ThermoFisher SCIENTIFIC

Optimum Settings for EDS Mapping

Patrick Camus, PhD

December 2012

Why Optimum Settings are Important

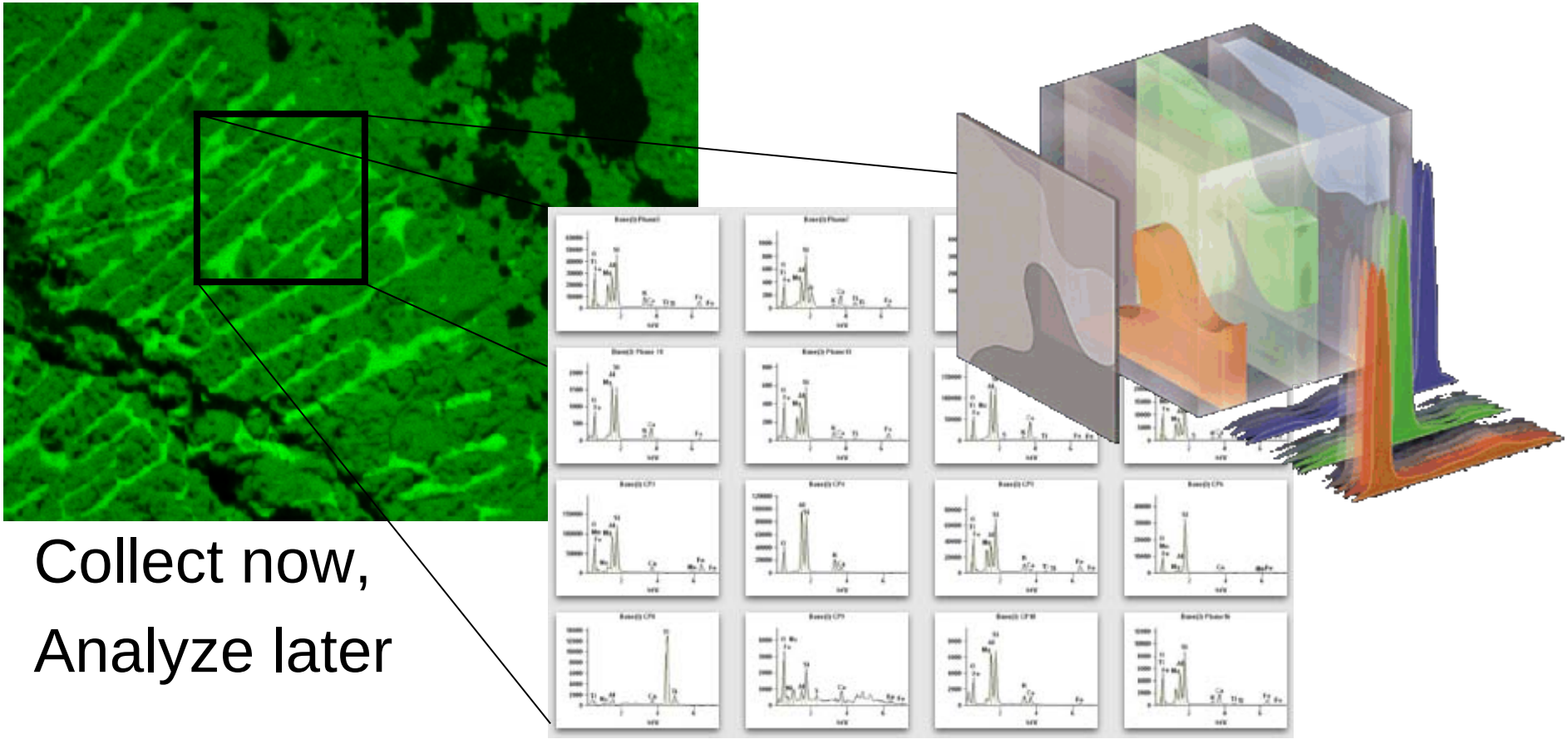
- Most complete sample description in shortest analyst time
  - SEM conditions and EDS parameters determine spatial resolution, spectral resolution, and statistics level.
  - Acquisition time is important but only a small portion. Analysis time may take longer.
  - Confidence in analyst interpretation is very important.

Conclusions

- Optimum settings for EDS mapping are very important.
- “Optimum” is subjective due to the number of variations that are possible.
- The optimum settings for one experiment will be different than those for another experiment.

Spectral Imaging Mapping

- Electron image with x-ray data cube histgram
  - Full x-ray spectrum at each scan location (position in map)

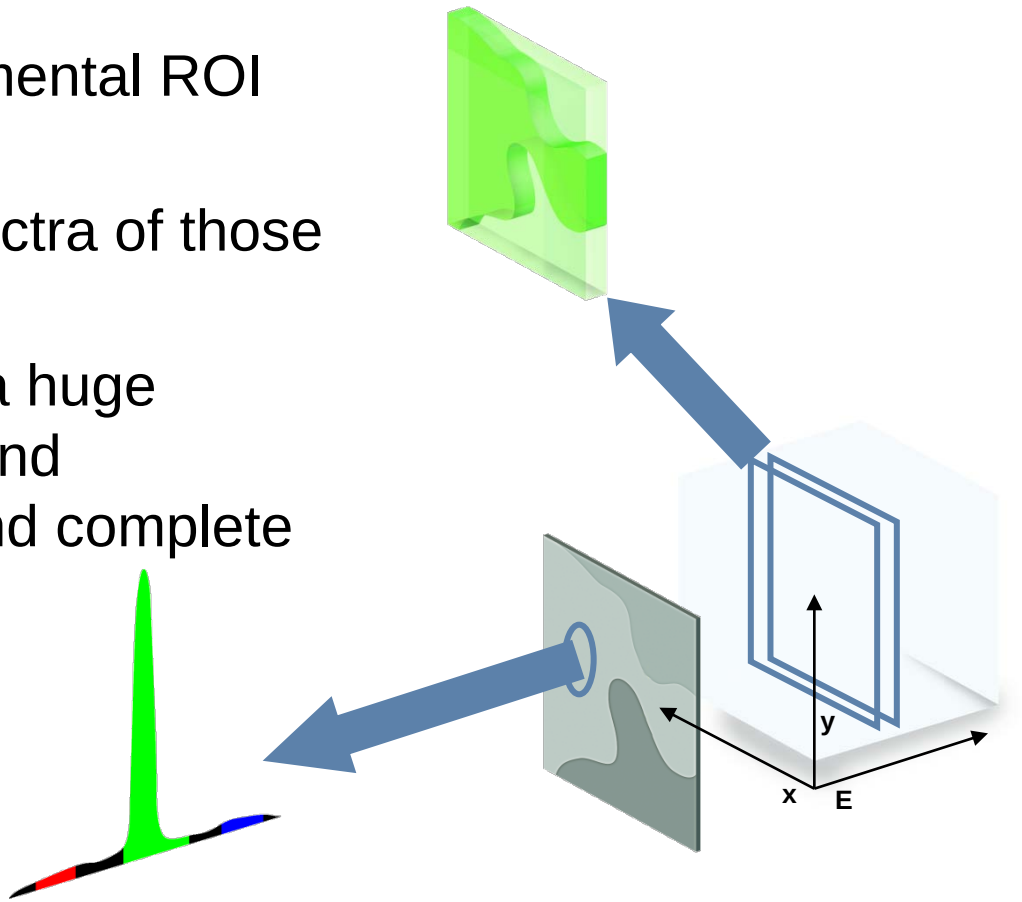


Collect now,

Analyze later

Spectral Imaging Histogram Processing

- Extractions
  - Energy axis provide elemental ROI maps
  - Image plane provide spectra of those regions
  - These methods require a huge amount of analyst time and experience for correct and complete interpretation.



- Whole data cube statistical analyses

X-ray Hardware Considerations

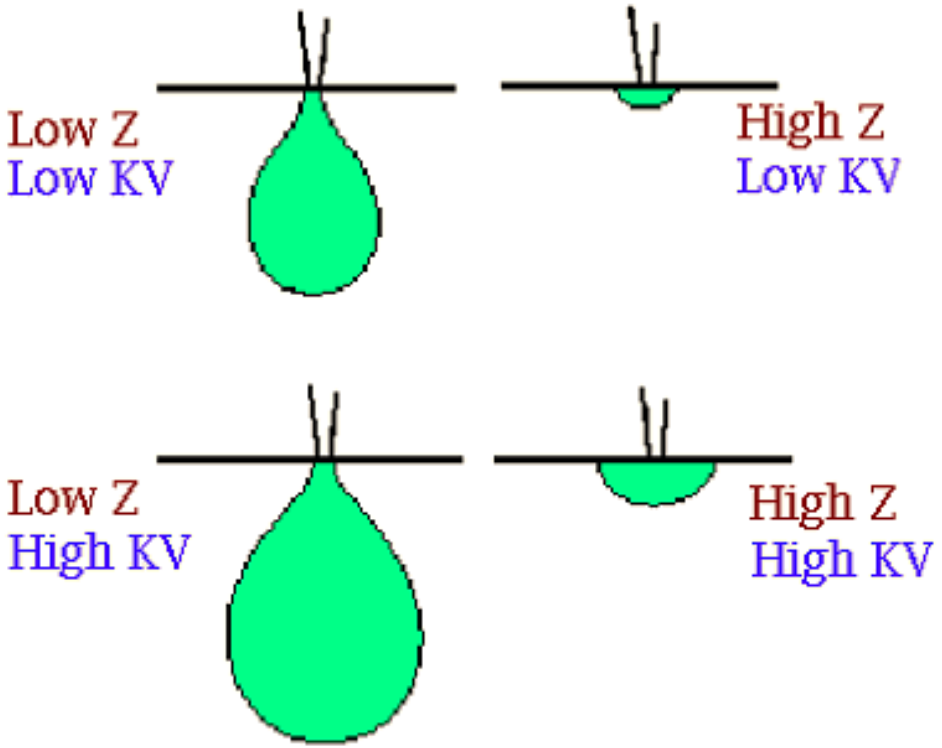
- High detector solid-angle increases input count rate
  - $\Omega \sim A / STD^2$
  - Short sample-to-detector (STD) distance
  - Large area (A) detectors
    - Be wary of housing diameter and needed STD
    - Multiple detectors
- High output x-ray electronics needed with high input rates
  - Output rate = *f*(input count rate, electronics deadtime)
  - An input rate of 100kcps at 121eV resolution and 90% deadtime is only <10kcps output rate!
  - An input rate of 100kcps at 135eV resolution and 45% deadtime provides 55kcps output rate
  - Output or storage rate is most important for analyst.

Acquisition Considerations

- Spatial resolution
  - Am I collecting x-rays from only my feature?
- Spectral resolution
  - Are peaks overlapped or separate?
- Statistics level
  - How confident am I in the measurements?
- Mapping pixels
  - How many are needed?

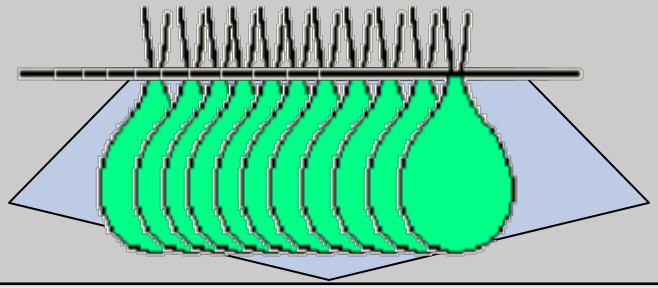
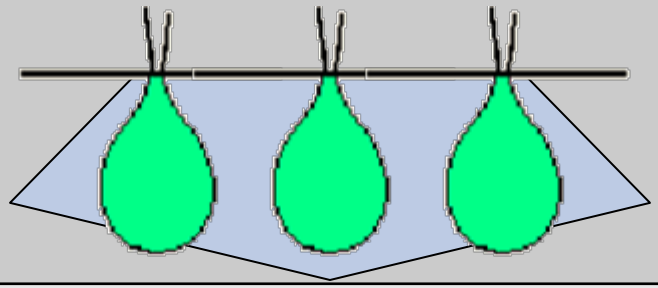
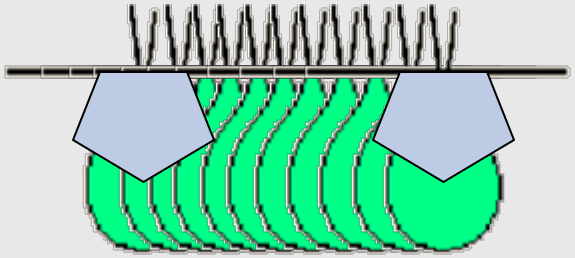
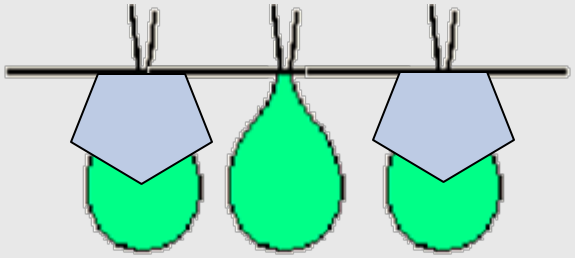
Electron Beam & Sample Interaction

- Interaction Volume Size
  - Determined by two factors:
    - Density of the sample. Average atomic number. (Z)
    - Energy of the electron beam. Accelerating voltage. (KV)



Spatial Resolution Considerations

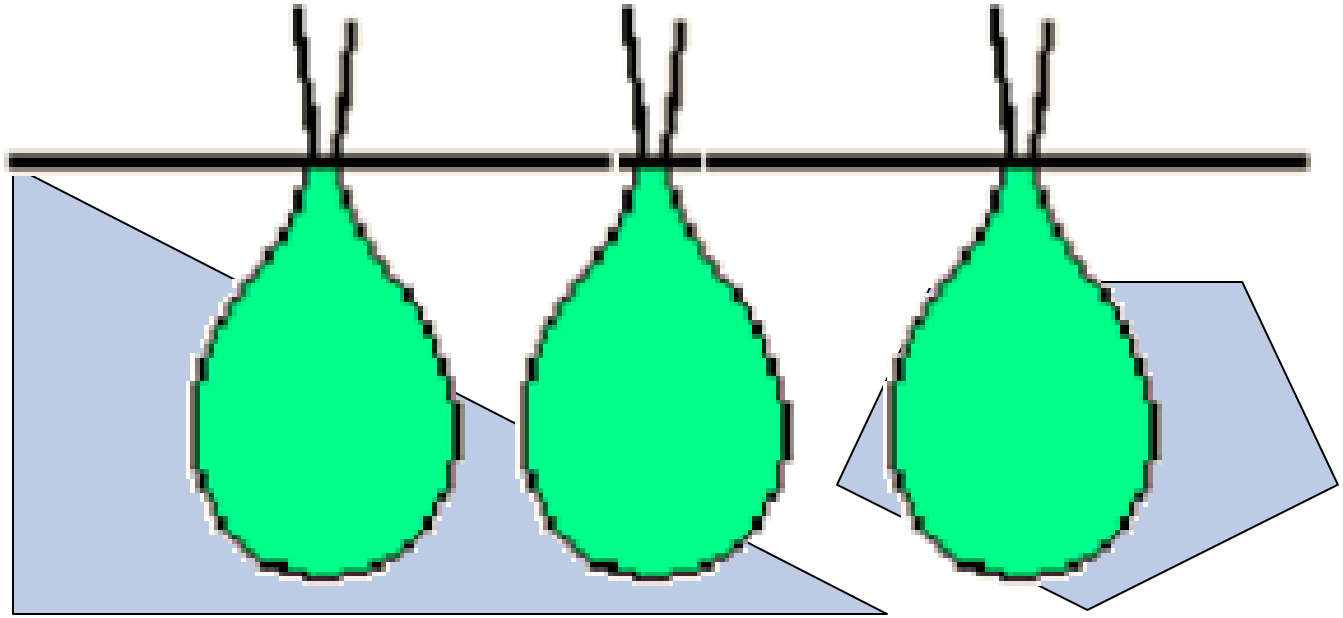
- Interaction volume + feature size = beam energy + sample density + pixel size

	Close pixels	Wide Pixels
Small Volume vs Feature		
Large Volume vs Feature		

- Select magnification to see smallest important feature.
- Select pixel size/spacing to optimally analyze that feature.
- Select beam energy to analyze only feature.

Spatial Resolution Depth

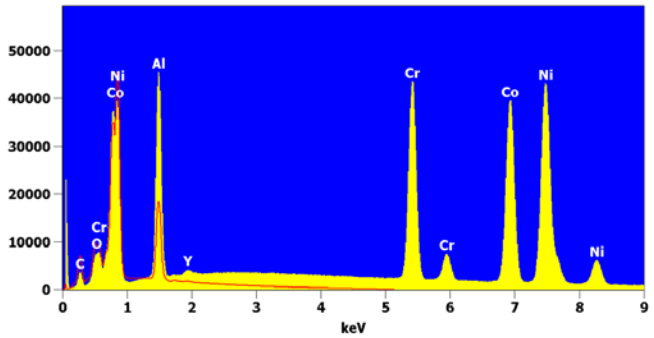
- The interaction volume may generate x-rays from unseen features.

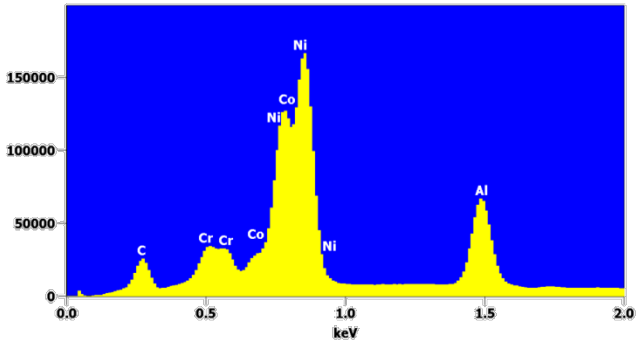


- Extremely important when different density materials (interaction volumes) in the same sample.
- Complication for settings selection and interpretation.

Beam Voltage Considerations

- Select to collect x-rays from all important elemental families.
  - Overvoltage should be maintained > ~2x for all of the important x-ray lines for optimal x-ray intensity.
  - High beam voltage (typically) accesses all x-ray lines.
  - Low beam voltage restricts available x-ray lines.
    - Peak overlaps become more common.





- Evaluate how elemental x-ray families help and hinder method of interpretation.

Spectral Resolution Considerations

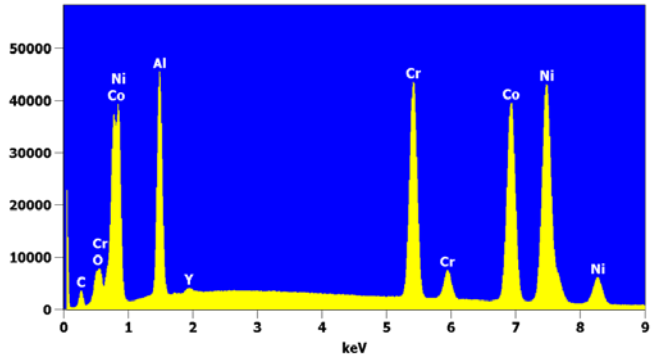
- High detector *specified* resolution typically preferred
  - Indication of quality of x-ray detection system
  - Only useful if fully separated peaks to baseline
    - Very important for trace elements
    - Very important if visual interpretation is primary analysis method
    - Advantageous if does not compromise speed
  - Peak overlaps and composition quantification require software separation
    - Spectral resolution is of minor consequence
    - Analyst confidence in Peak ID and Quant routines
- Low detector *operational* resolution typically accepted
  - Higher collection rates, less acquisition time
  - Software performs most analyses independent of resolution

Spectral Resolution Techniques

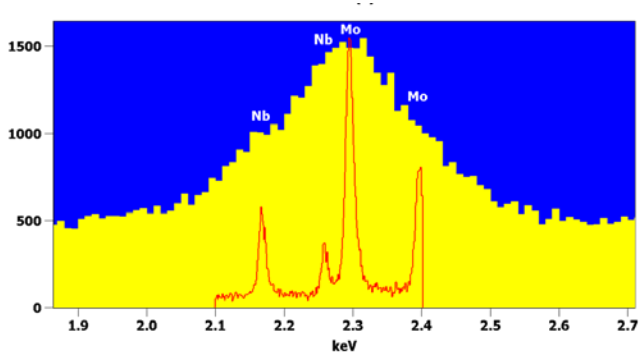
- WDS
  - Very high resolution
  - Single element only
  - Useful for single peak separation
  - Advantageous for trace elements
- EDS
  - Higher total x-ray storage rate
  - Relatively lower resolution
    - Electronics setting balances resolution vs. output rate
  - Advantageous for most materials

Spectral Resolution Considerations – 2

- Method of analysis determines level of importance
  - Visual interpretation = very important
  - Software interpretation = not important



Spectral resolution is almost unimportant for K-lines. Optimize for interaction volume or storage rate.



<36 eV resolution at Mo-L (<57 eV at Mn-K) required. EDS must rely on software.

- Judge the importance of resolution on method of interpretation.

Statistics Level Considerations

- Minimum peak contrast for analytical method
  - Minimum detection should equal enough counts to NOT impact measurement uncertainty
  - Peak/background in spectrum
  - Feature contrast in map (composition contrast in features)
  - Poisson statistics: $\sigma = SQRT(N)$

Statistics Level Considerations – 2

- Minimum detection = acquisition time * output (storage) rate
- Output rate = *f*(beam current, sample density, electronics speed
  - Beam current is major user setting
    - Affects spot size on sample
    - Affects x-ray generation rate inside sample
  - Same time using different rates = different statistics
  - Same rate using different time = different statistics
  - Termination on stats gives flexible time (count threshold / storage rate)
- Time is a poor termination criterion for acquisitions; statistical termination is much more powerful, consistent, and useful.

Statistics Level Considerations – Termination

- Statistics threshold depends on analysis technique of data
  - Metric: total x-ray counts per pixel spectrum (cpp)
  - Elemental mapping requires minimum of 200 cpp
  - Quantitative mapping requires minimum of 500 cpp
  - Statistical analyses require minimum of 50 cpp
- Total map acquisition time = pixels * pixel dwell time
  - Dwell time = statistics threshold / storage rate
  - If beam current or electronics setting changes, the statistical quality of the acquisition remains the same!

Statistics Level Considerations – Mapping Size

- 512 x 384 pixels @ 10kcps output for 100 cpp: < 2000 sec
  - Best-case traditional mapping using statistical analyses
- 512 x 384 pixels @ 100kcps output for 100 cpp: < 200 sec
  - Modern mapping using statistical analyses
- 1024 x 768 pixels @ 100kcps output for 100cpp: < 800 sec
  - High-quality modern mapping using statistical analyses
- 1024 x 768 pixels @ 100kcps output for 500cpp: < 4000 sec
  - High-quality modern mapping using elemental quant maps
- 4k x 3k pixels @ 100kcps output for 500cpp: < 63000 sec
  - < 17 hours
  - Highest-specification modern mapping using elemental quant maps

Map Size Optimizing

- Termination of 500 cpp at 100kcps output requires 5 ms pixel dwell time
- Analysis width of 1 mm requires 100x

- Beam voltage of 20 kV provides spatial resolution of 2 µm
- 512 pixels gives max info content in ~ 1000 sec
  or
  1024 pixels gives slight spatial oversampling in ~ 4000 sec
- More pixels provide no more real information for much longer acquisition time

- Beam voltage of 5 kV provides spatial resolution of 0.5 µm
- 2k pixels gives maximum info content in ~ 16000 sec
  or
  4k pixels gives slight spatial oversampling in ~ 64000 sec
- Interpretation of large maps by zoom-and-pan
- Select termination, output rate, beam voltage, mag and pixels wisely.

Desired Results for Report

- Analysis of raw x-ray data into interpretable form
  - Analysts typically think in terms of alloy/mineral/compounds, even if only single element.
- Elemental Maps
  - Elemental x-ray line spatial distributions
  - Traditional report format because easiest computational method, not best interpretable form.
- Phase Maps
  - Alloy/mineral/compound distributions
  - Modern report format because best interpretable form.

Elemental Map Results for Report

- High experience level needed for complete list of elements
  - Peak overlap detection, small peak amplitude (trace) detection
  - Very high level of statistics required
- Gross counts maps
  - Simple display
  - Simple processing
  - Potential misinterpretation of intensity and phase distribution
- Quantitative elemental maps
  - High contrast display
  - Full-spectral quantification processing, correct elemental distribution
  - Potential misinterpretation of phase distribution

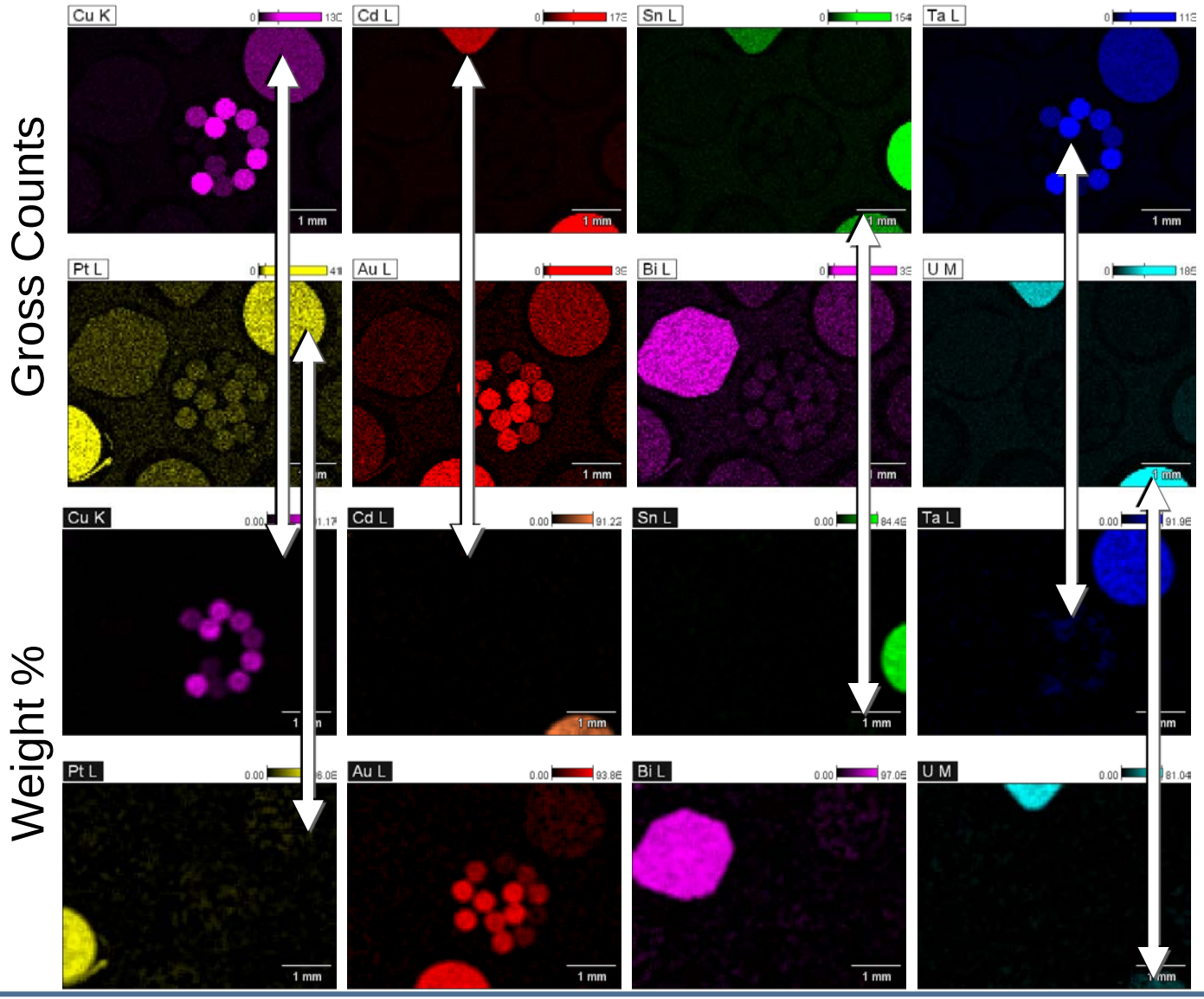
Phase Map Results for Report

- Alloy/mineral/compound distributions and spectra
  - The preferred interpretation for customers
- Experience level requirements and interpretation quality depends on raw data format and phase creation method.
  - Phase determination by elemental maps.
    - All of the restrictions and limitations of elemental maps apply.
    - Time prohibitive when more than ~5 elements
  - Phase determination by statistical methods
    - No user-bias on data selection (whole SI data set).
    - Users of all experience levels produce same results.
    - Lowest level of statistics needed for correct interpretation.
    - Peak deconvoluting routine.
    - Finds ALL compositionally unique features
    - Fastest analysis time.

Example Reports

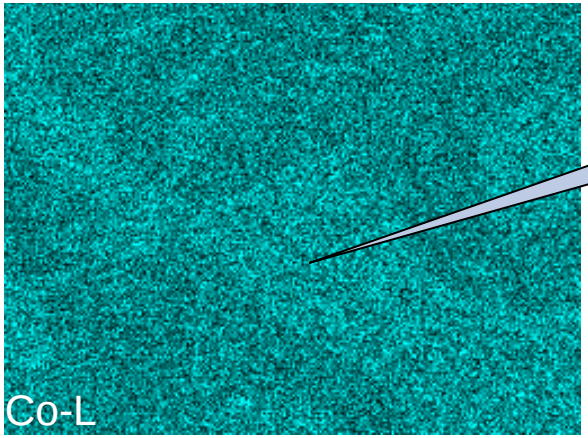
- Elemental Maps
- Quantitative elemental maps
- Phases using elemental maps
- Phases using statistical methods

Taylor Standard Elements

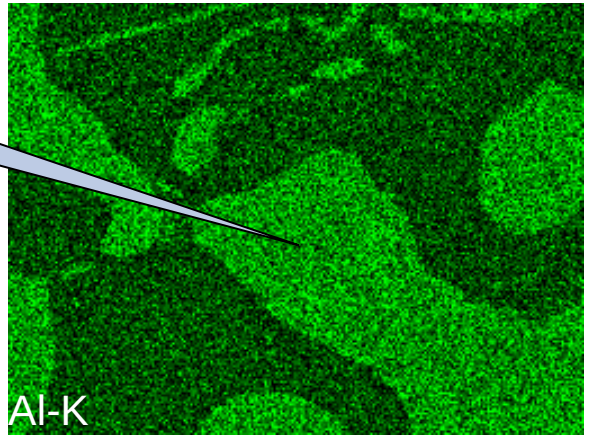


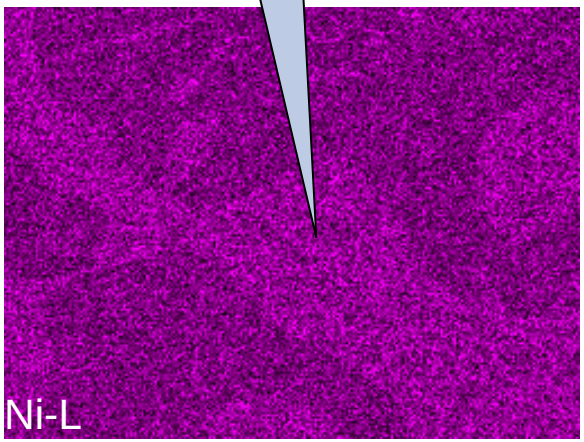
ThermoFisher SCIENTIFIC

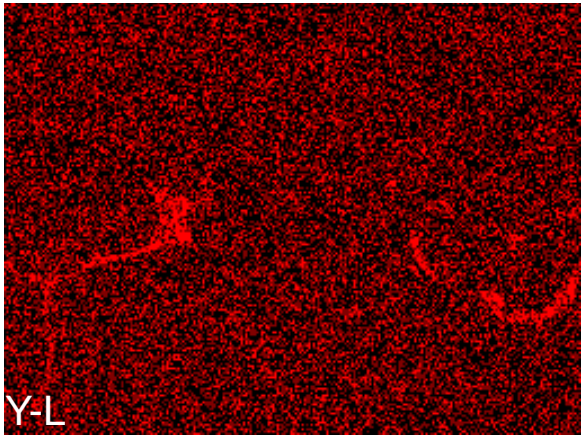
Turbine Raw Count Maps at 7kV

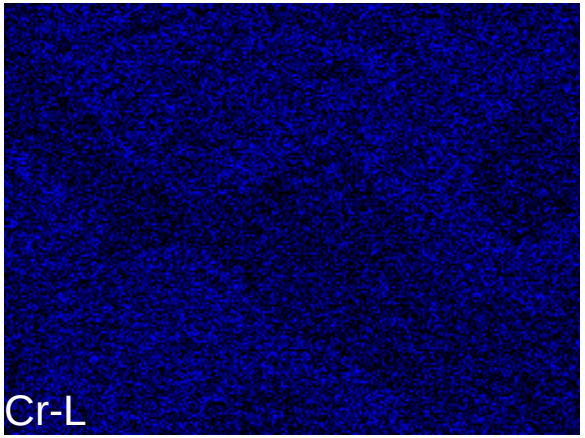


Similar maps !



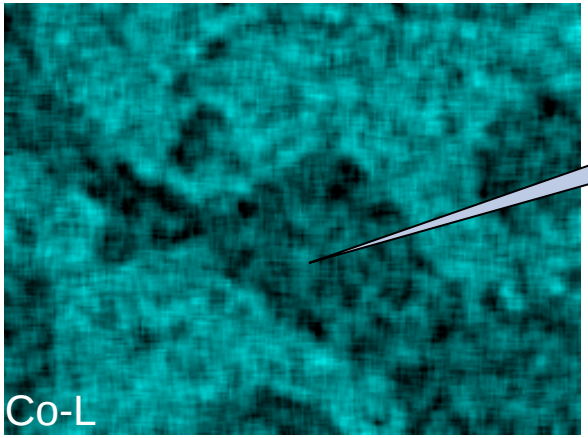




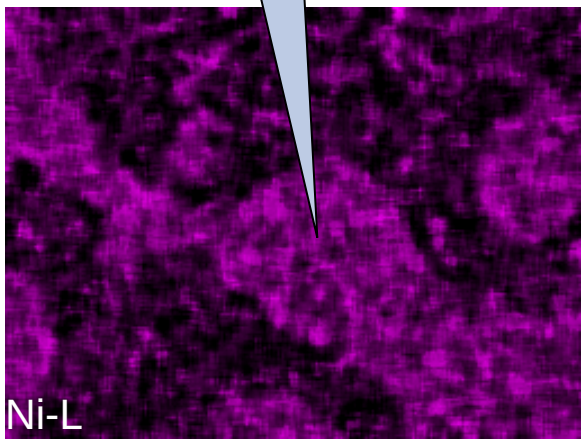


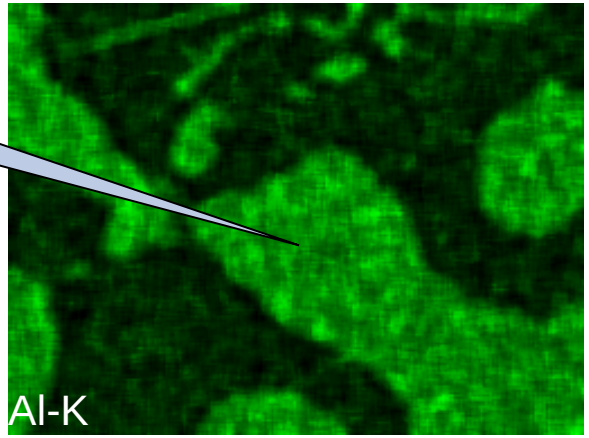
- Co, Ni and Al coexist.
- Y has high background.

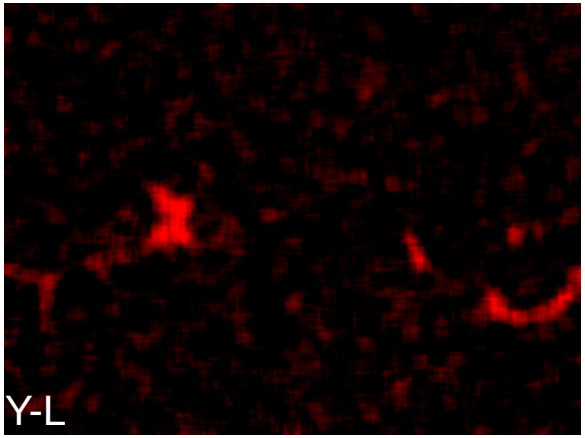
Turbine Quantitative Maps at 7kV



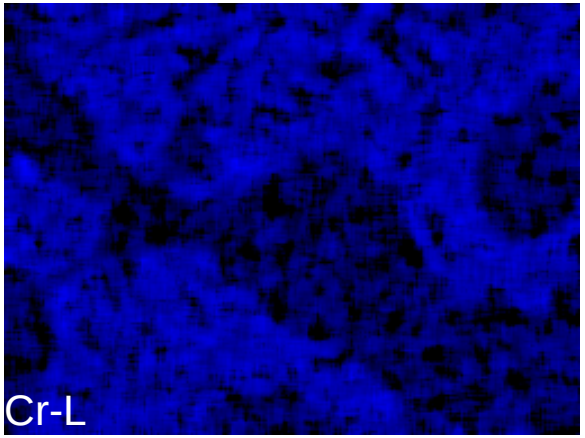
Different maps !





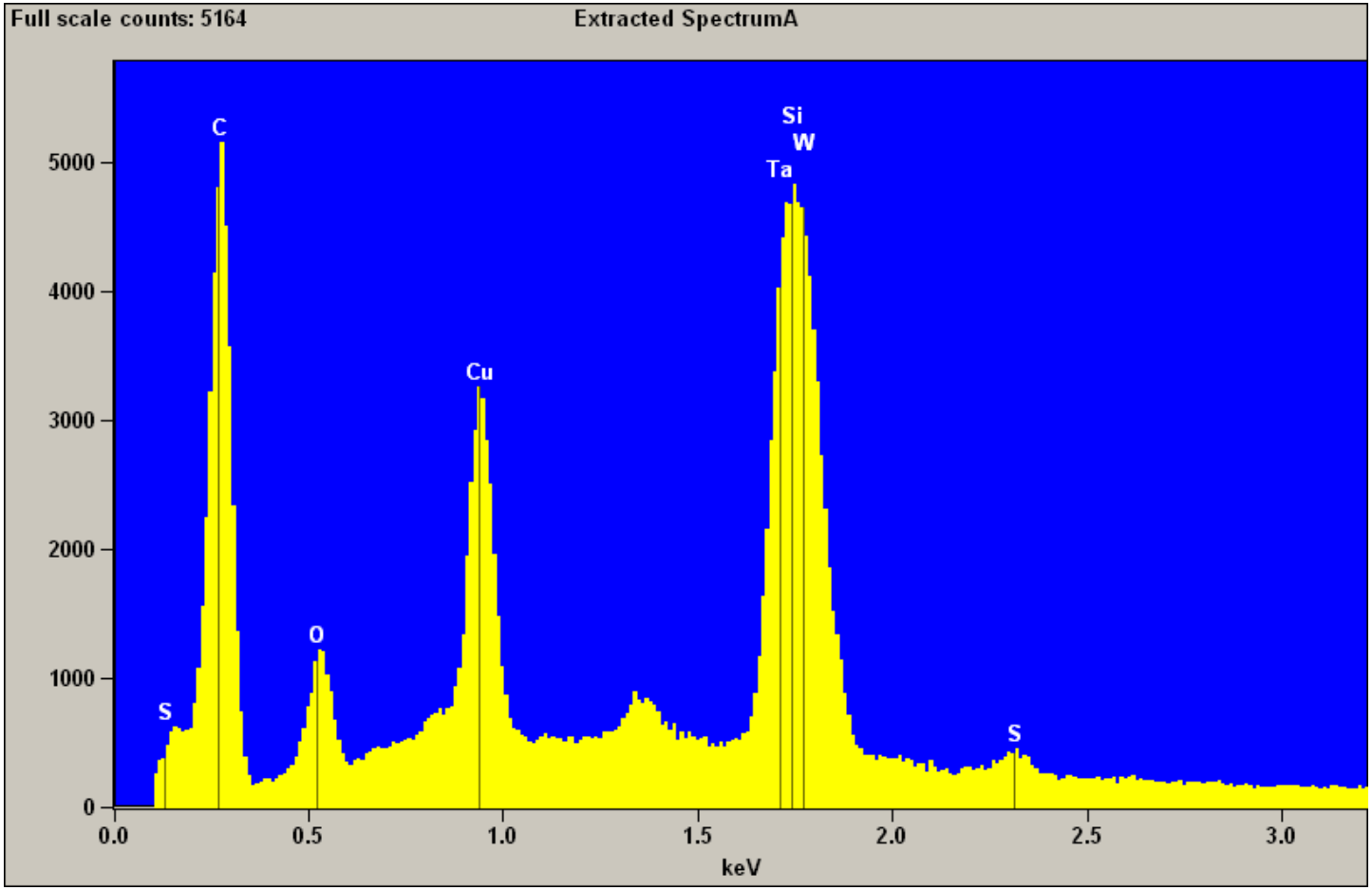


- Co-Cr and Ni-Al coexist!
- Y background eliminated!



Overlap of Si-K, Ta-M and W-M

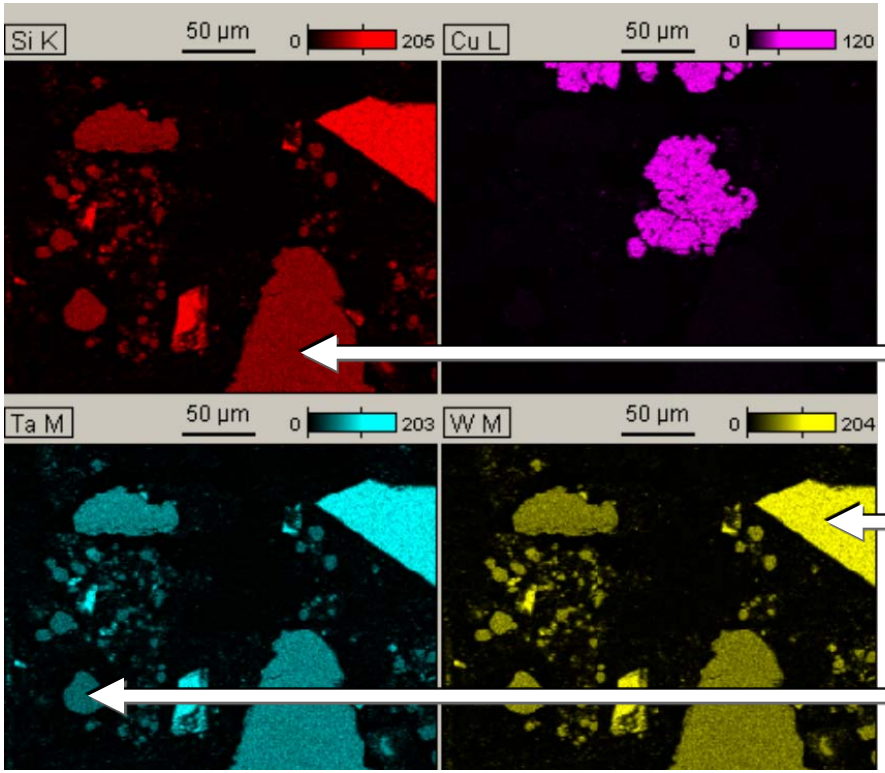
- Heavy peak overlap that needs < 30eV resolution

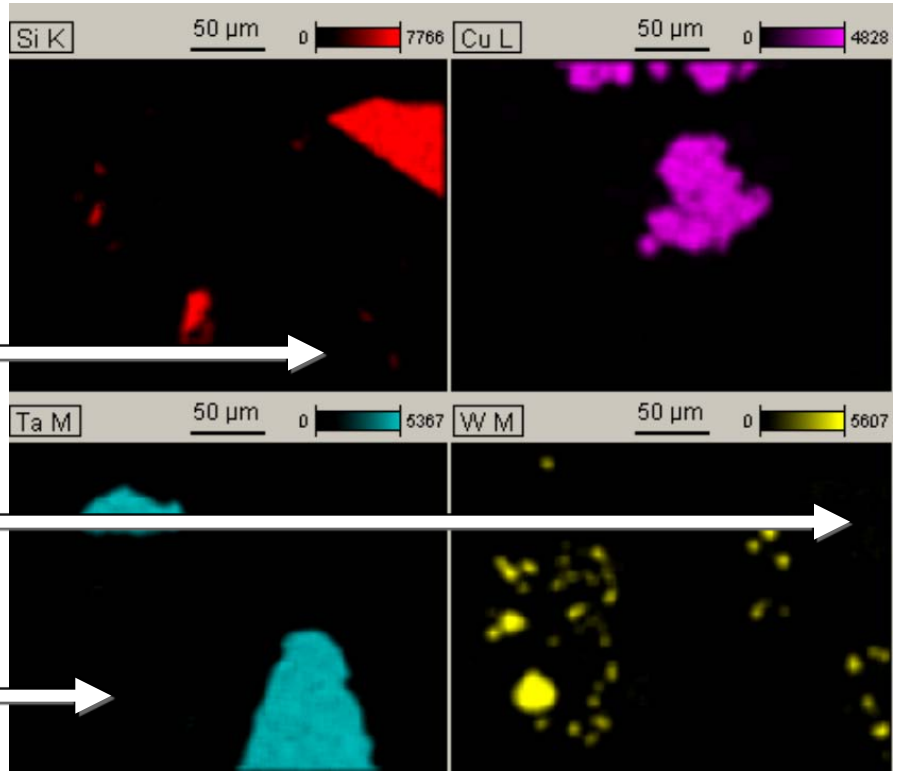


- Element validation is experience driven

Elemental Maps of Si-Ta-W-Cu

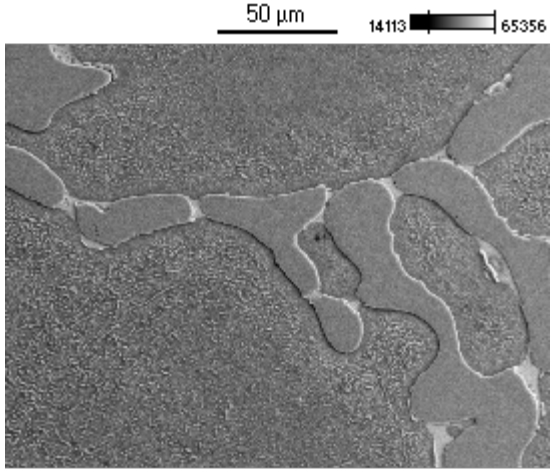
- Gross Count Maps
- Net Count Maps

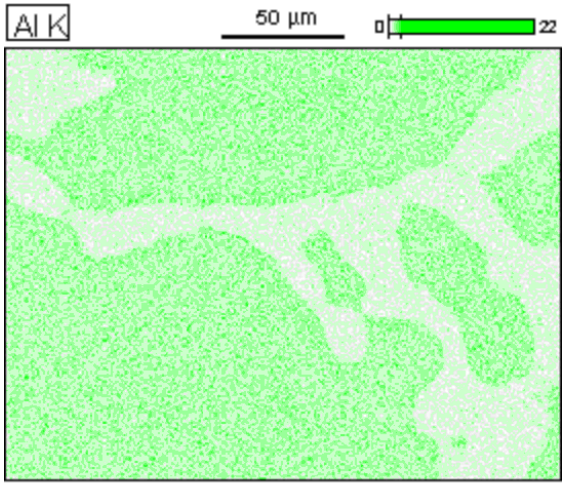


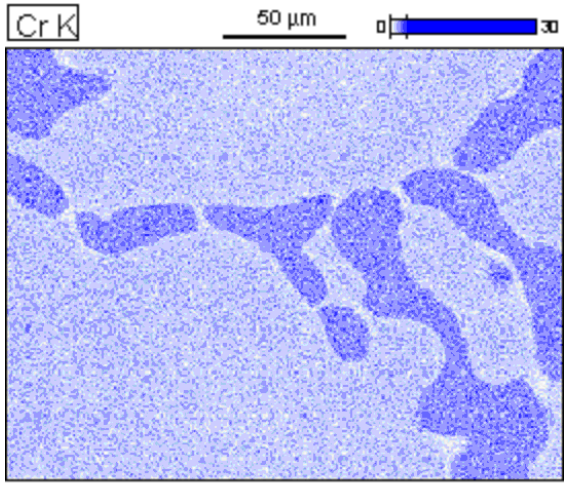


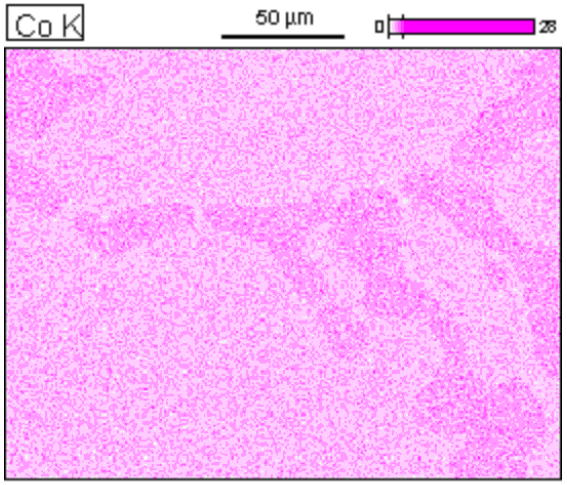
ThermoFisher SCIENTIFIC

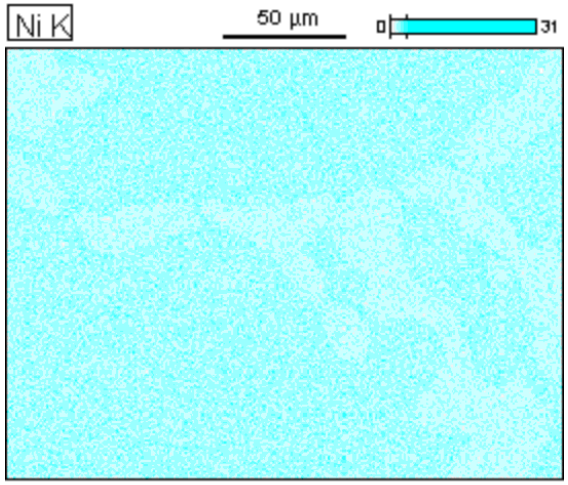
Turbine Spectral Imaging Maps



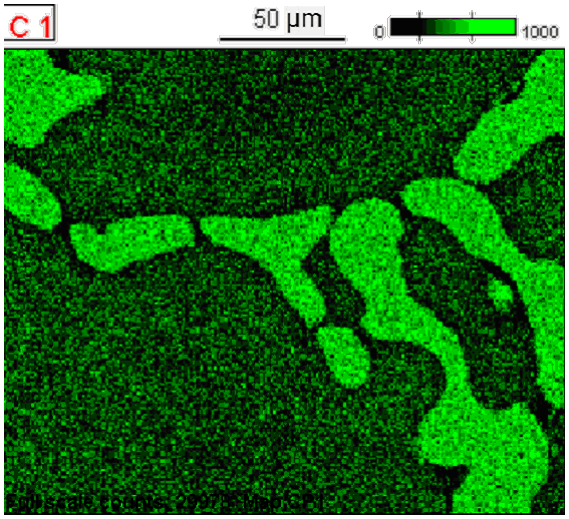


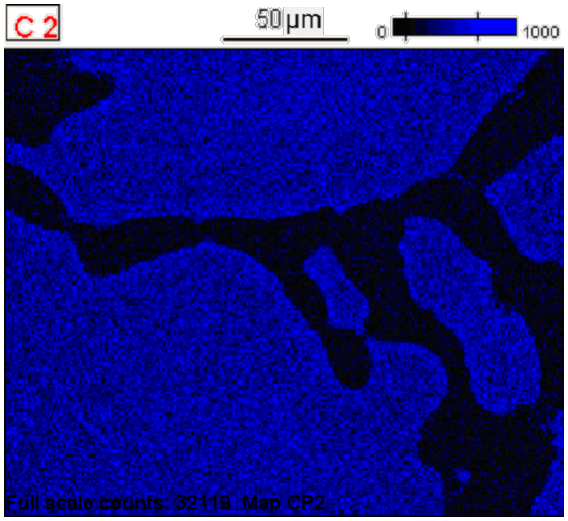


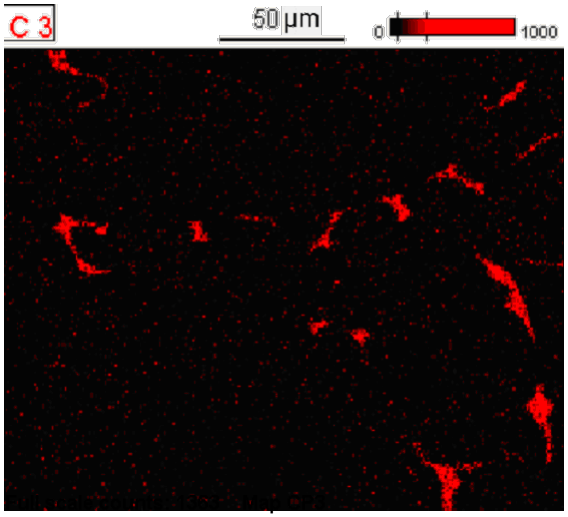


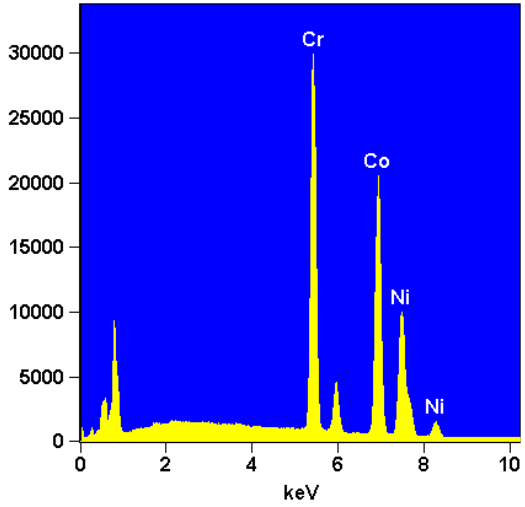


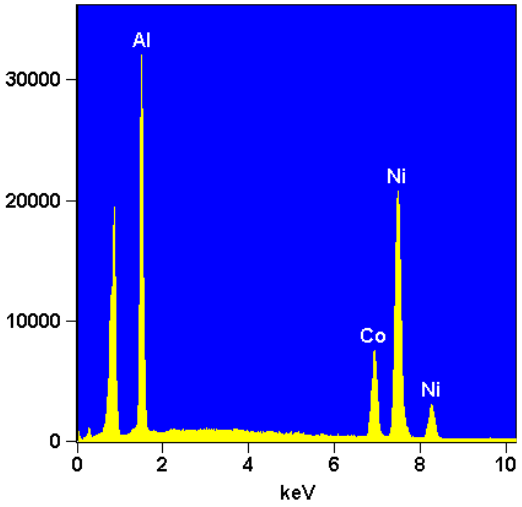
Turbine Statistical Phase Analysis

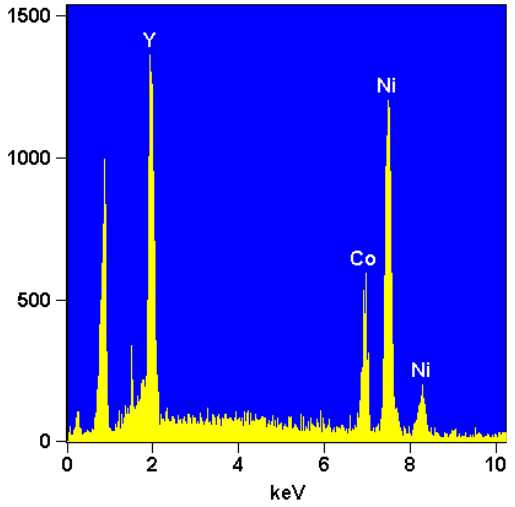






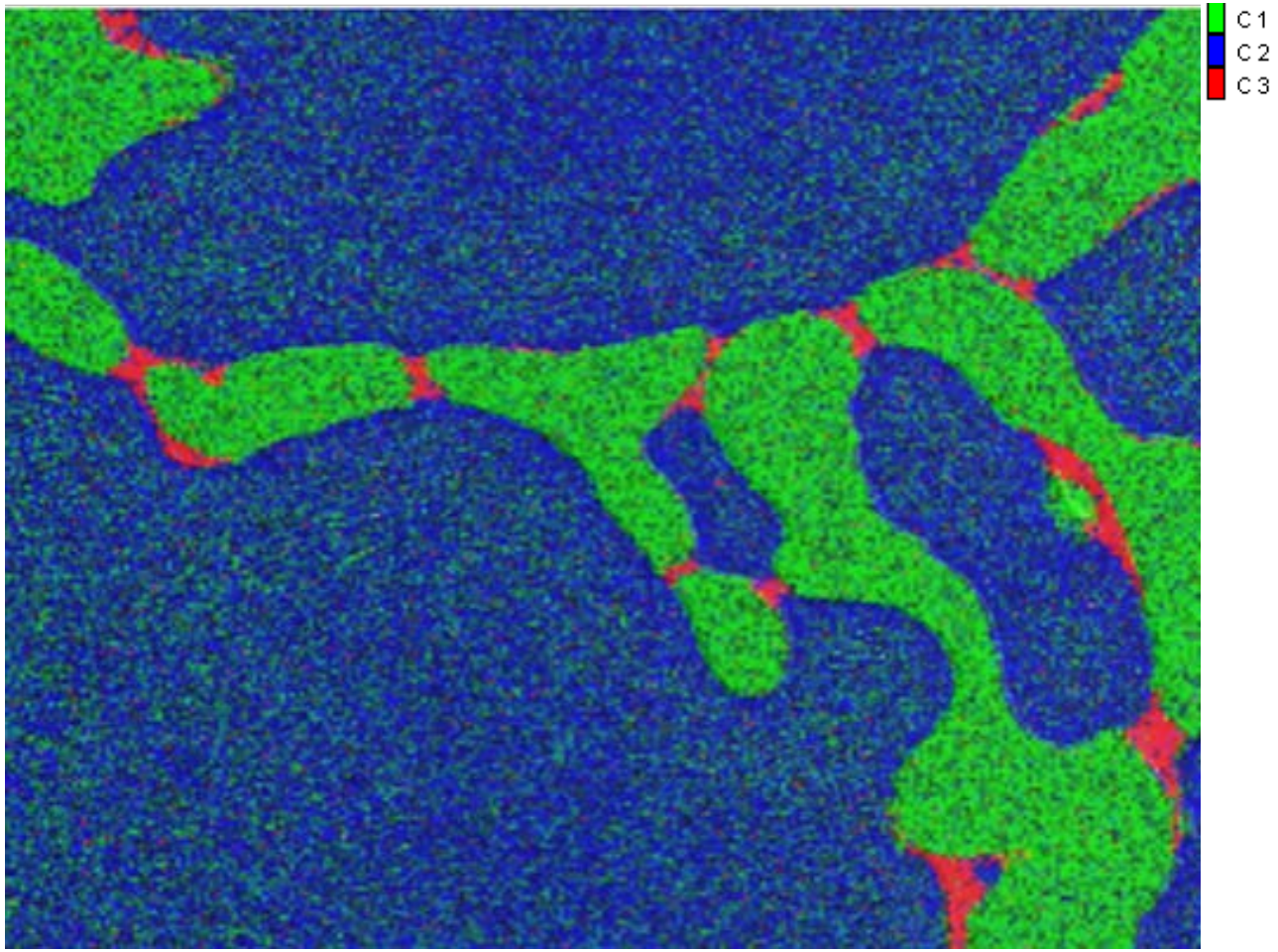






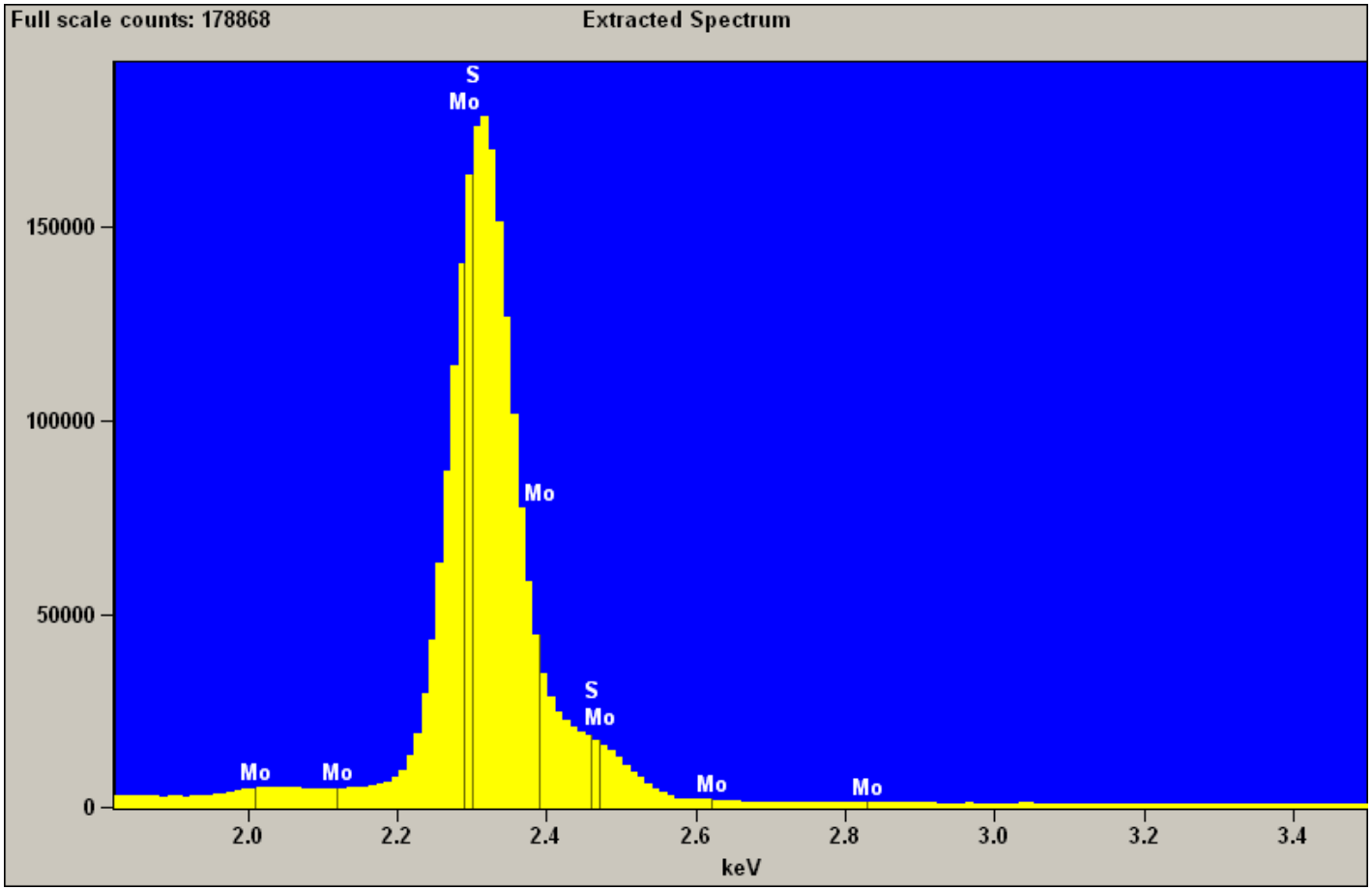
Turbine Statistical Phase Composite

- Unexpected red phase found!



Overlap of Mo-L and S-K

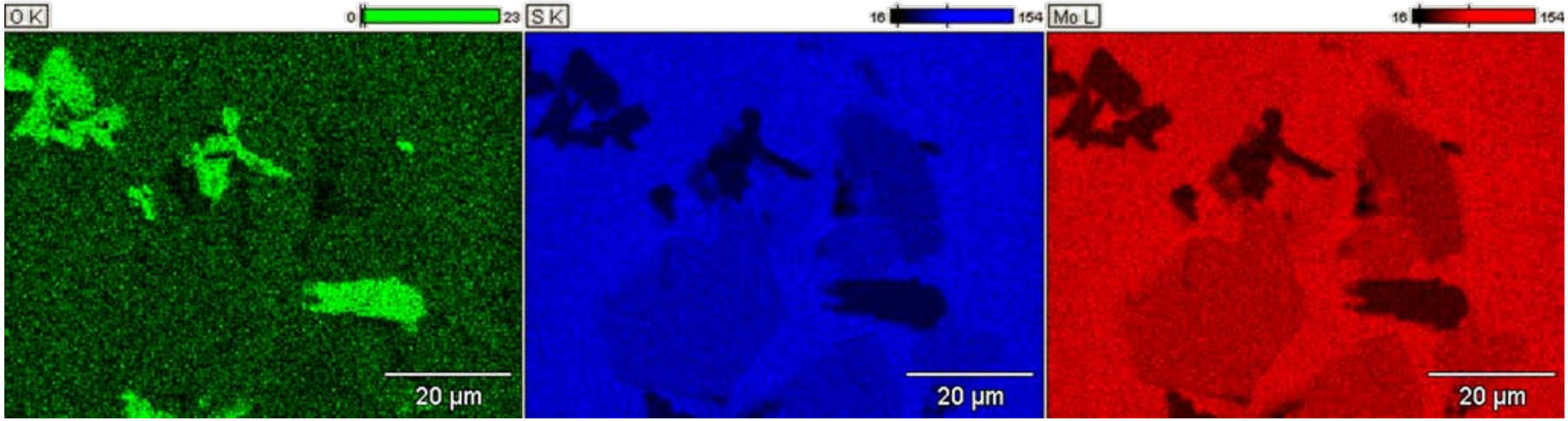
- Heavy peak overlap that needs < 20eV resolution



- Element validation is experience driven

Traditional Elemental Maps

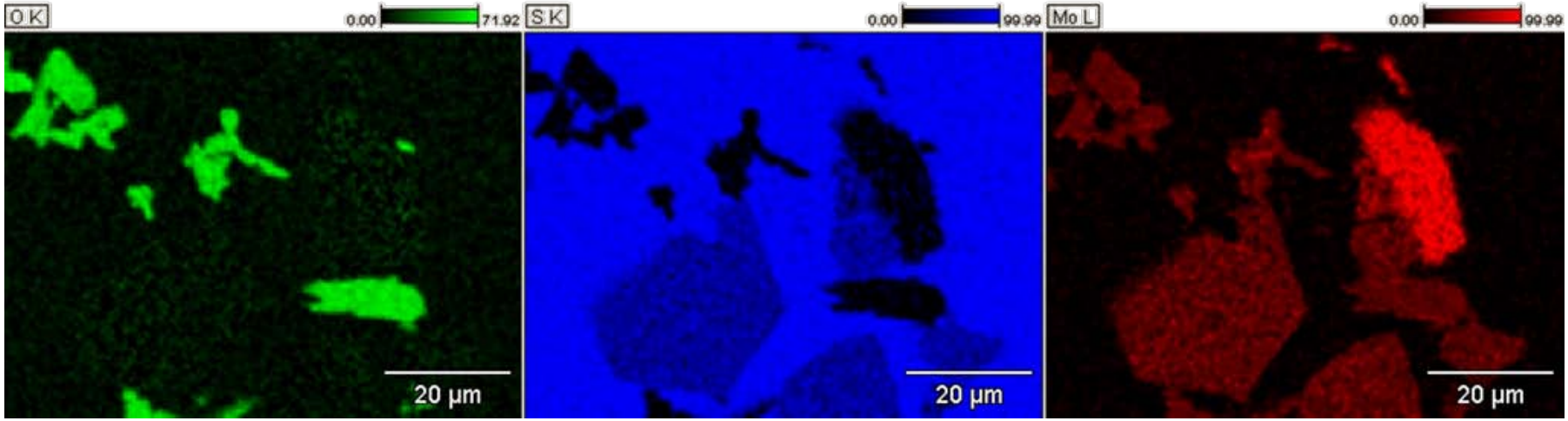
- Elemental gross-count maps
  - Excessive spectral background
  - Peak overlaps
  - Proper element selection



- Results are interesting but confusing

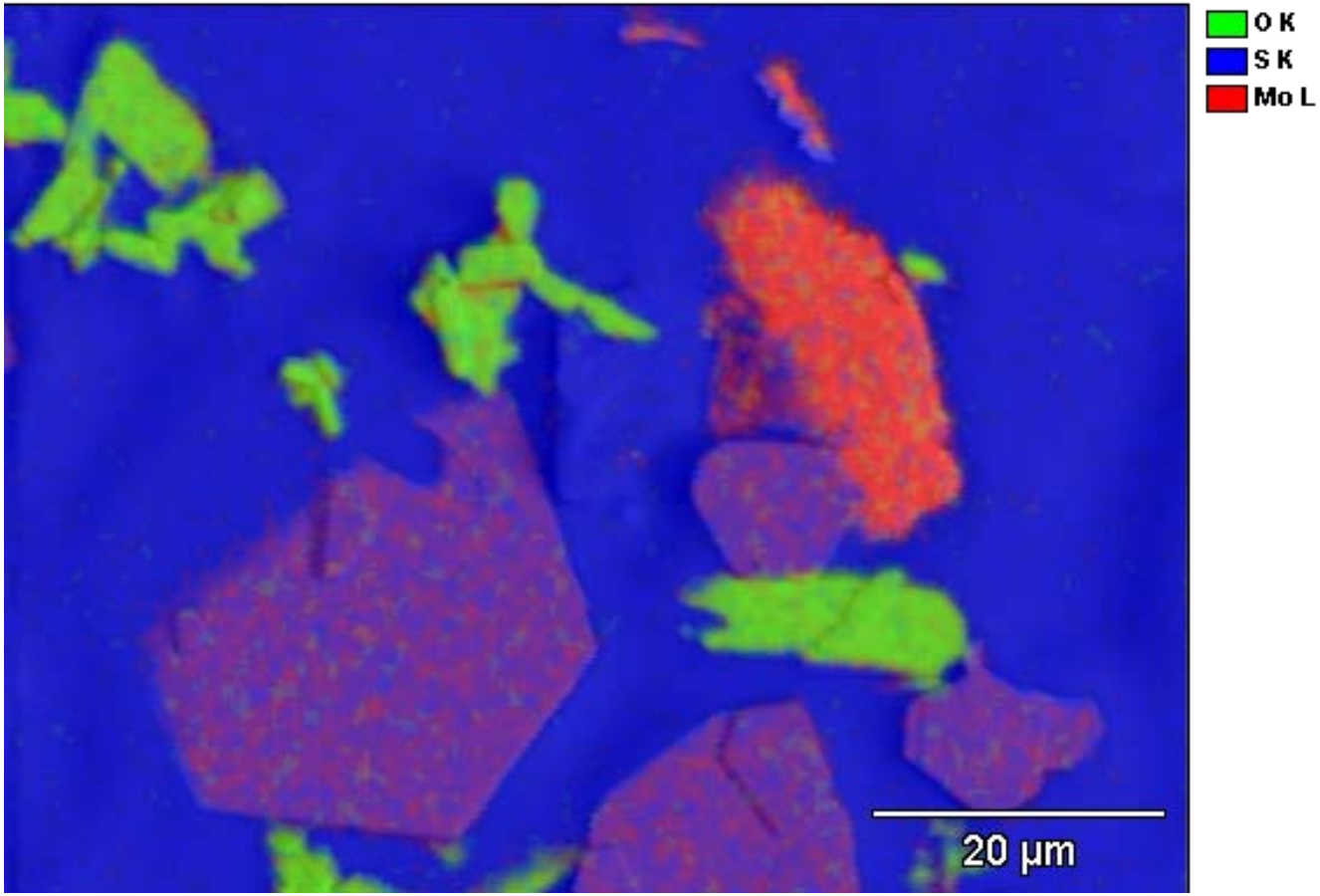
Quantitative Element Maps

- Apply full range of spectrum quantitative methods
  - Background subtraction
  - Peak deconvolution
  - Matrix correction



- Significant information content
- Correct composition intensity
- Spatial overlap complications

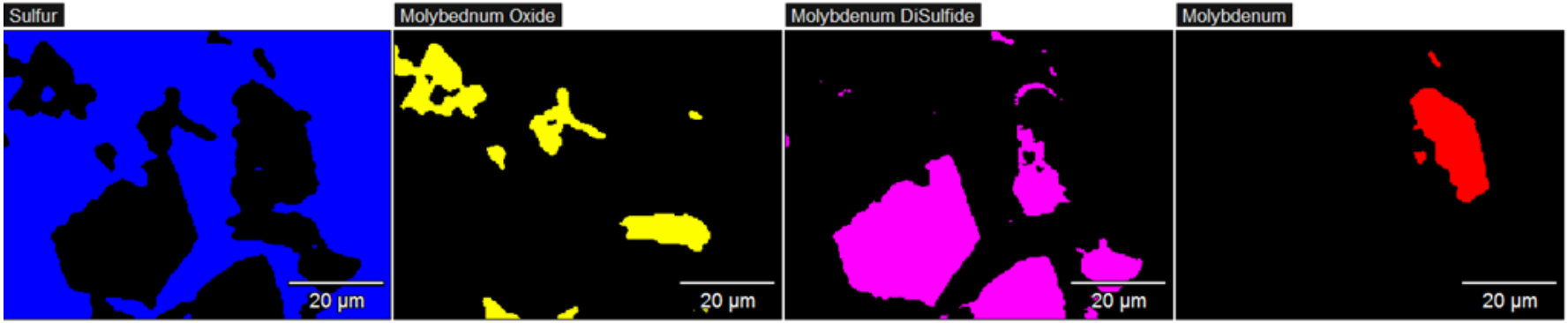
Quantitative Map Summary



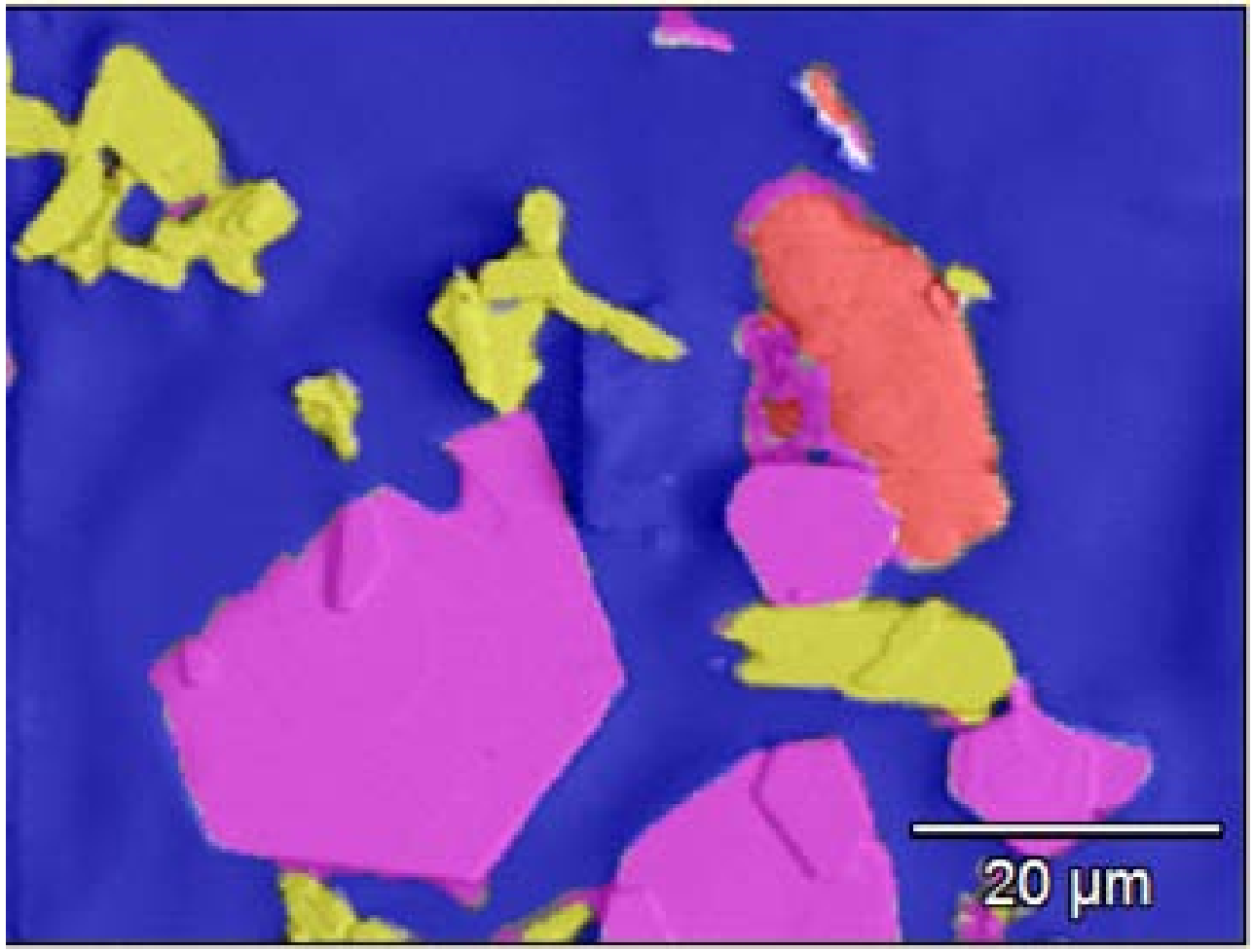
- Spatial overlap complications:
  - Unknown multi-element compound phases

Phase Analysis using Elemental Maps

- Input of user-selected maps
- Analyzes for pixel overlaps
  - Finds multi-element compounds
- Provides maps and spectra of compounds



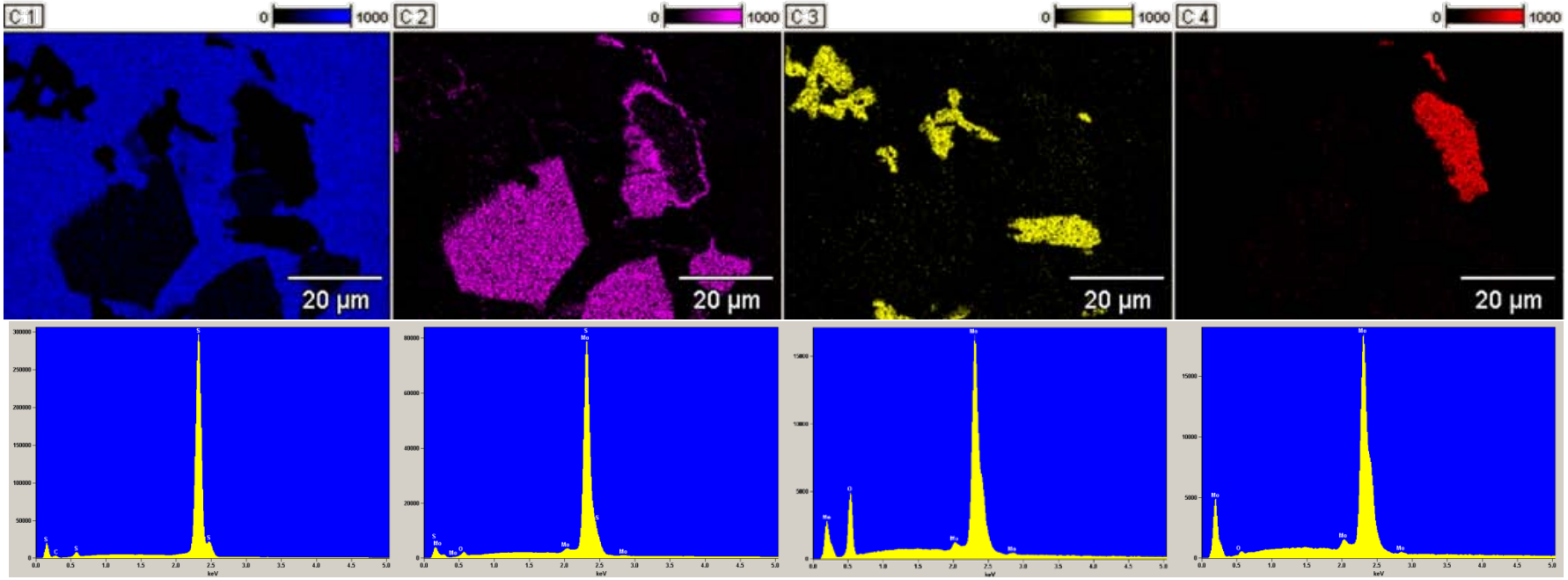
Phase Analysis Summary



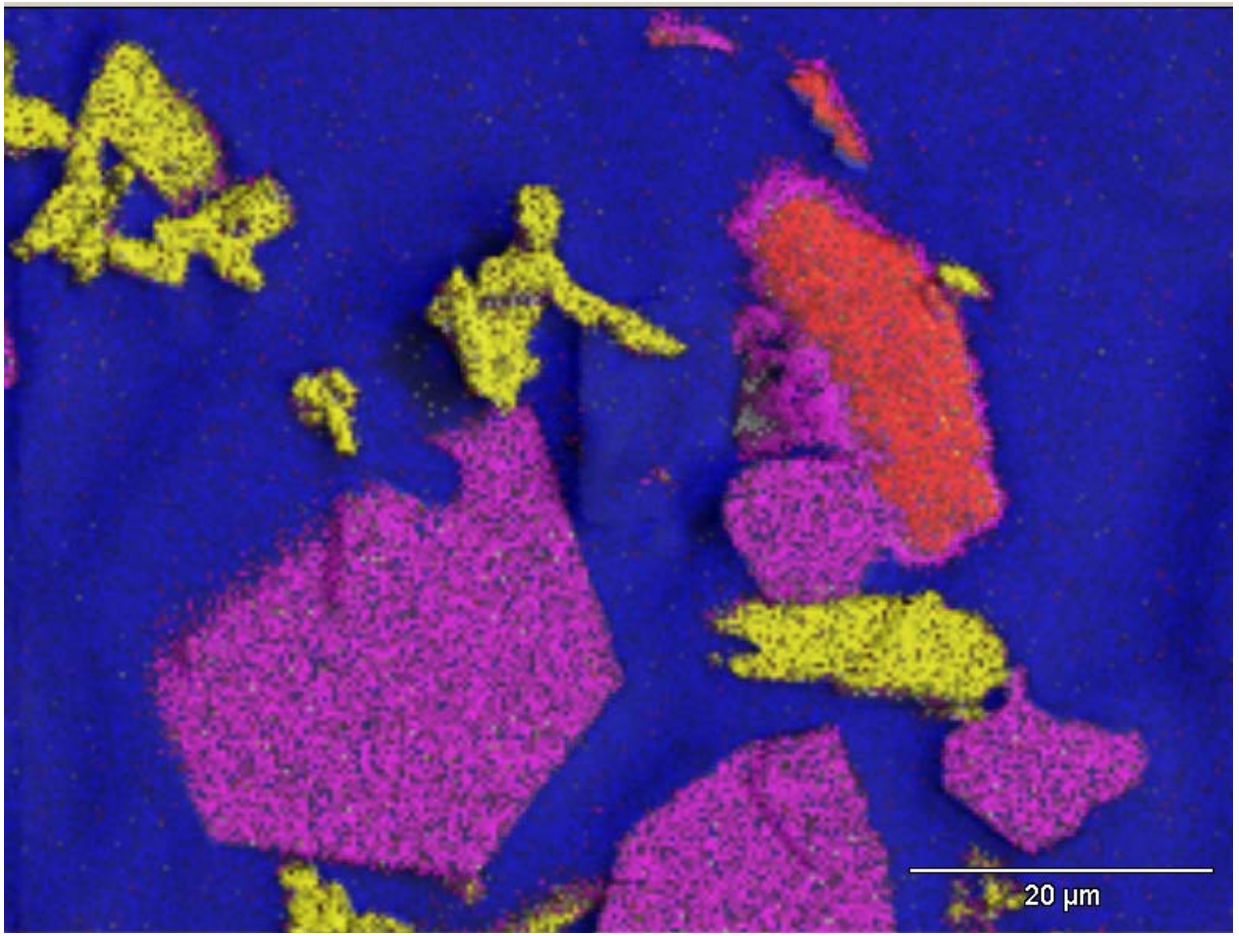
- Clearly delineated and identifiable phases

Statistical Phase Analysis

- Statistical analysis of whole data cube
  - No user bias on input to calculation
- Compares every pixel spectrum for similarities
- Provides unique component maps and spectra
- Spectral peak deconvoluting

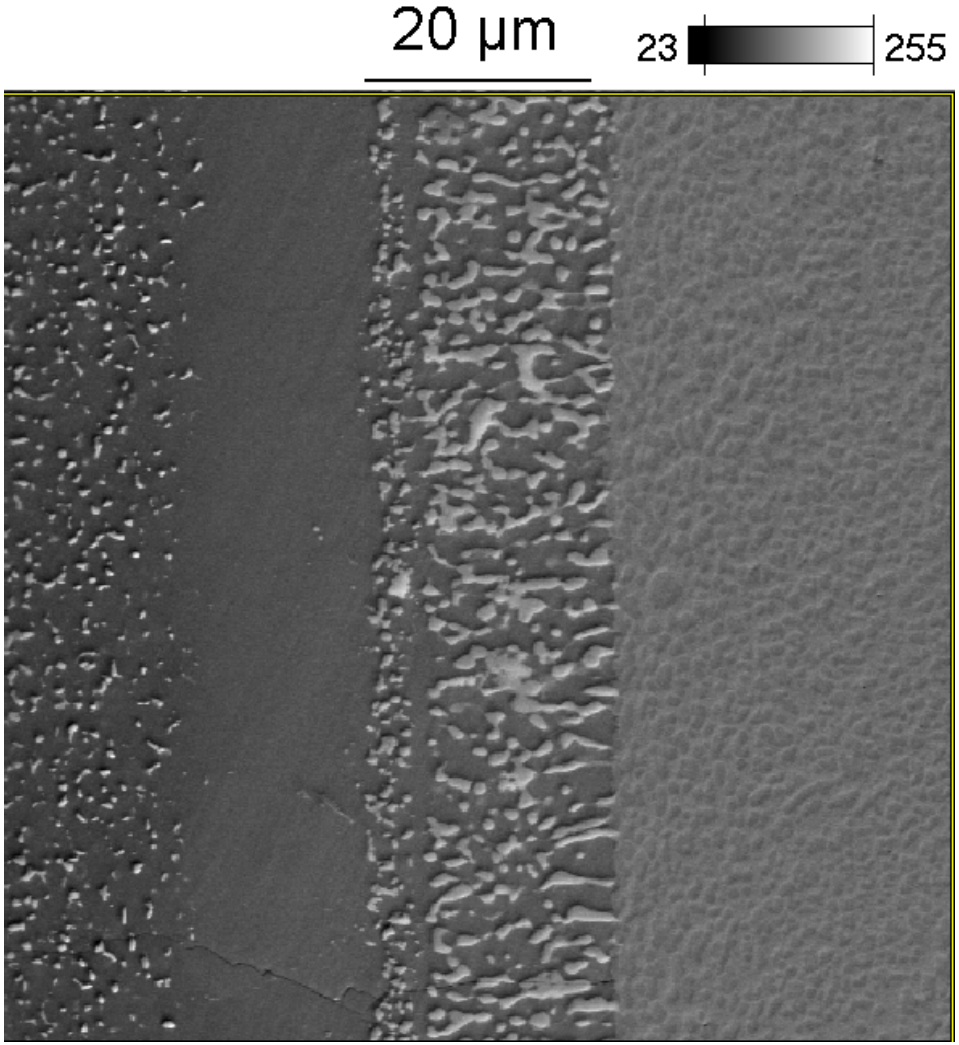


Statistical Phase Summary

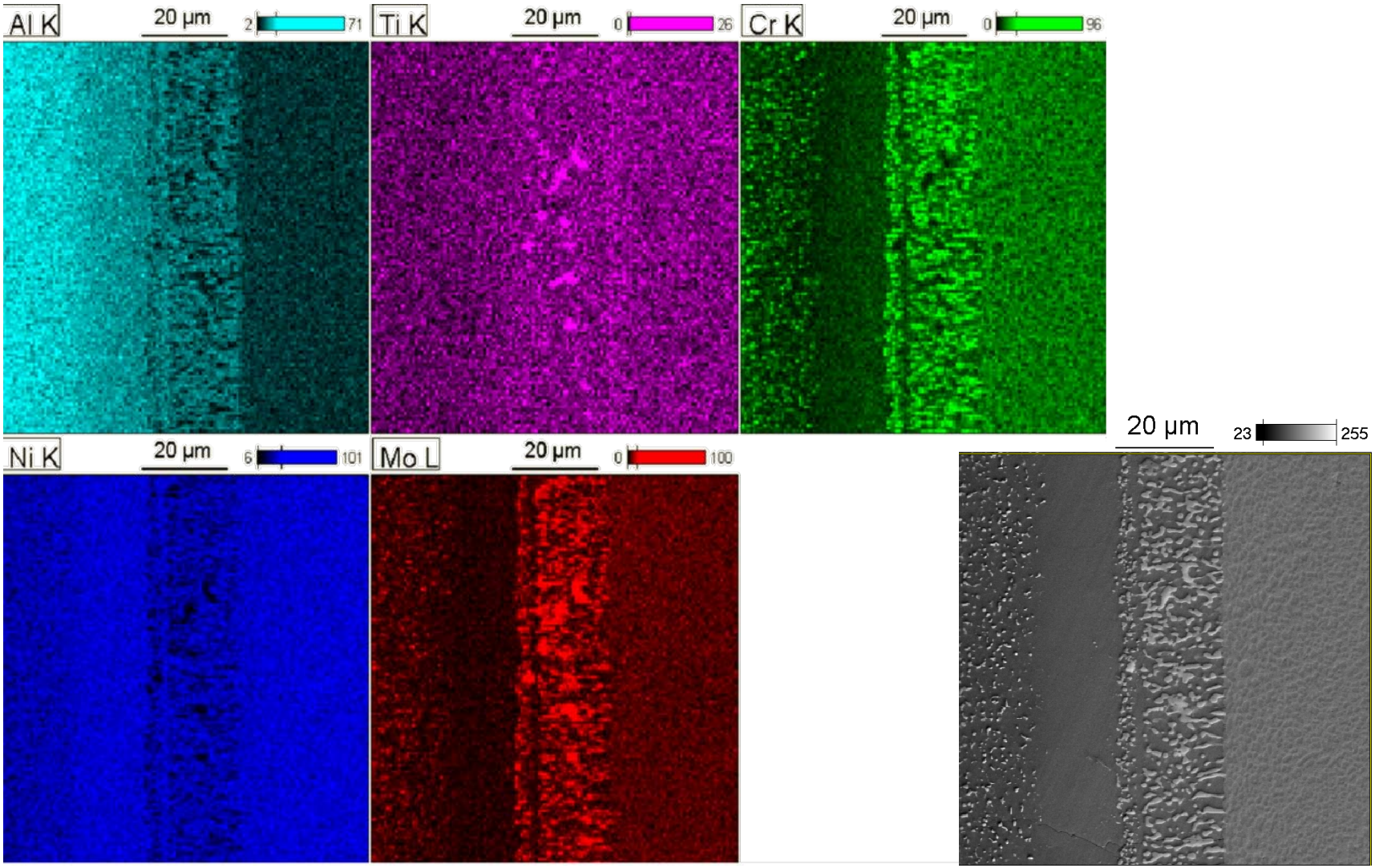


- Reduces huge data cube to a manageable and interpretable amount of information

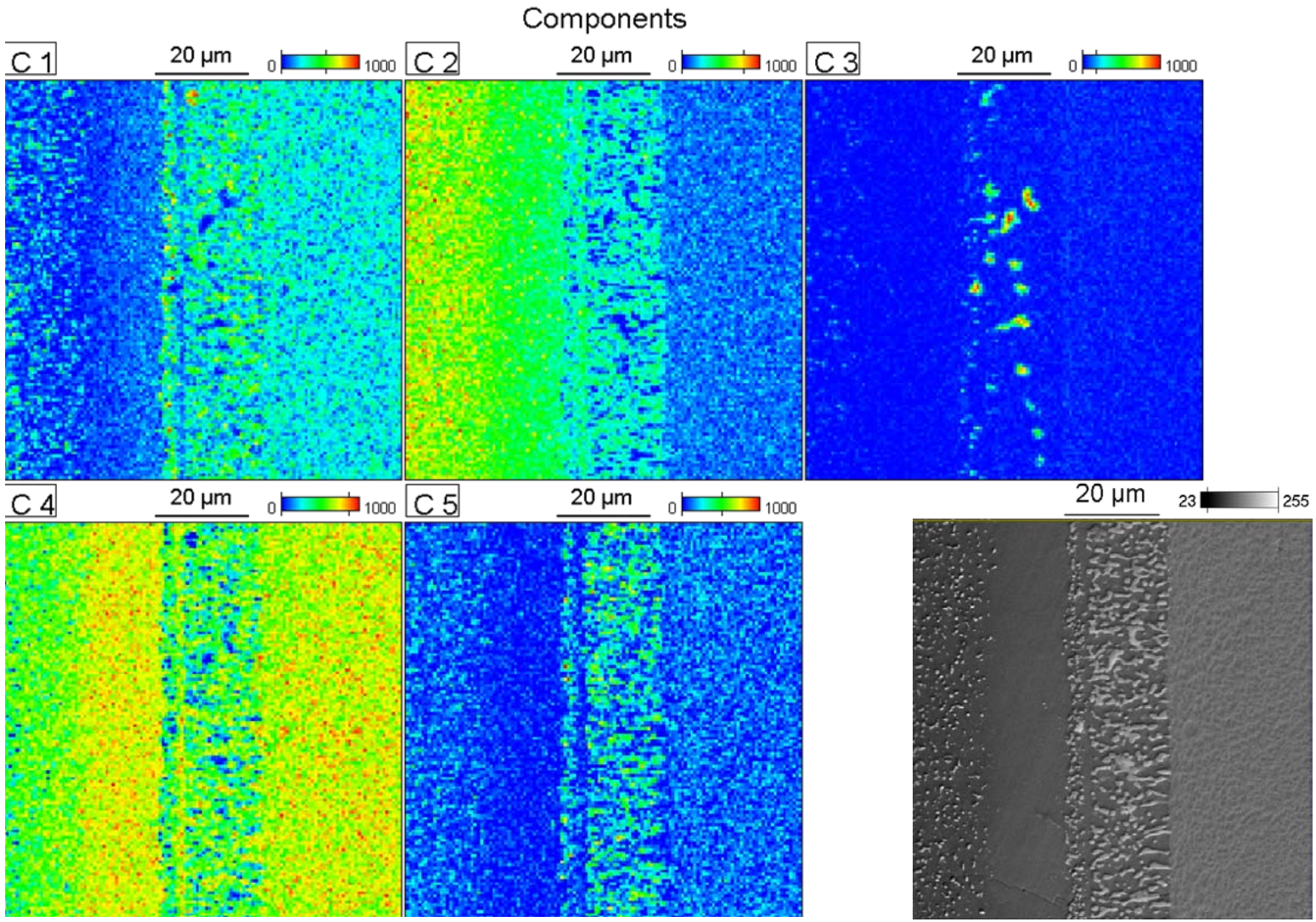
Analysis of Superalloy



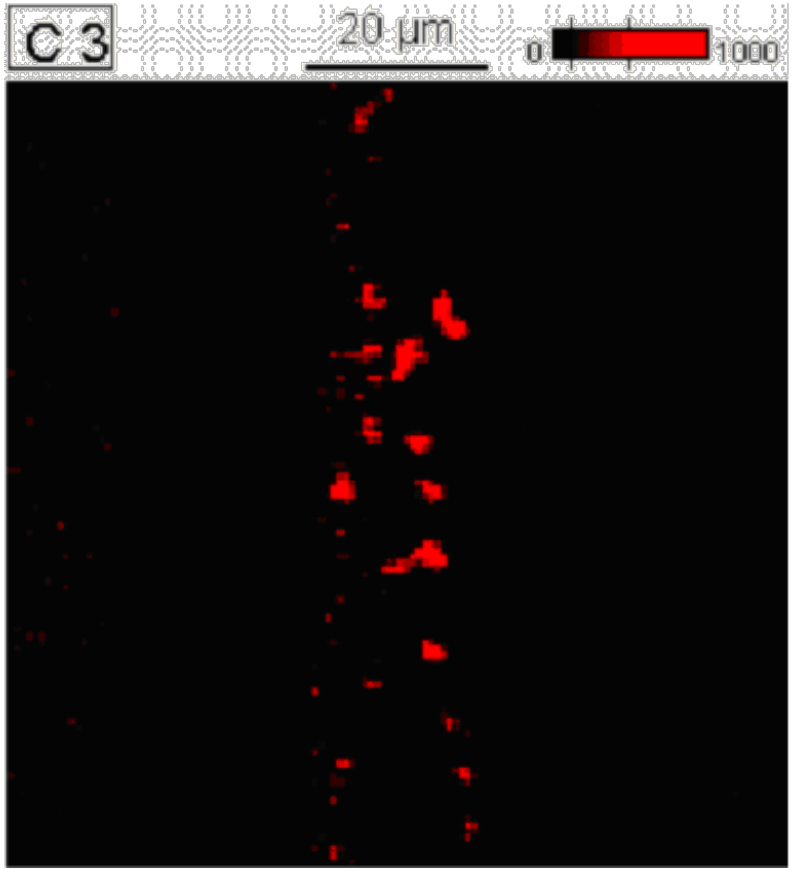
Superalloy Elemental Maps

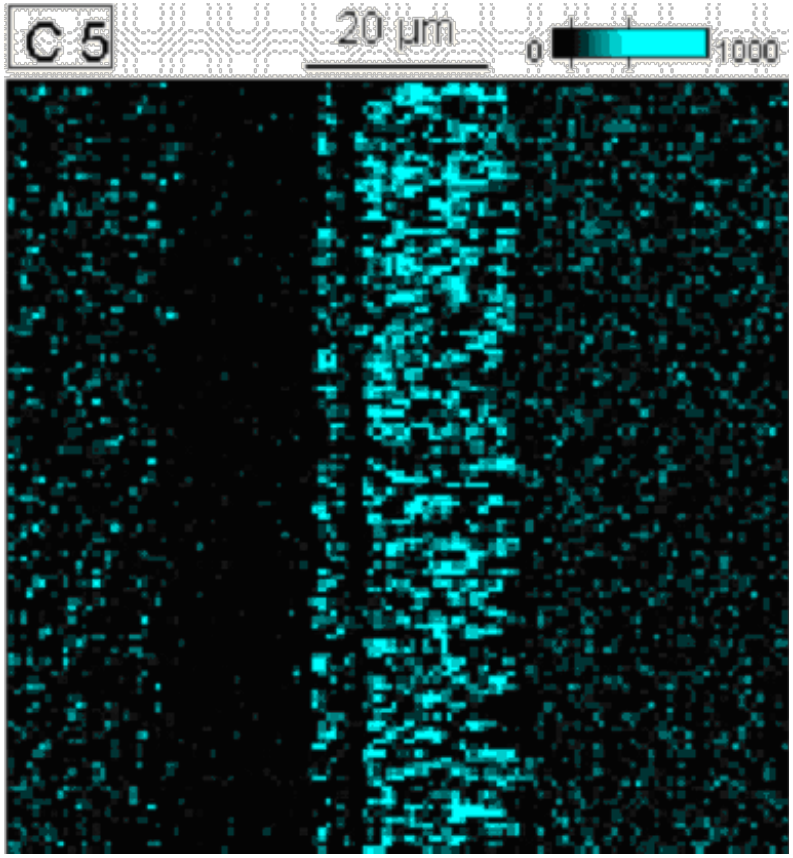


Superalloy Statistical Phase Analysis

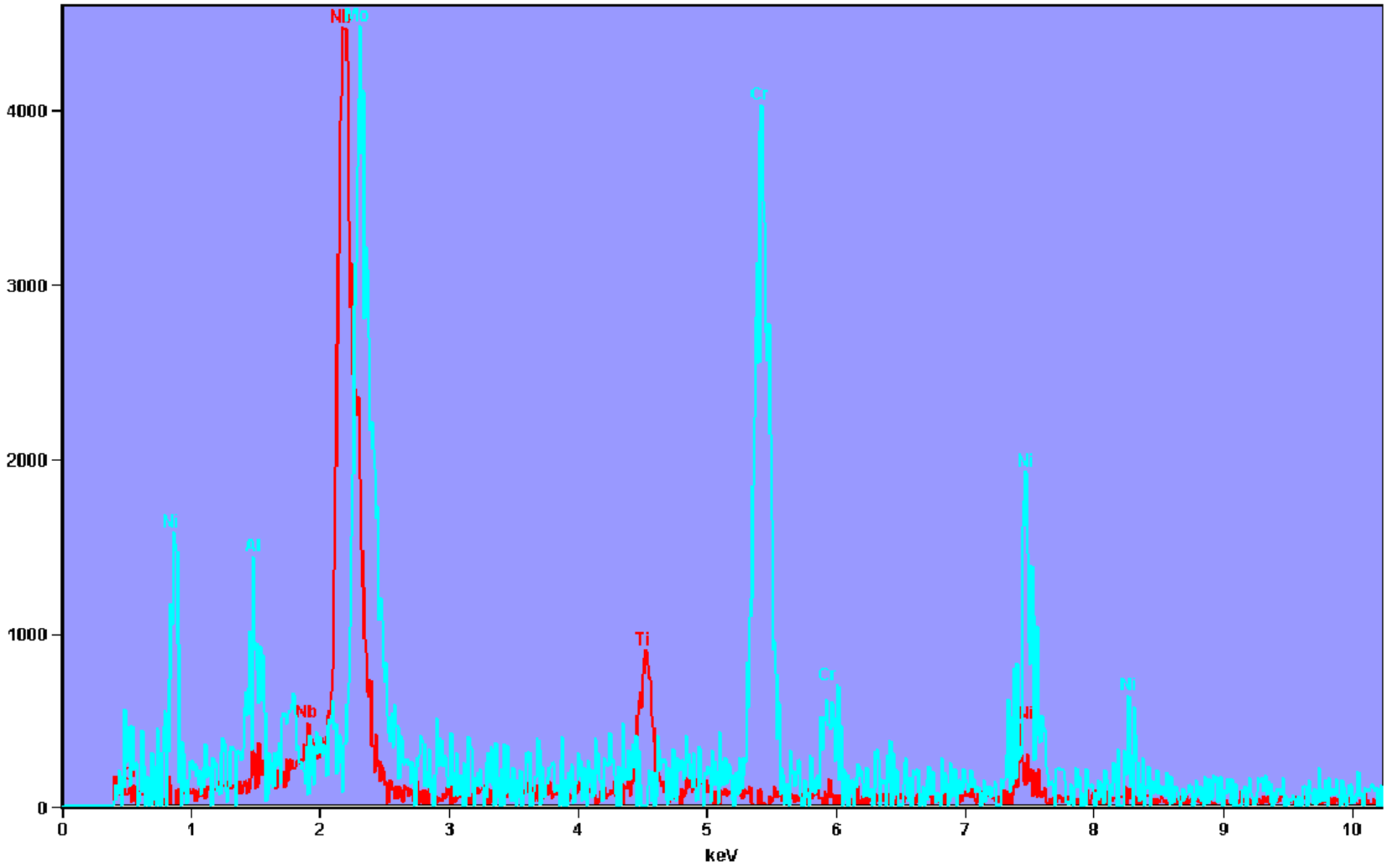


Superalloy Particle Spatial Deconvolution

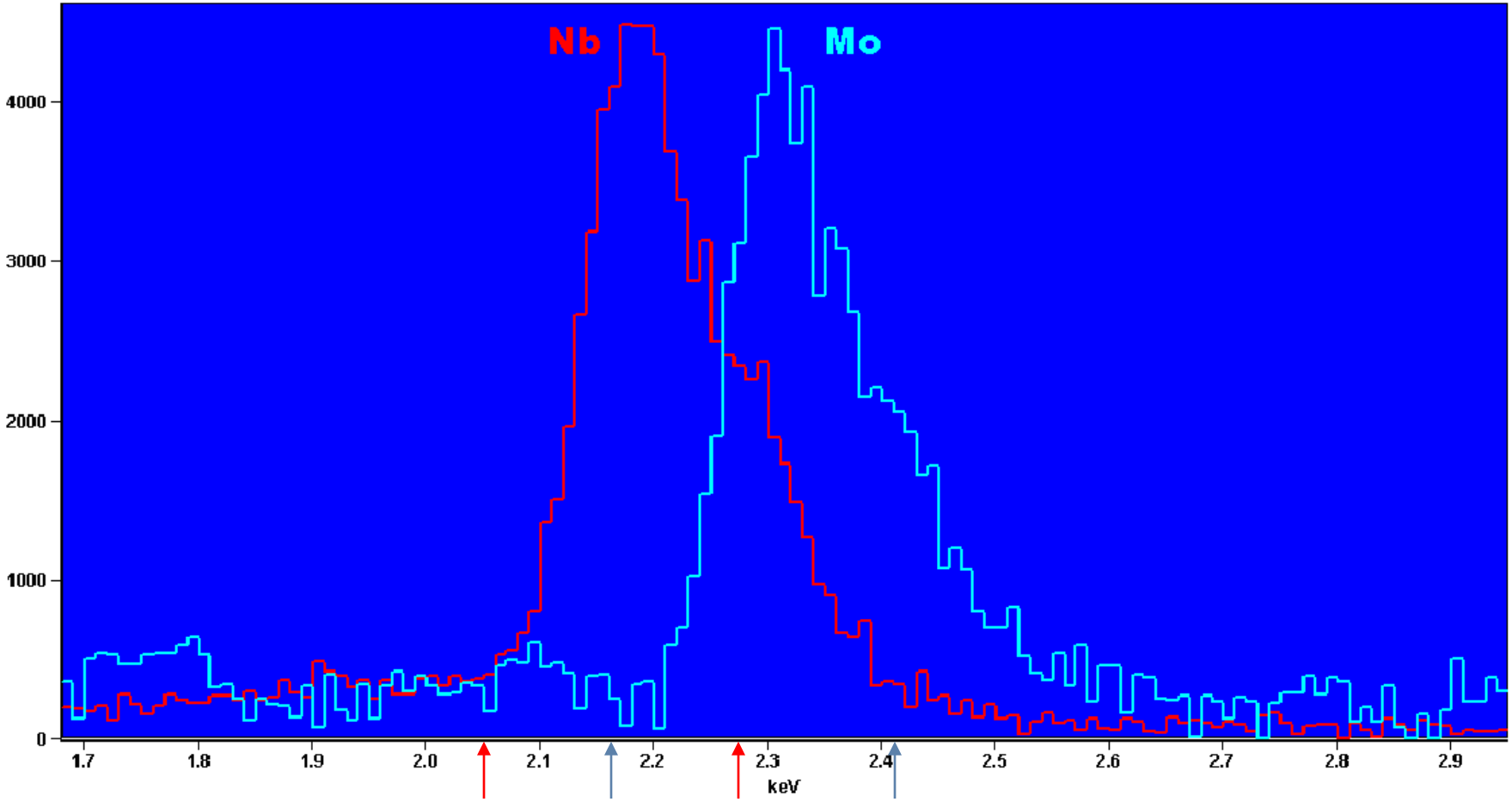




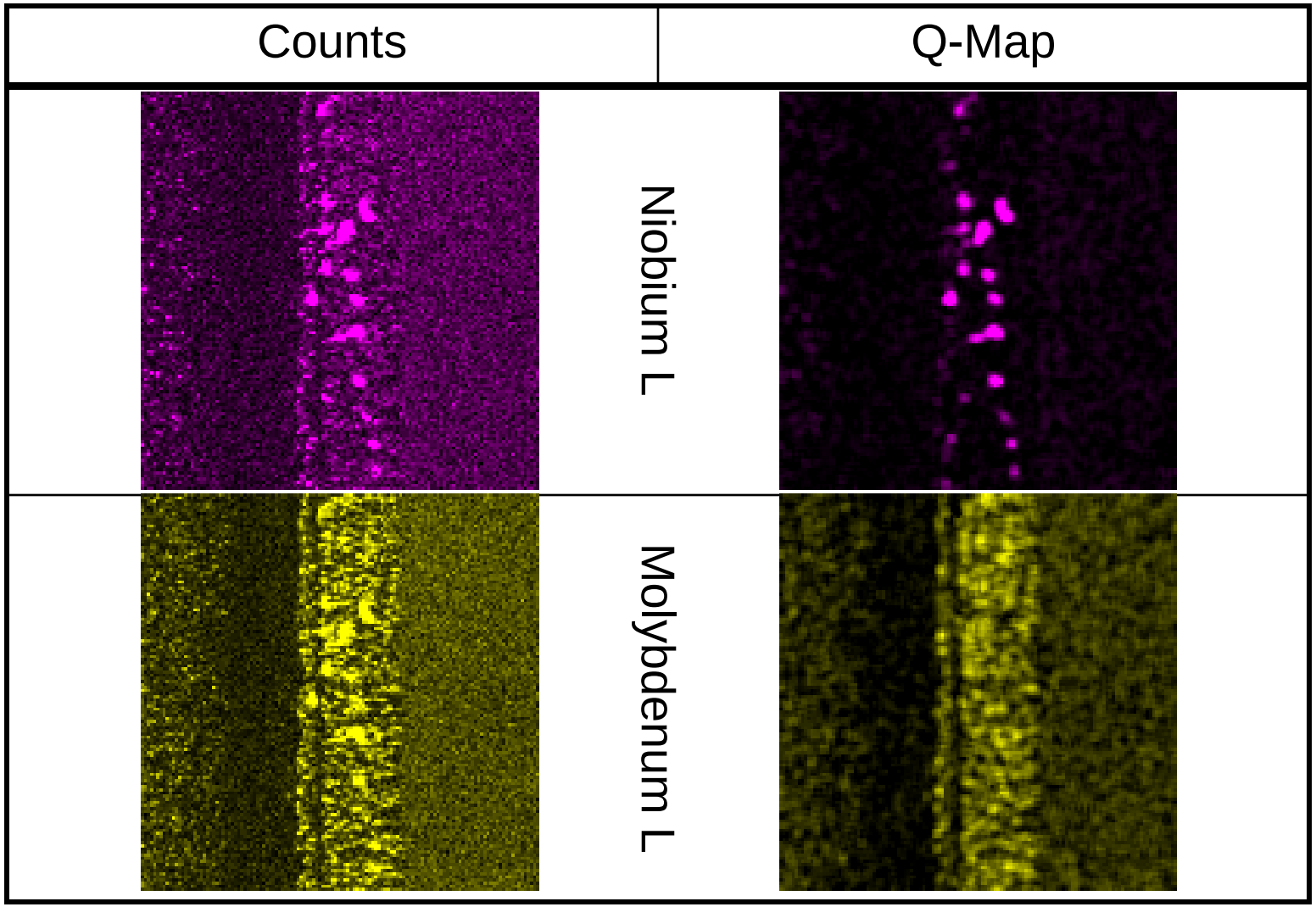
Superalloy Particle Spectral Deconvolution



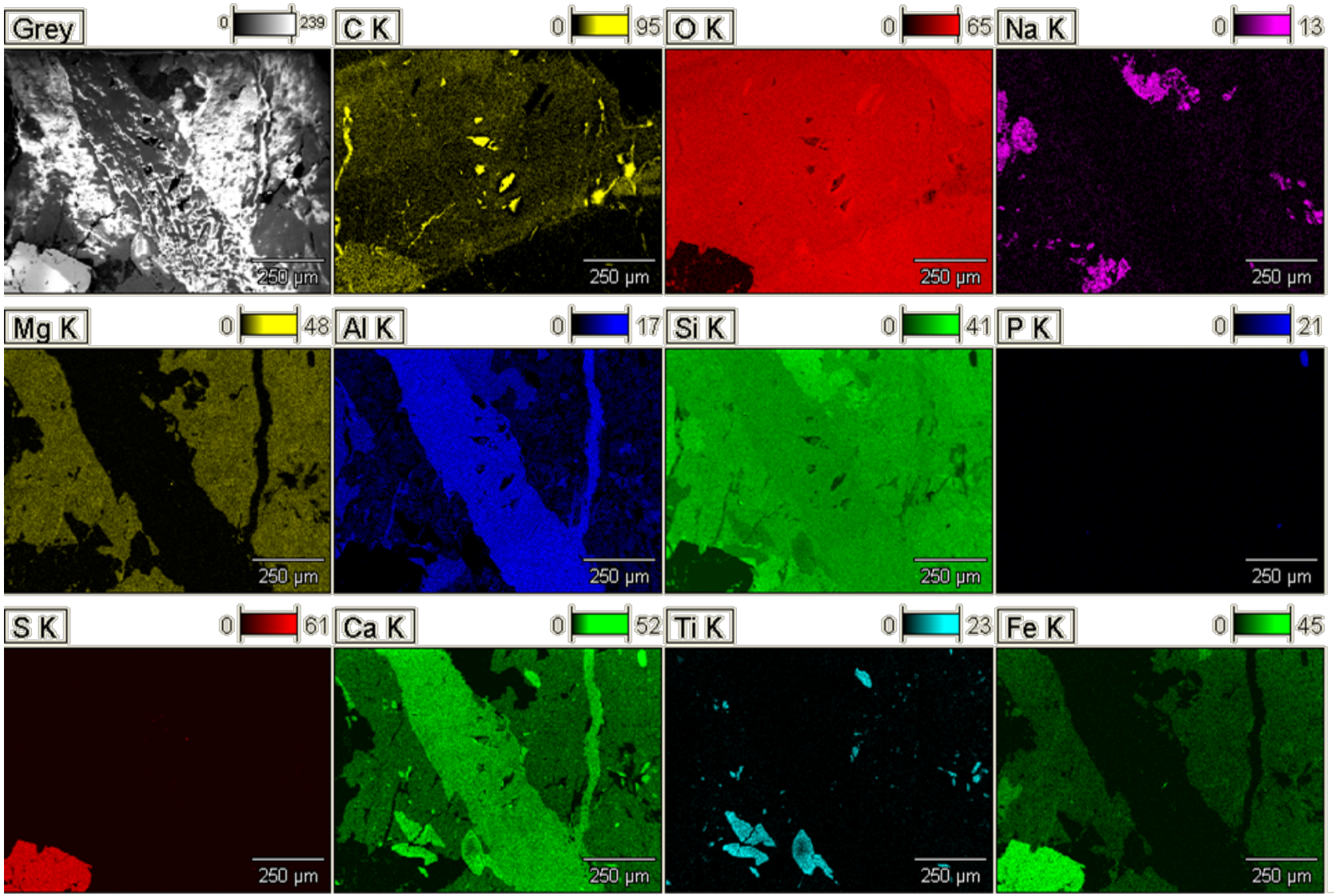
Superalloy Particle Spectral Deconvolution – 2



Superalloy Quantitative Elemental Mapping

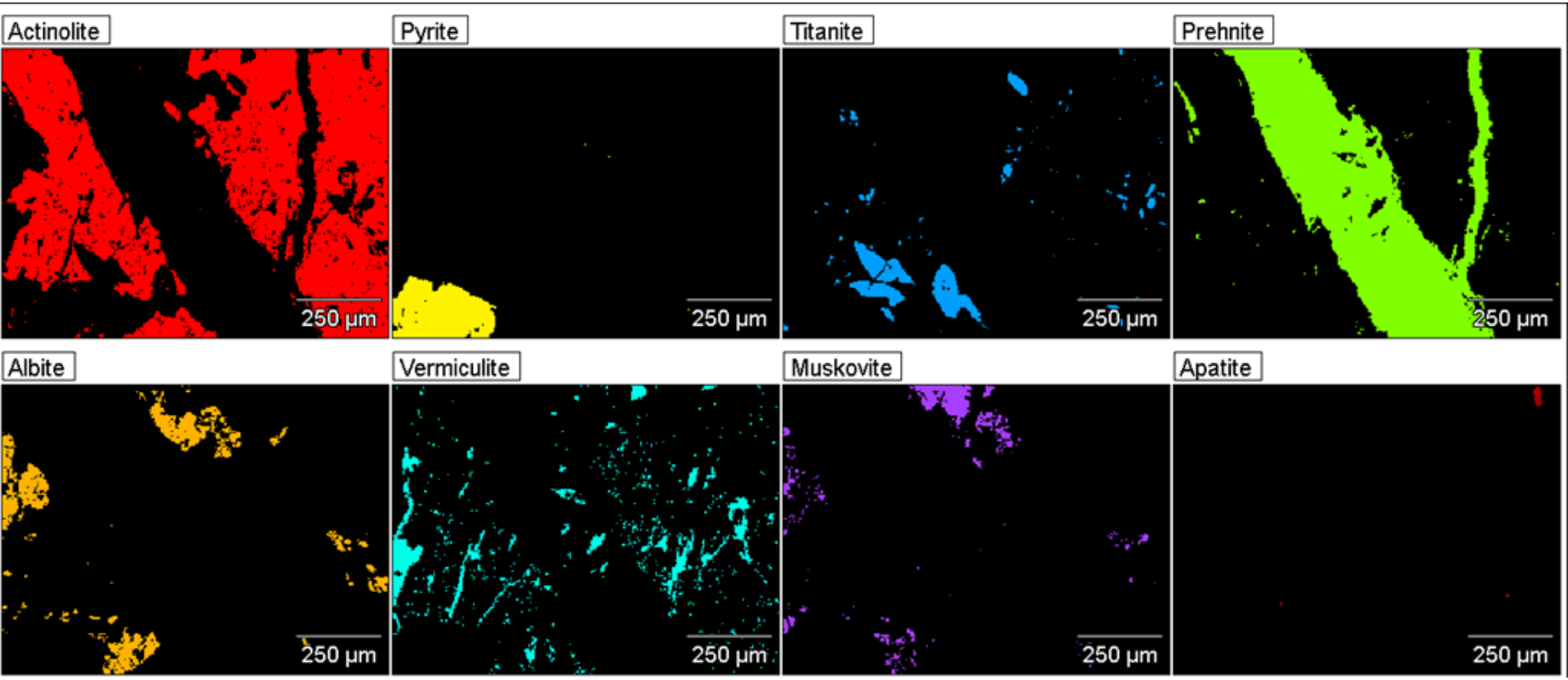


Stony Meteorite Elemental Maps

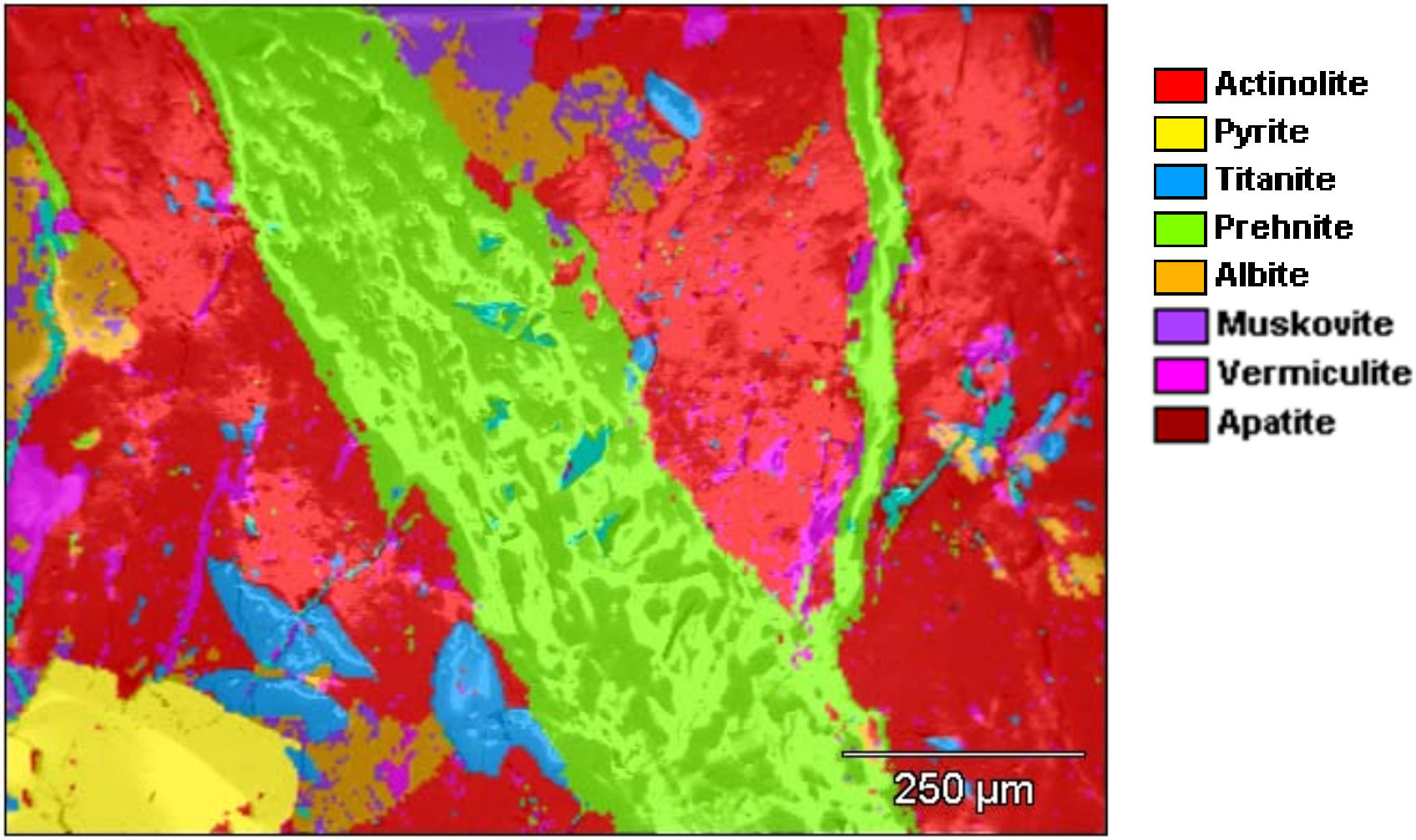


Stony Meteorite Statistical Phase Maps

- All phases found



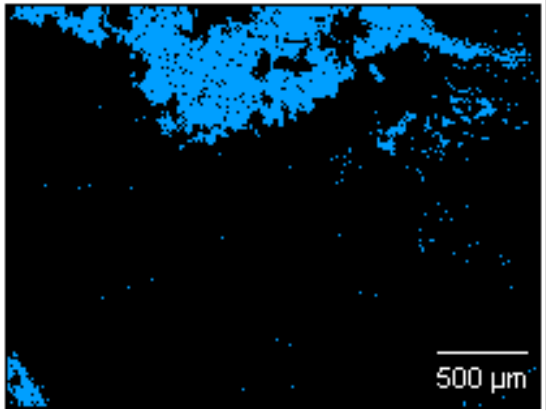
Stony Meteorite Statistical Phase Map Summary

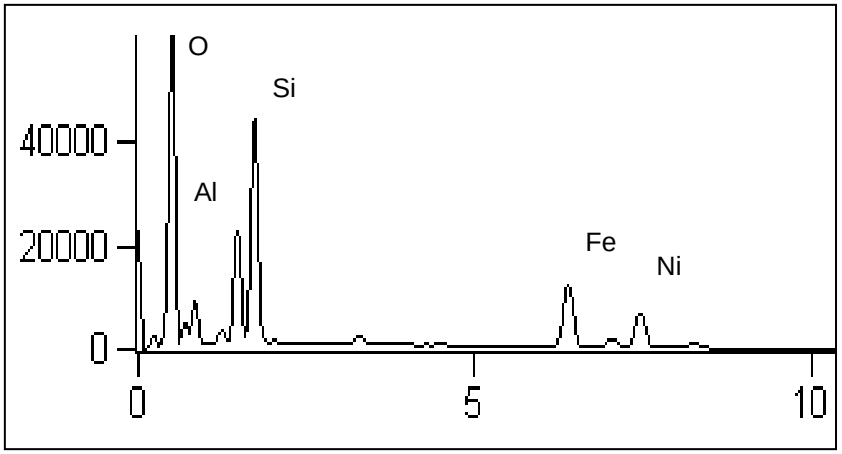


- Phase distributions overlaid on the electron image

Stony Meteorite Statistical Phase Map Details – 1

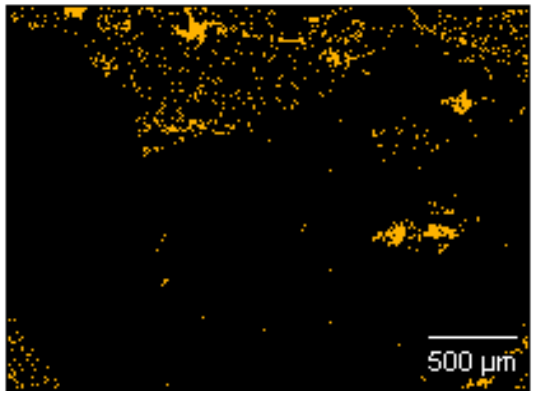
SiAlFeNi - O

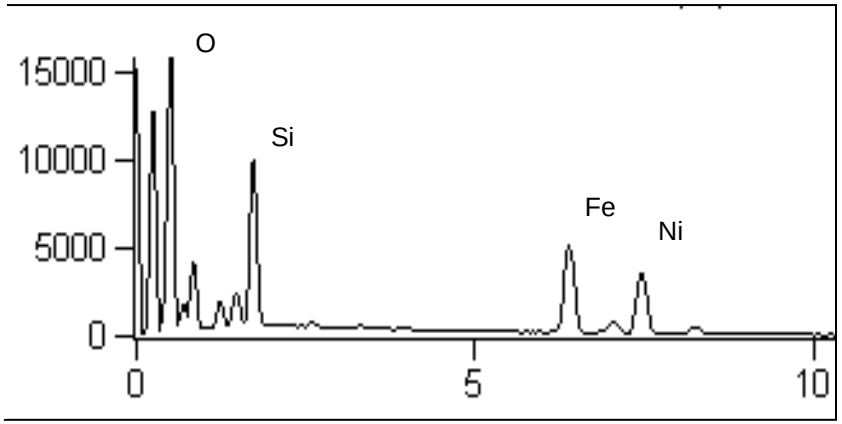




SiAlFeNi - O phase		
Element	X-ray Counts	Atomic percent
O K	296282	61.4
Mg K	17069	1.2
Al K	177934	8.1
Si K	393884	15.4
Ti K	4008	0.1
Fe K	188800	7.5
Ni K	115434	6.3

NiSiFe - O





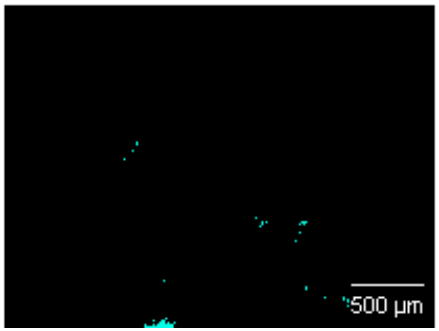
SiFeNi - O phase		
Element	X-ray Counts	Atomic percent
O K	103582	62.7
Mg K	11959	3.8
Al K	5432	1.1
Si K	86081	11.9
Fe K	78001	10.2
Ni K	56059	10.3

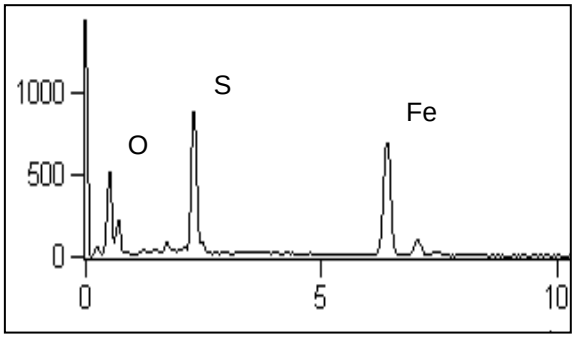
- Spatial distribution, spectrum and quantification for each phase

Stony Meteorite Statistical Phase Map Details – 2

- 2 Unexpected phases with very low area coverage

FeS - O

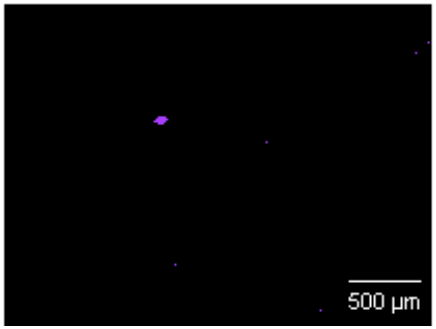


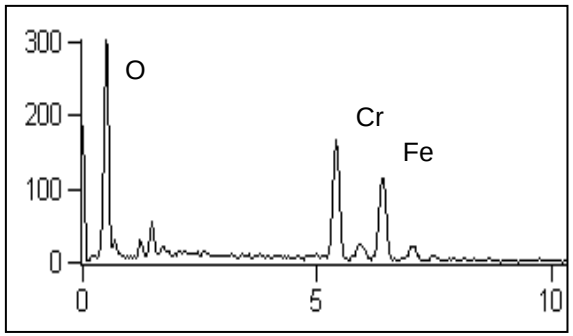


FeS - O phase		
Element	X-ray Counts	Atomic percent
O K	3412	52.5
Si K	473	0.7
S K	9449	16.0
Fe K	10955	30.8

Note the low counts < 0.1% of the total sample counts

FeCr - O





FeCr - O phase		
Element	X-ray Counts	Atomic percent
O K	1963	59.5
Mg K	91	1.7
Al K	172	2.1
Cr K	2386	18.4
Fe K	1744	18.3

- All users get this answer!
- Statistical methods provide the highest confidence of fully understanding your sample.

Conclusions

- Highest quality report in the shortest analyst time
  - Acquisition and analysis time
- Operational settings depend upon sample
- “Optimal” settings are a balance of capabilities
- Terminate by statistics
- Report include phase analysis by statistical method

Q & A

THANK YOU

QUESTIONS?