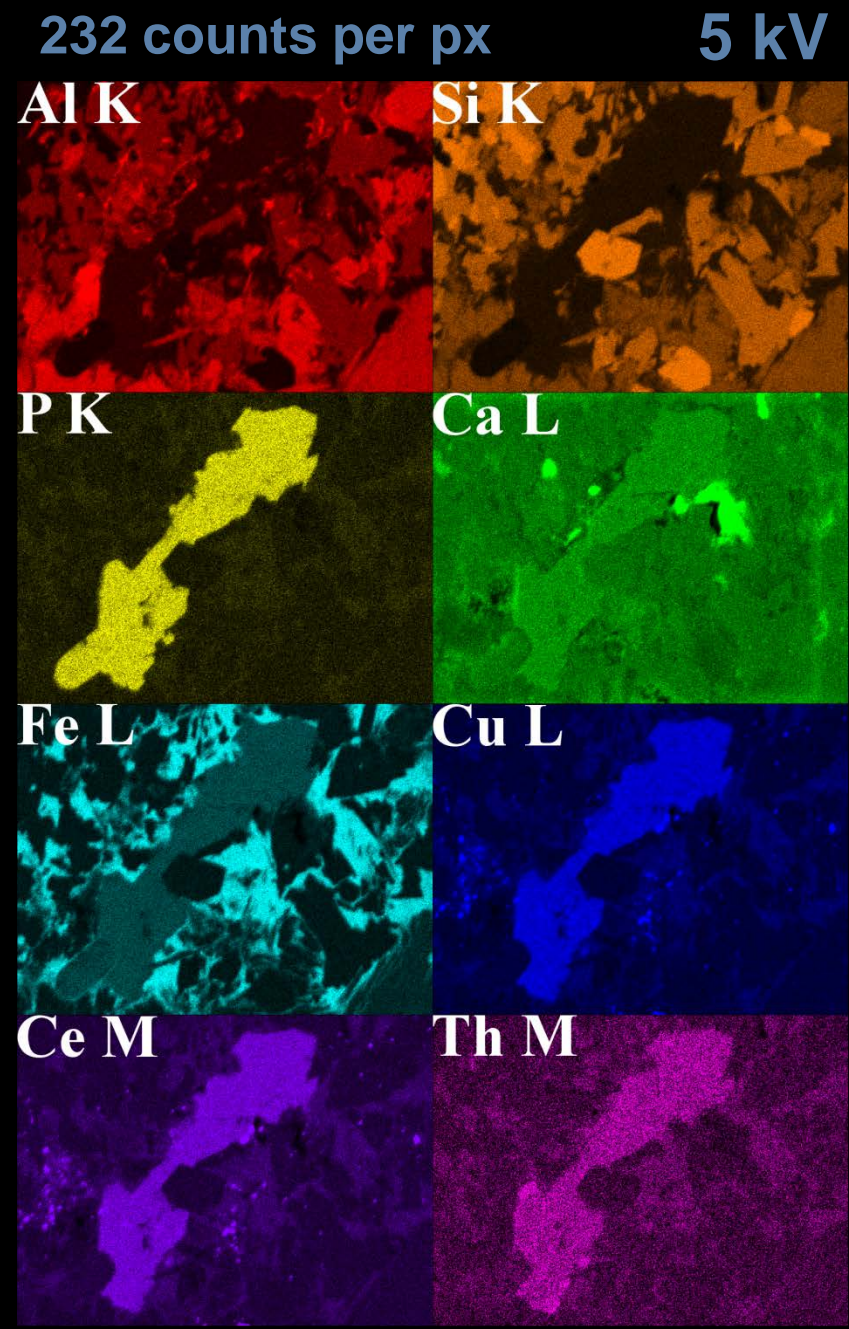
10 μm



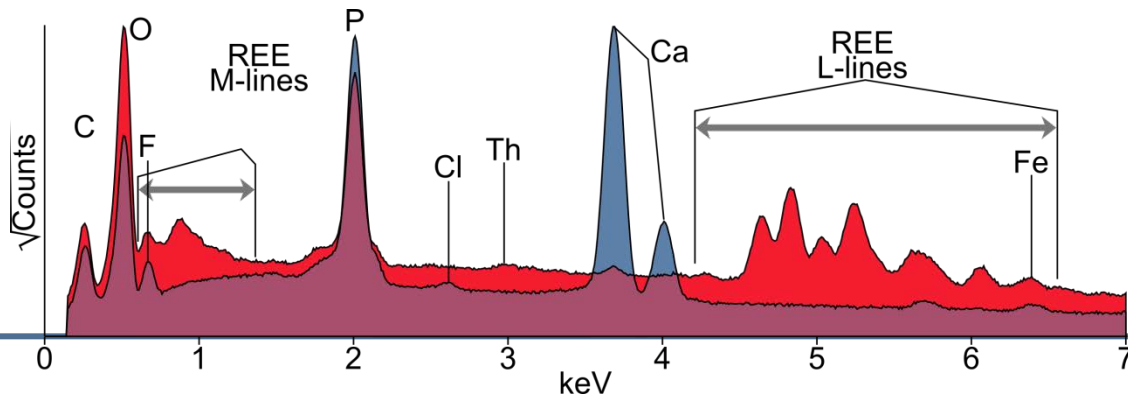
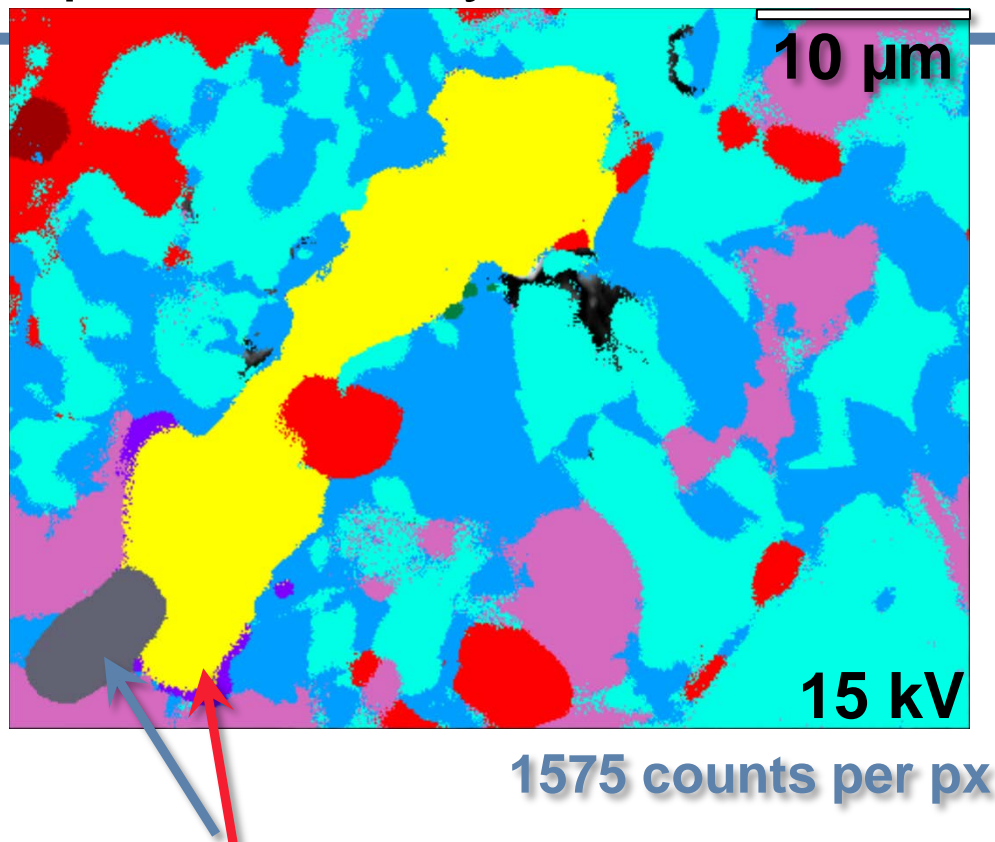
Both mapping runs were acquired for 2.5 hr



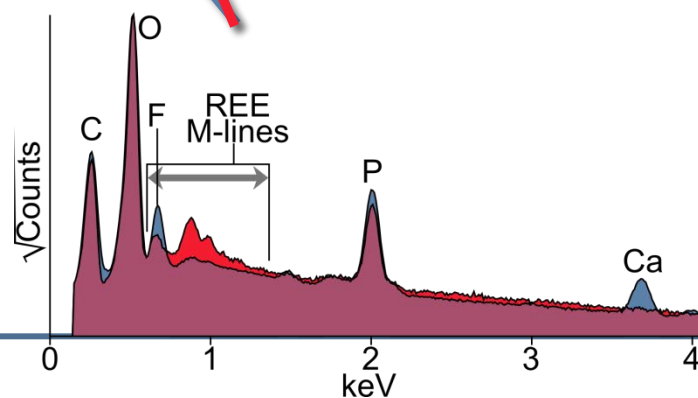
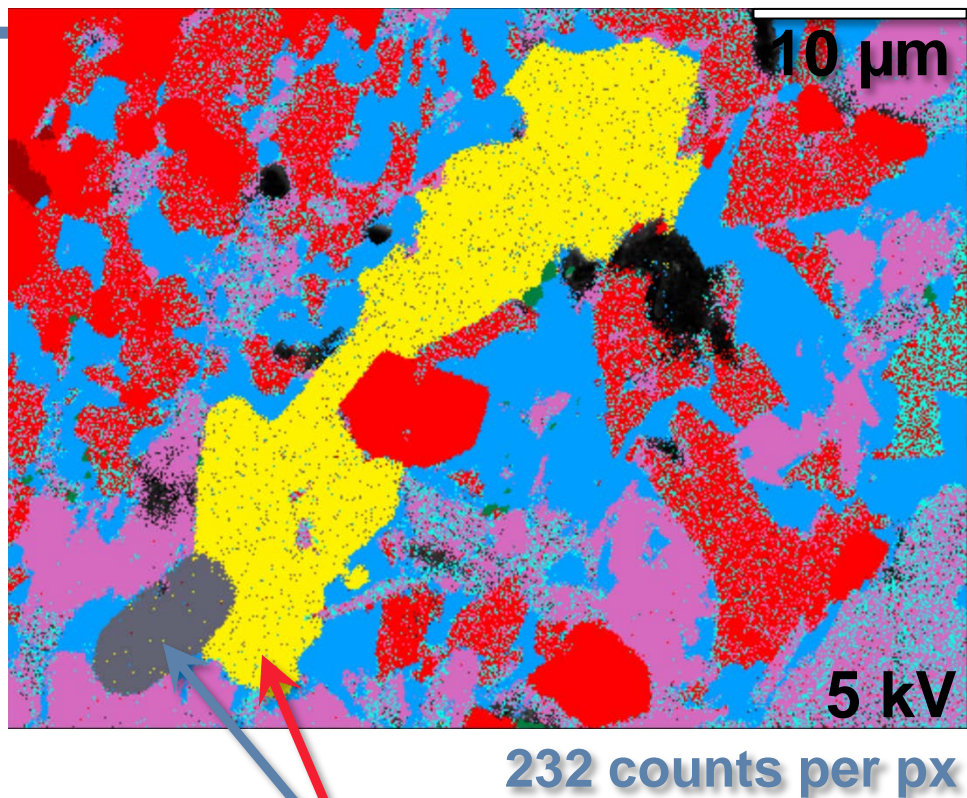
10 μm



Principal Component Analysis



Principal Component Analysis

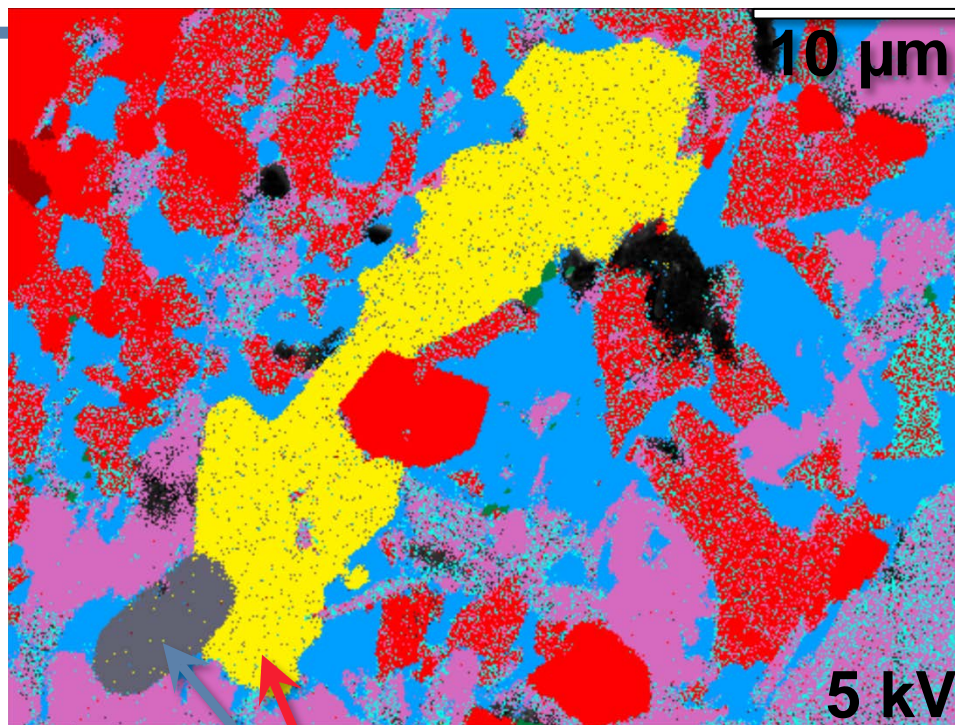




Principal Component Analysis

12

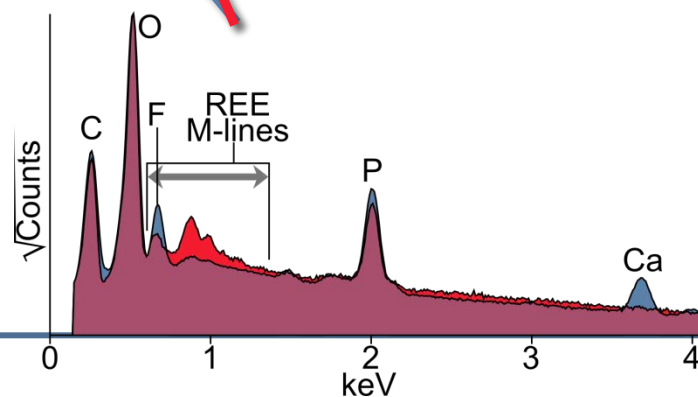
COUNTS PER
PIXEL!!!



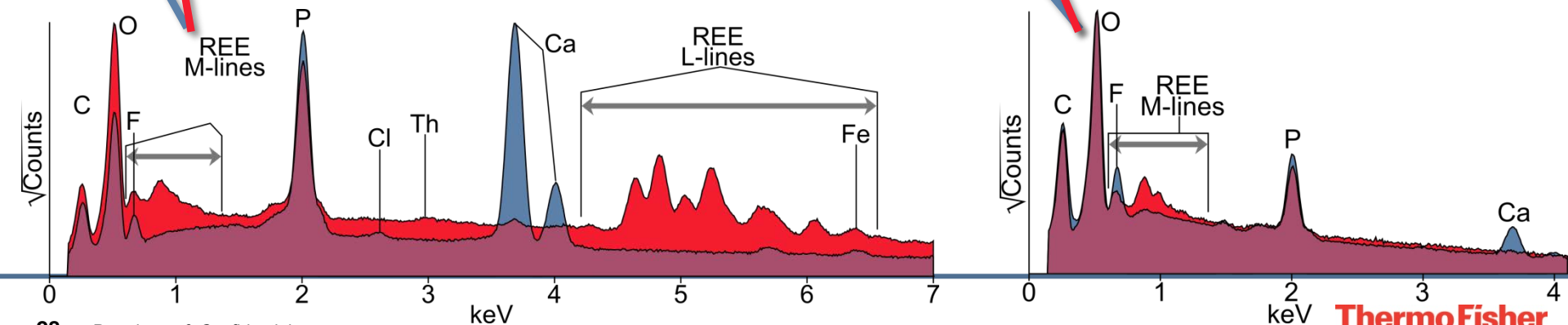
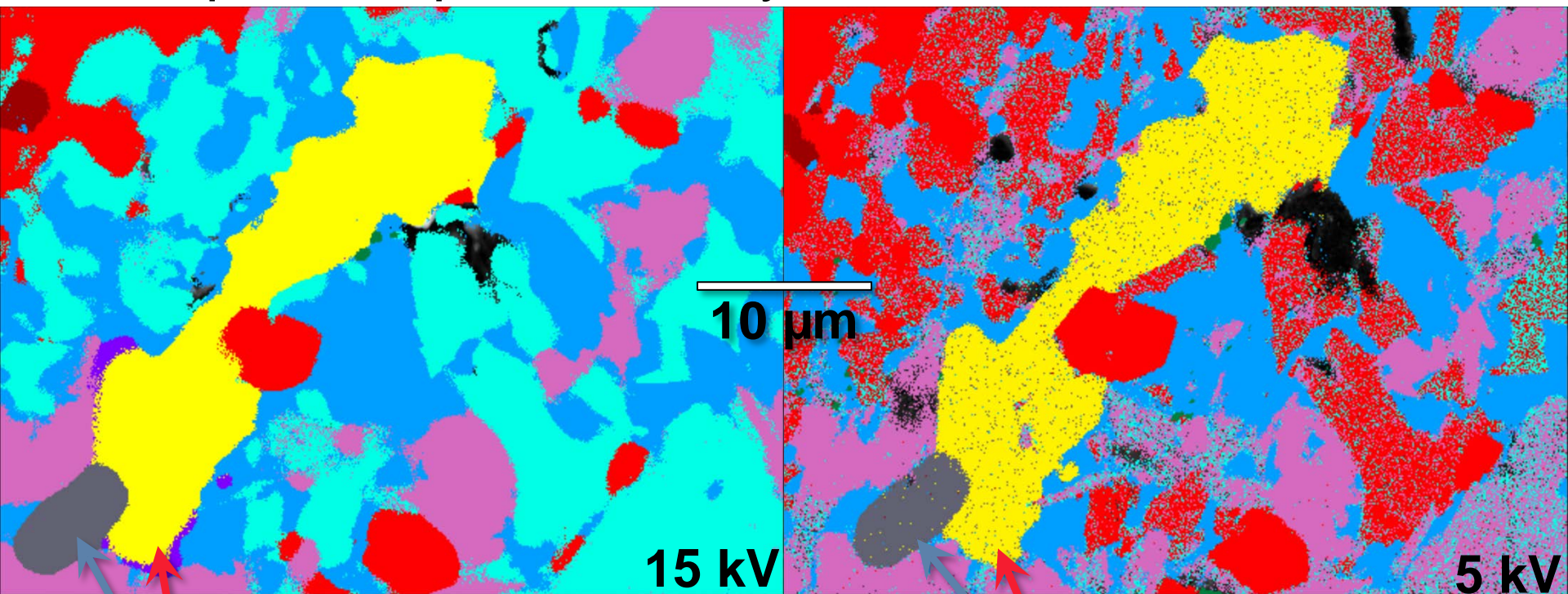
232 counts per px

12

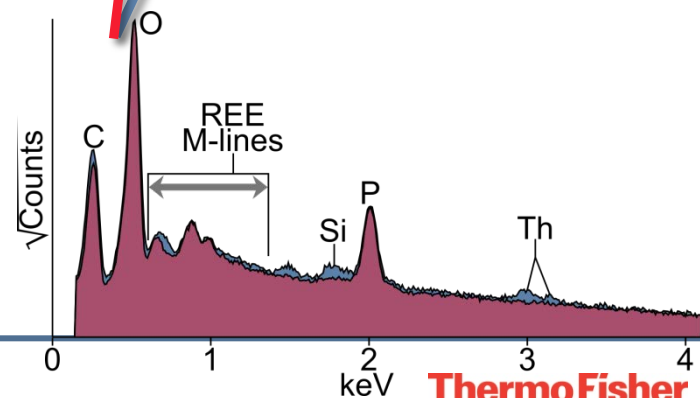
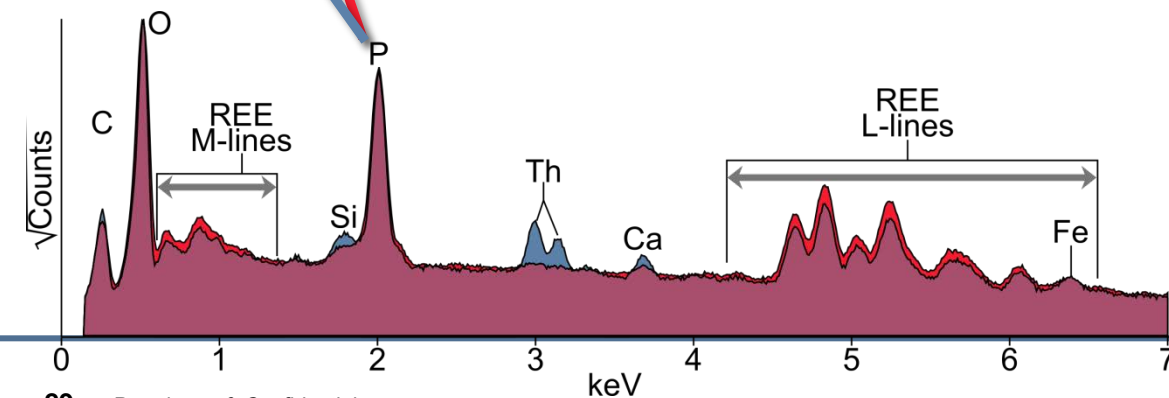
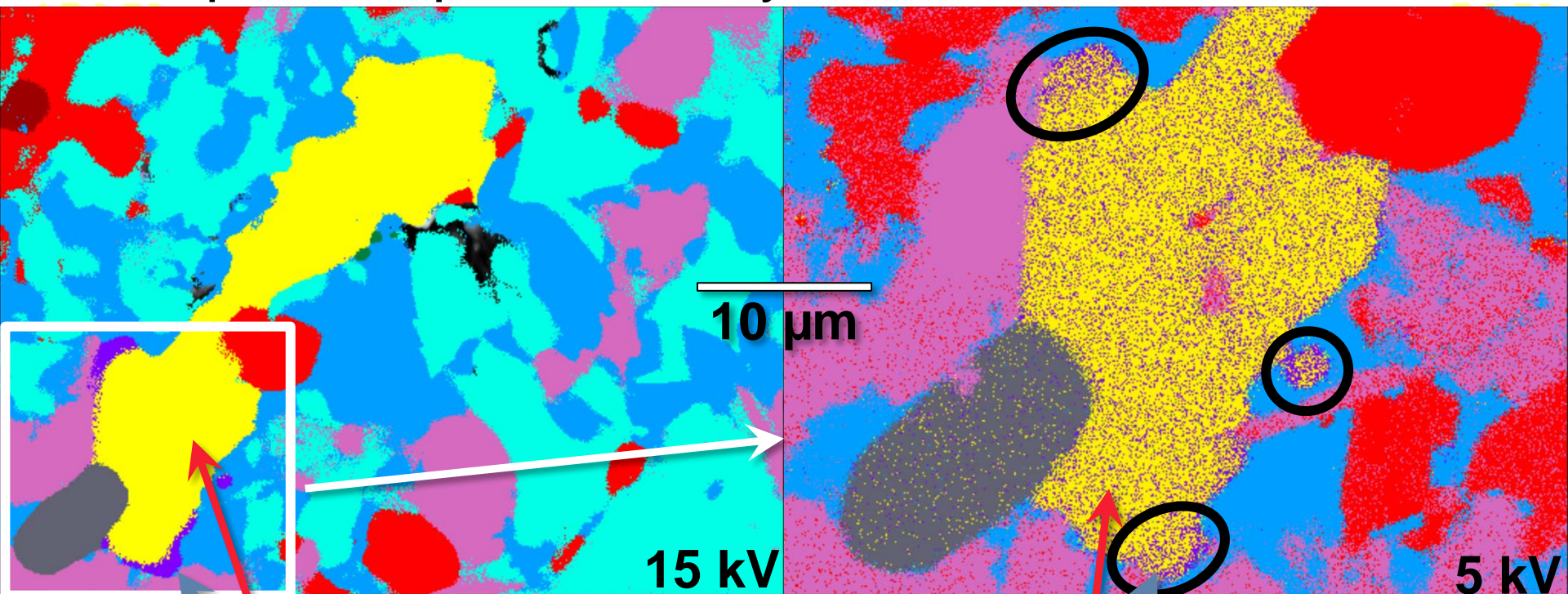
COUNTS PER
PIXEL!!!



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

