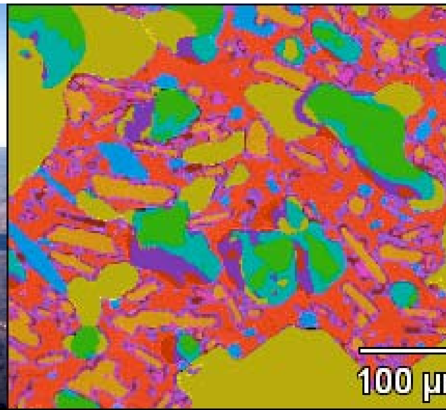
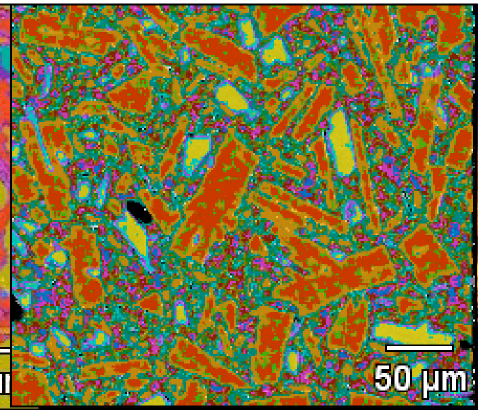




Useful Methods for Processing N-dimensional X-ray Datacubes

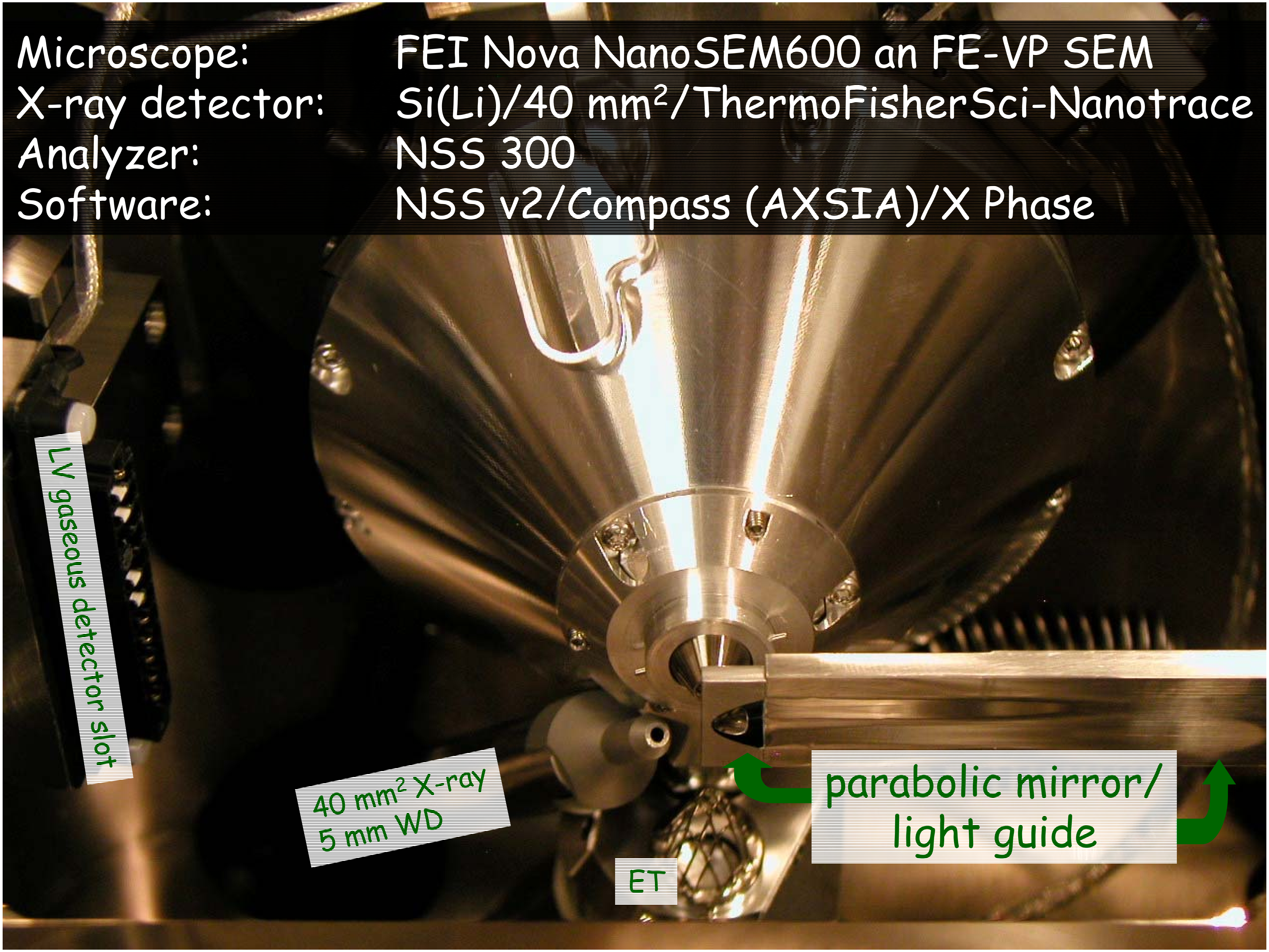
A Volcanological Example

Smithsonian
National Museum of Natural History

Ed Vicenzi
Department of Mineral Sciences
Washington, DC

Outline

- ✓ Concept of localized bulk chemistry on the microscale
- ✓ Introduction to MVS, the spatial simplicity method, and paths to chemical phase analysis
- ✓ The tale of Parícutin Volcano
- ✓ Phase results from Parícutin specimens


Microscope: FEI Nova NanoSEM600 an FE-VP SEM
X-ray detector: Si(Li)/40 mm2/ThermoFisherSci-Nanotrace
Analyzer: NSS 300
Software: NSS v2/Compass (AXSIA)/X Phase
LV gaseous detector slot
40 mm2 X-ray
5 mm WD
ET
parabolic mirror/
light guide

Ultimate Analytical Objectives

- Measure area (volume) fraction of all chemical phases present
- Measure composition of all phases of interest (POI)
- Normalize volume fractions and weight phase microchemistry accordingly

Sounds simple! and leads to the determination of a sample's Local Bulk Chemistry (LBC)

Local Bulk Composition?

Determination of the chemical nature of a sub-volume of a sample. It often yields information about the specimen's history e.g. by way of comparison with bulk properties

Traditional approaches

- Estimate area fractions by segmenting BSE image, perform representative point analyses of each POI Fraught with problems
- Analyze sum raster Fahgetaboutit!

Ideal approach

Base area estimate on segmentation of 10^3-10^4 X-ray analyses. POI composition from aggregate of spectra at all locations, yielding improved statistics

Some Applications

Earth Sciences

• reconstruction of trapped liquid composition in complex melt inclusions (eg w/daughter crystals)

• crystal- melt geothermometry where glass composition is not accessible owing to groundmass crystallization (element partitioning in general)

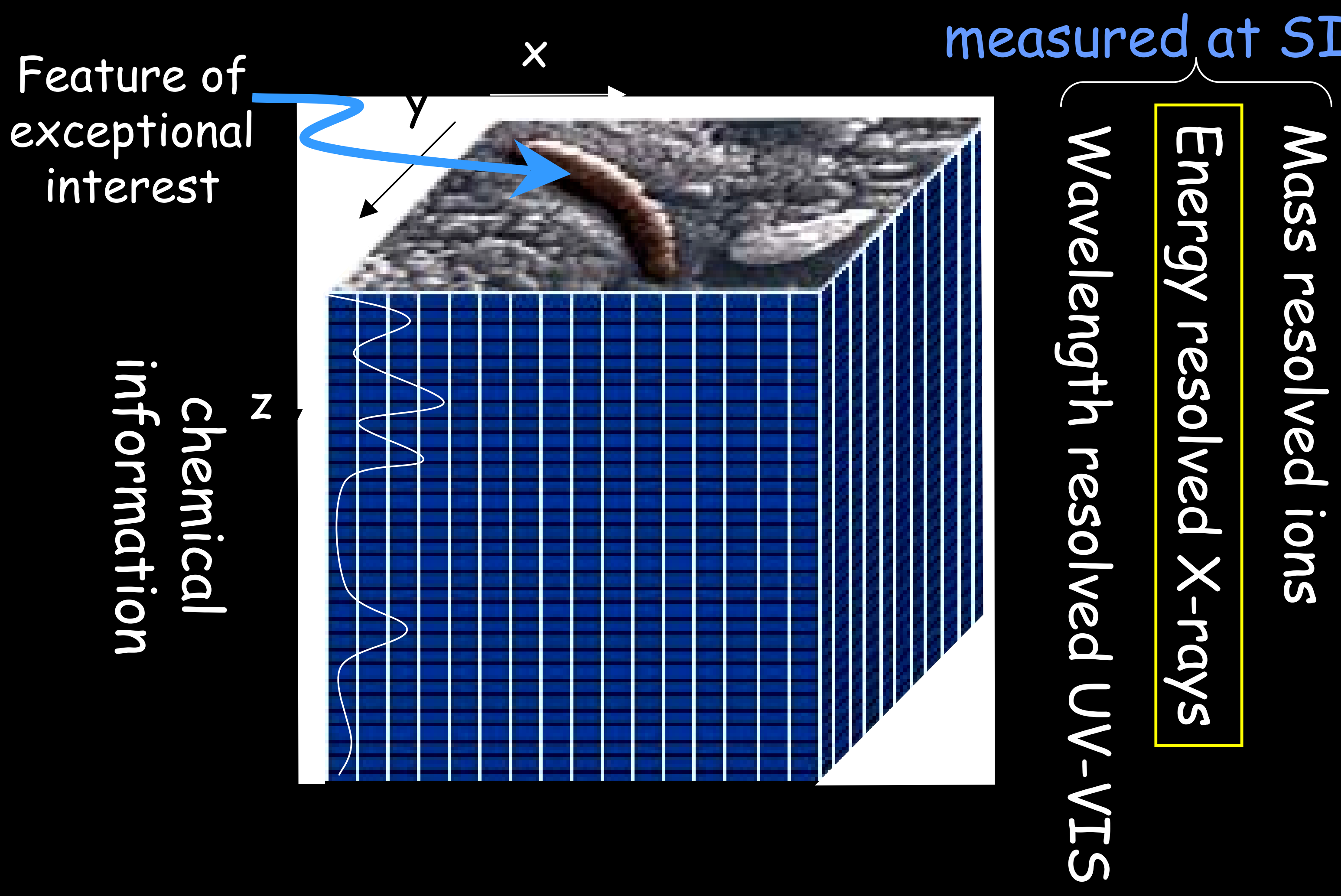
• estimation of fluid chemistry by summing all precipitated material in a vein

Materials Sciences

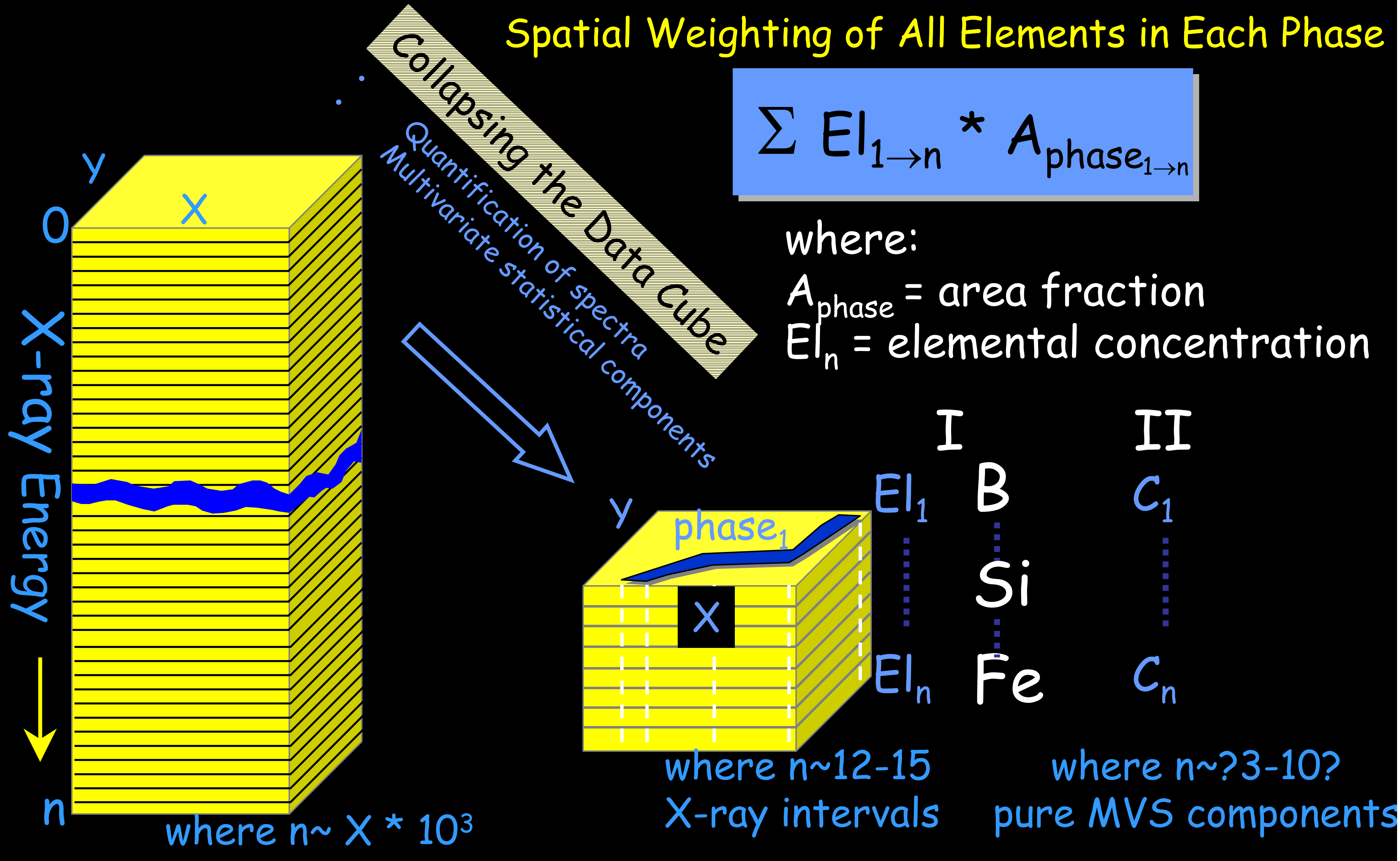
• heterogeneity of welds

The Hyperspectral Data Cube

Hyperspectral ≡ more than 20 spectral bands

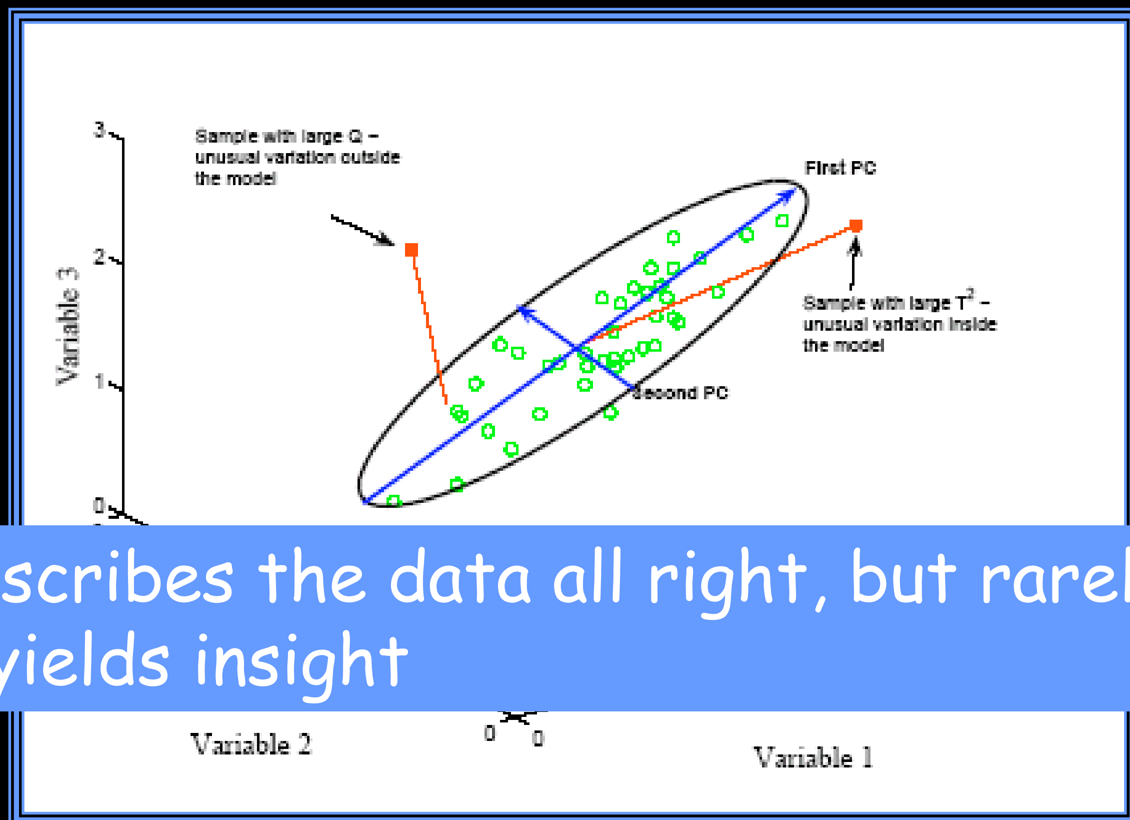


Simplification of the Data Cube Prior to Computing the LBC



Method I: Mining Hyperspectral Datasets in N-Dimensional Compositional Space

Traditional Factor Analysis: Classical Principal Components

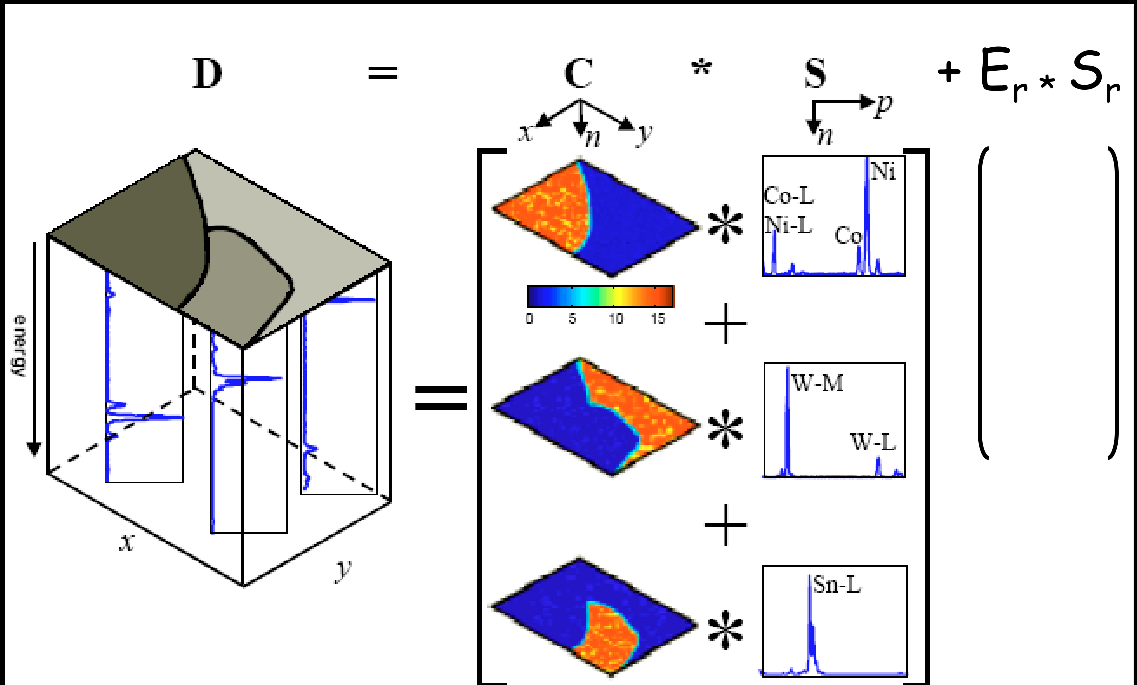


Describes the data all right, but rarely yields insight

The Alternate Approach of Keenan & Kotula

Spatial or Spectral Simplicity Solutions

An infinite # solutions possible (rotational ambiguity) in N dimensions. We seek only those that give us insight.



after *Kotula et al. (2002)

Spectral simplicity*

High spectral contrast solution.

Spatial simplicity

High spatial contrast solution.

Spatial Simplicity (Keenan and Kotula, unpublished)

- $D = CS^T$ (Goal: Factor raw data into C and S…linear model)
  - D is an *m*-pixel × *n*-channel raw spectral-data matrix
  - S is an *n* × *p* matrix containing the *p* pure-component spectra shapes
  - C is an *m* × *p* matrix containing their spatial distributions/abundances
- Data is scaled to account for non-uniform (Poisson) noise*

  Allows for noise on signals of all levels to be accounted for

- PCA is performed on the scaled data such the the spatial components are orthonormal

  Instead of classical PCA (max variance in spectral domain), maximize variance in the spatial domain.

- Rotate the spatial components to maximize their mutual simplicity with the VARIMAX procedure

  Rotate PCA_{sp} solution in N dimensions to obtain maximum # zeros in one dimension of the matrix.

*M.R. Keenan and P.G. Kotula, *Surf. Int. Anal.* 36 (2004) 203-212.

Spatial Simplicity (contin.)

- Apply the inverse rotation to the spectral components

  Necessary to maintain the product [C x S]

  Note: The VARIMAX solution fits the data as well as the PCA solution, however yields more physical insight into the specimen by virtue of the assumption that simplicity is desirable and defined as maximized contrast.

- Perform non-negativity-constrained *classical* least squares (CLS) on the data, making spatial components all positive

  D (known) = C (constrained) x S
  Hence, set all neg. values for C to 0 and solve for S accordingly

- Inversely scale the components for Poisson noise

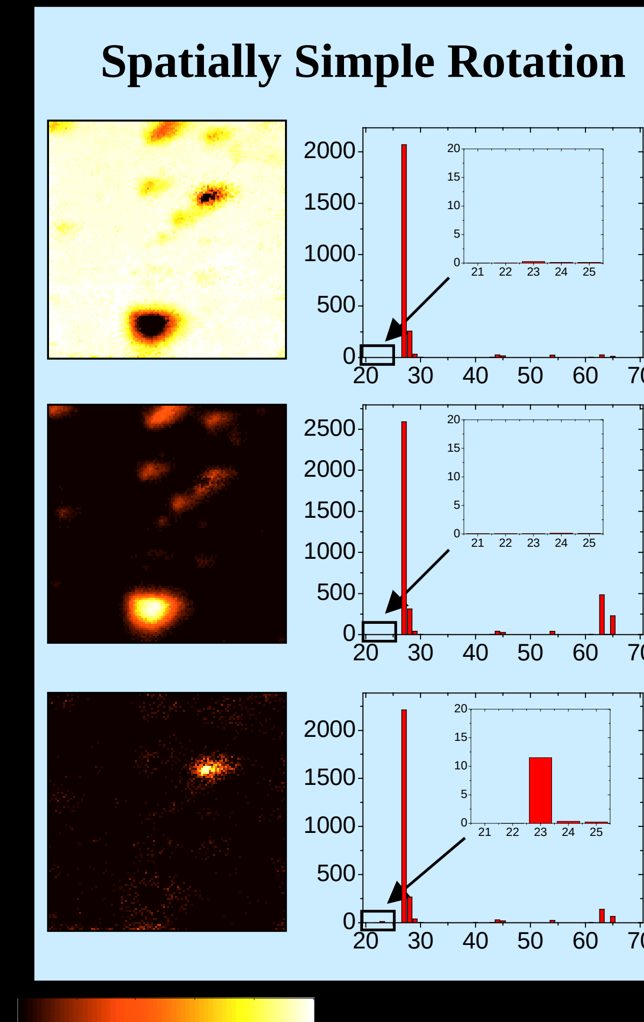
  Restores normalized count space back to real count space

Rotated PCA Delivers a Spatially Simple Analysis

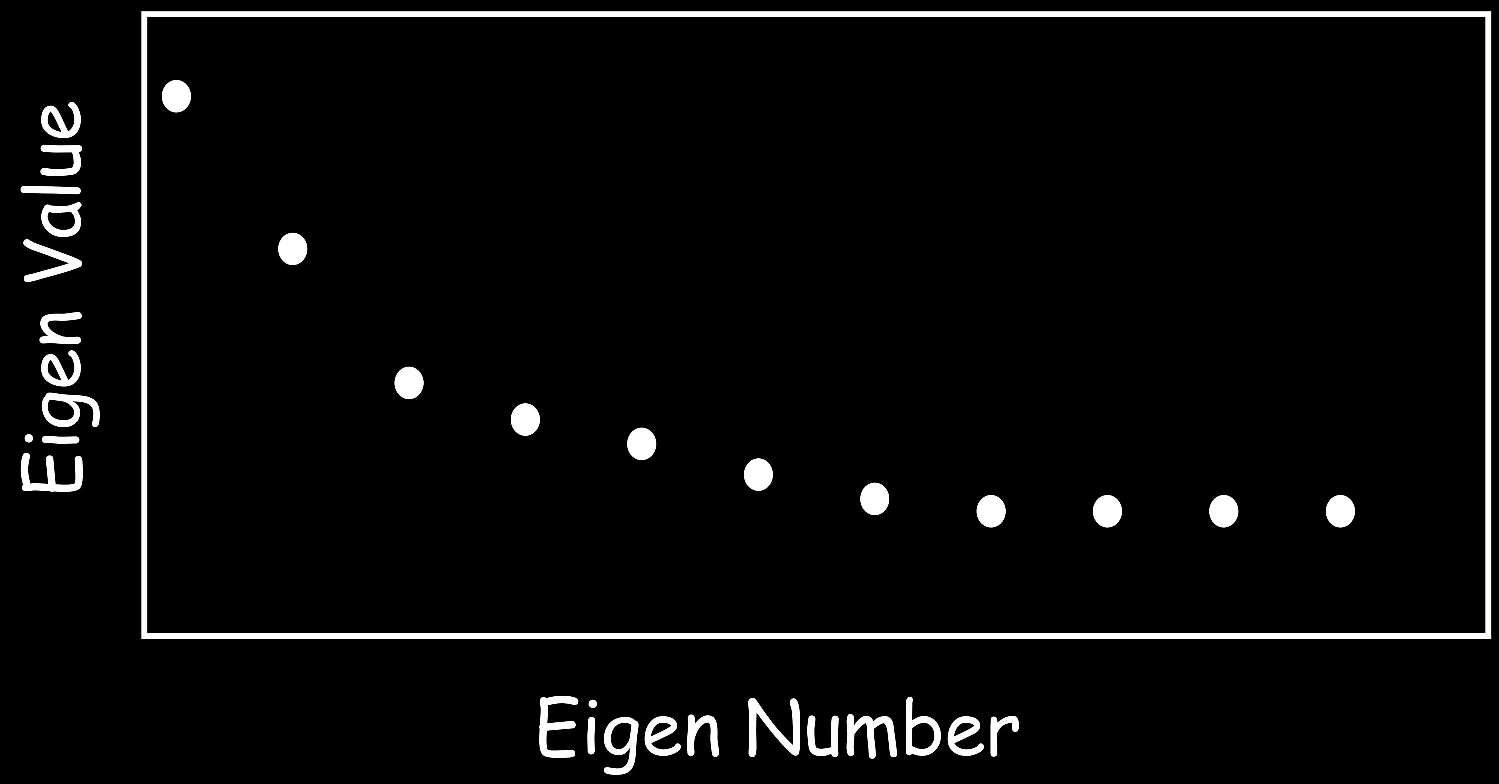
Rotated PCA

- Based on a Varimax rotation of PCA images
- Relaxes orthogonality of one dimension
  - Separates data based on simplifying images or spectra
  - Works well with data containing large spectral backgrounds (AES, XPS)
- Minor spectral features can be hard to find.

Q. Where is the spatial contrast in the image, and what is it?

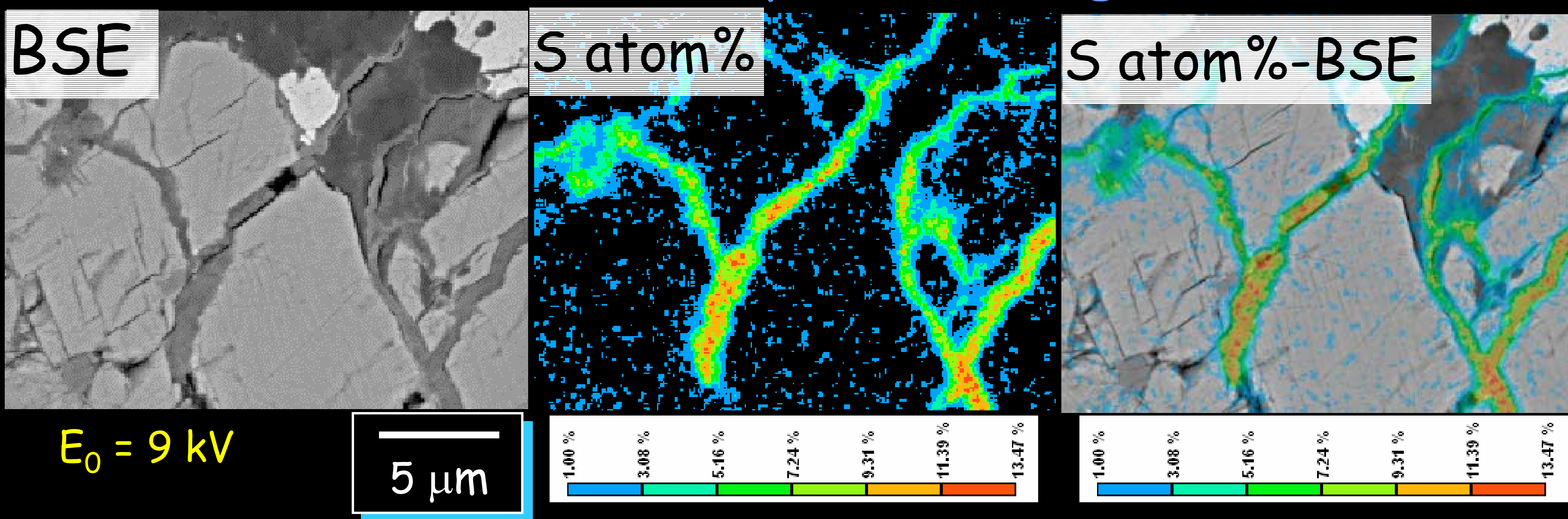


How Many MVS Components will Describe My Data?



Keenan-Kotula assume no more than 25 components

Method II: Elemental Maps & Quantified Spectral Images

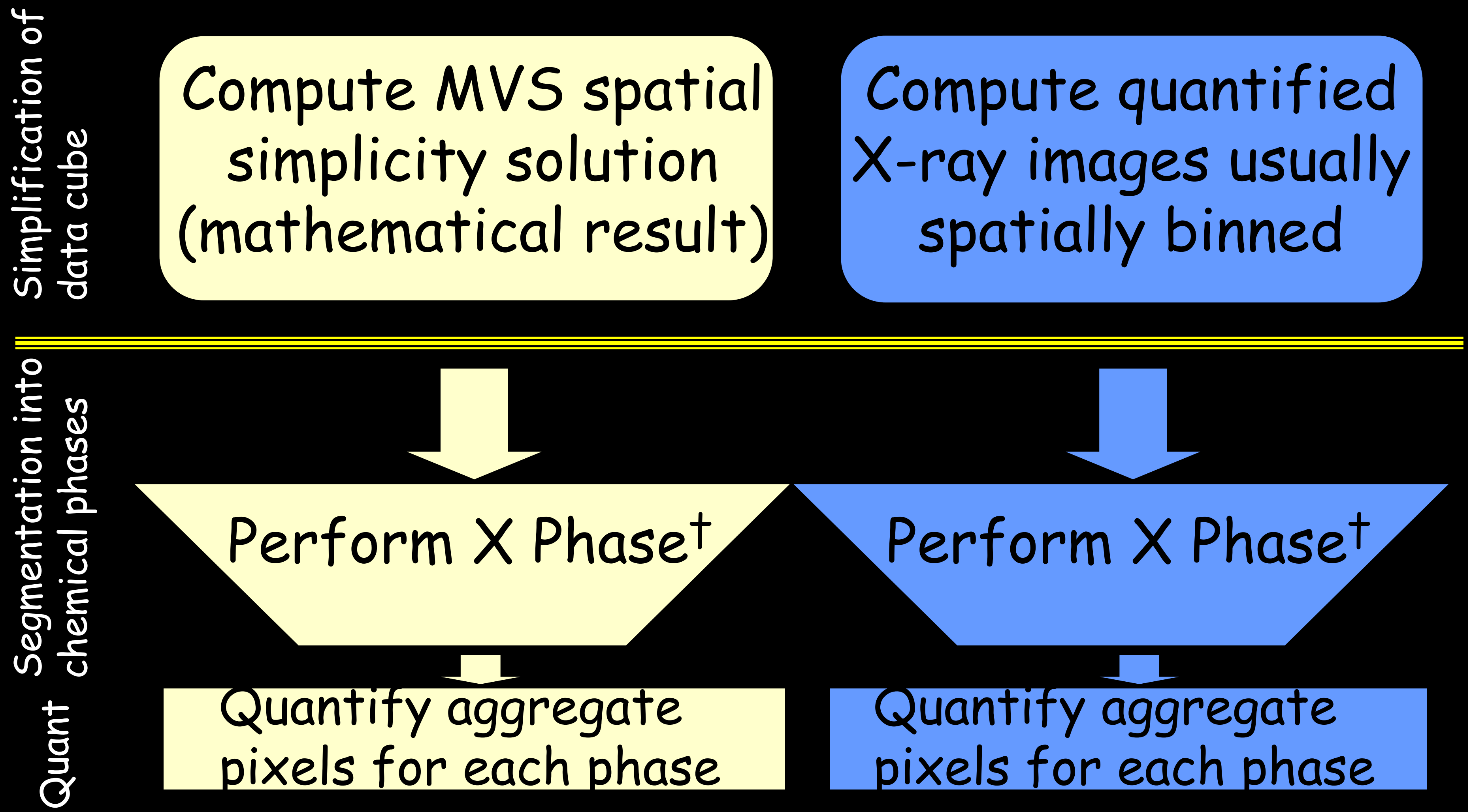


Spatial binning
enhanced spectral intensity

	13	

→ Background subtraction → Peak deconvolution → Matrix correction → Threshold and superimpose on BSE

Paths to Phase Analysis



†X Phase output: Binary masks showing location of phases and associated spectra (real data)

Phase Segmentation: X Phase

Input: Compass (Spectral/Spatial simplicity) results,
or, X-ray images (raw cts. or quantified)

- Define min area for a phase (default = 1.5%)
- Perform histogram stretch on each image
- Multiply each image by the others, and stretch resulting 16 bit image
- Threshold image and binarize
- If mask is >1.5% of tot. area, declare it a phase

More Phase Segmentation X Phase

• If overlap occurs then combine overlap into the first detected phase for that area

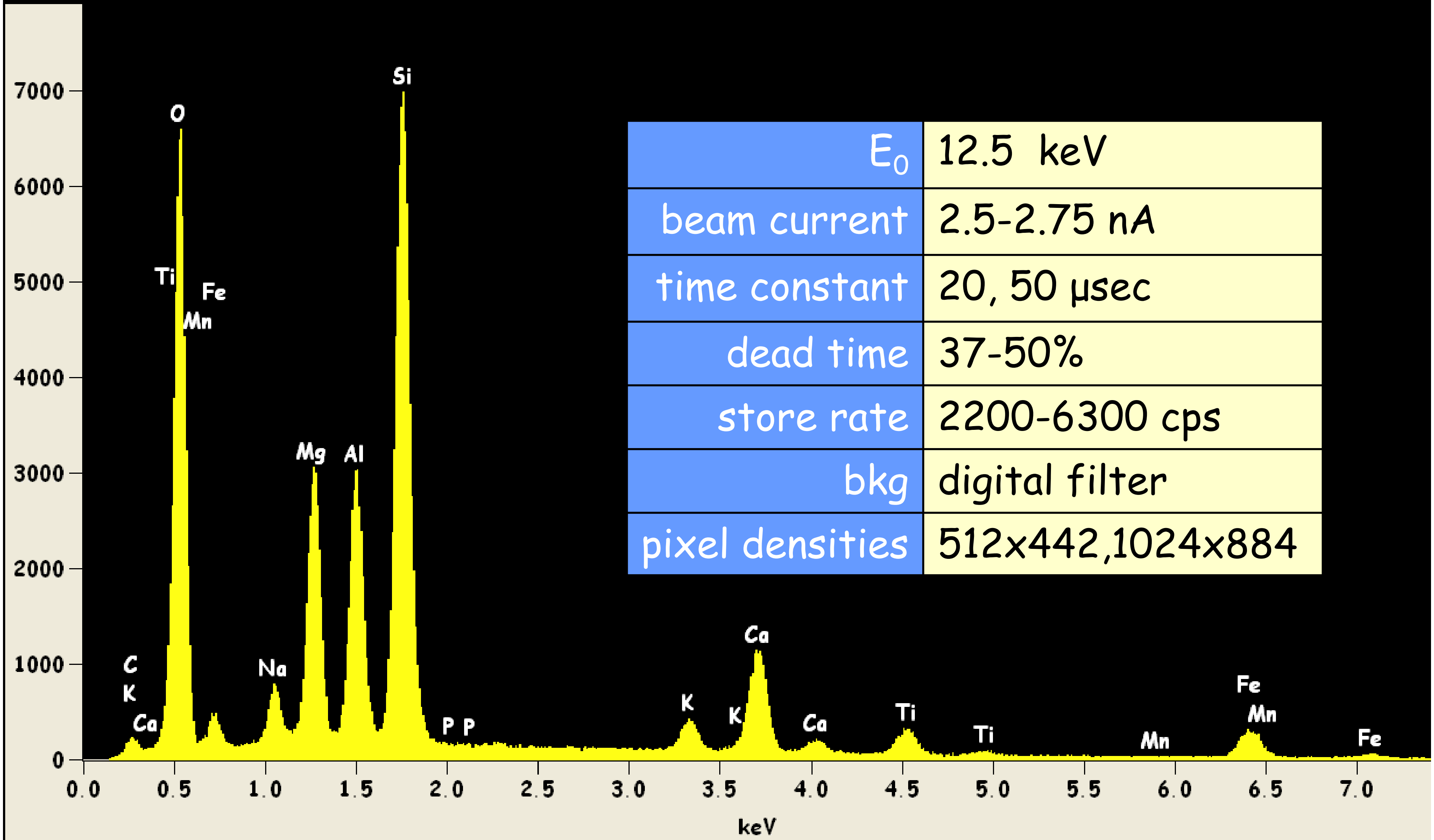
• From each binary mask extract a spectrum from the datacube

Now you have a image (showing the location) and spectrum (giving the composition) pair for each chemical compound, or phase.

• Compare phase spectra to a library of stored phases using conventional least squares fit and give it a name

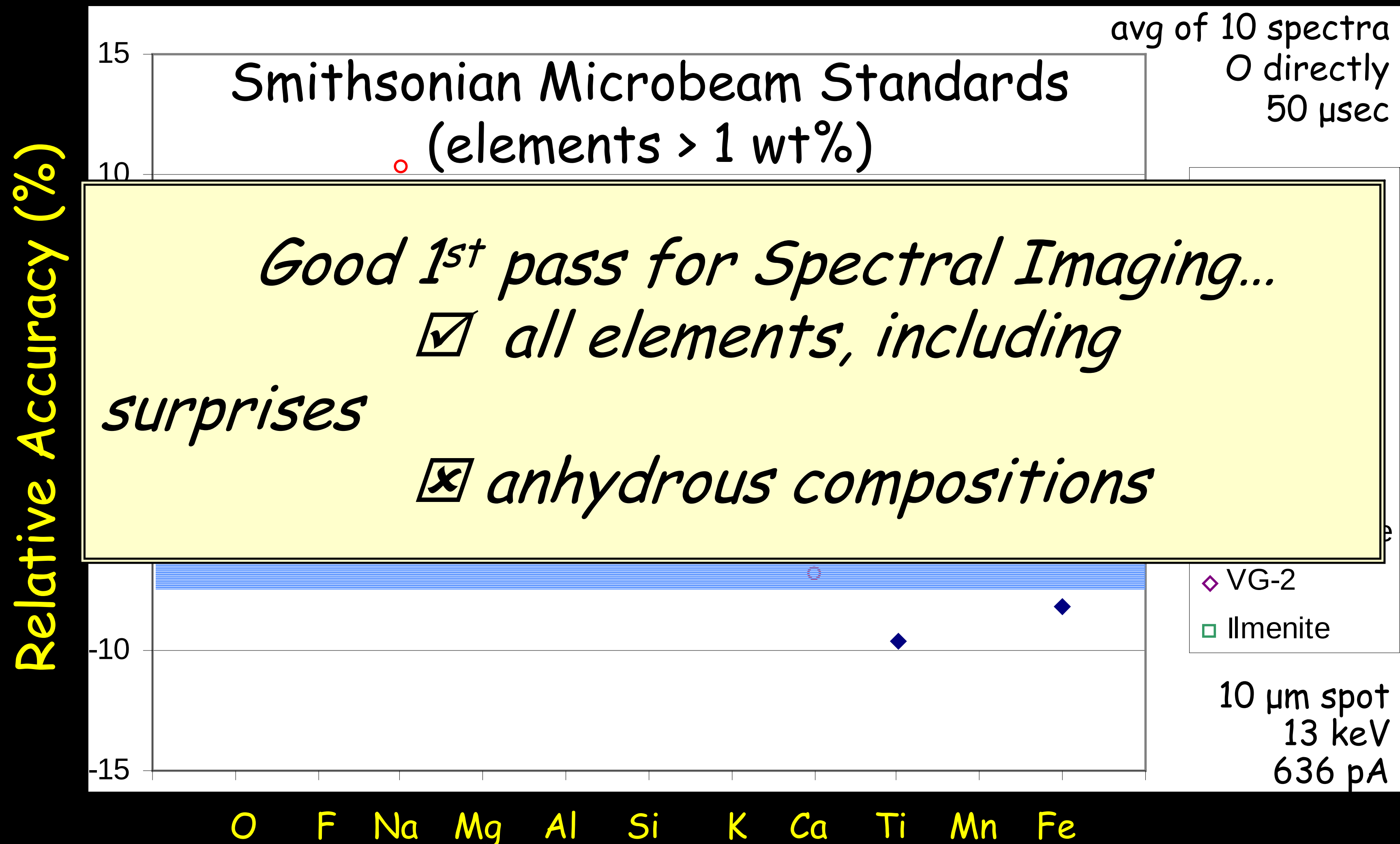
Note: Smithsonian mineral library will be available soon-

Quantification: Instrumental Conditions



E_0	12.5 keV
beam current	2.5-2.75 nA
time constant	20, 50 µsec
dead time	37-50%
store rate	2200-6300 cps
bkg	digital filter
pixel densities	512x442,1024x884

Quantification: "Standardless" EDS:
Useful or Worthless?



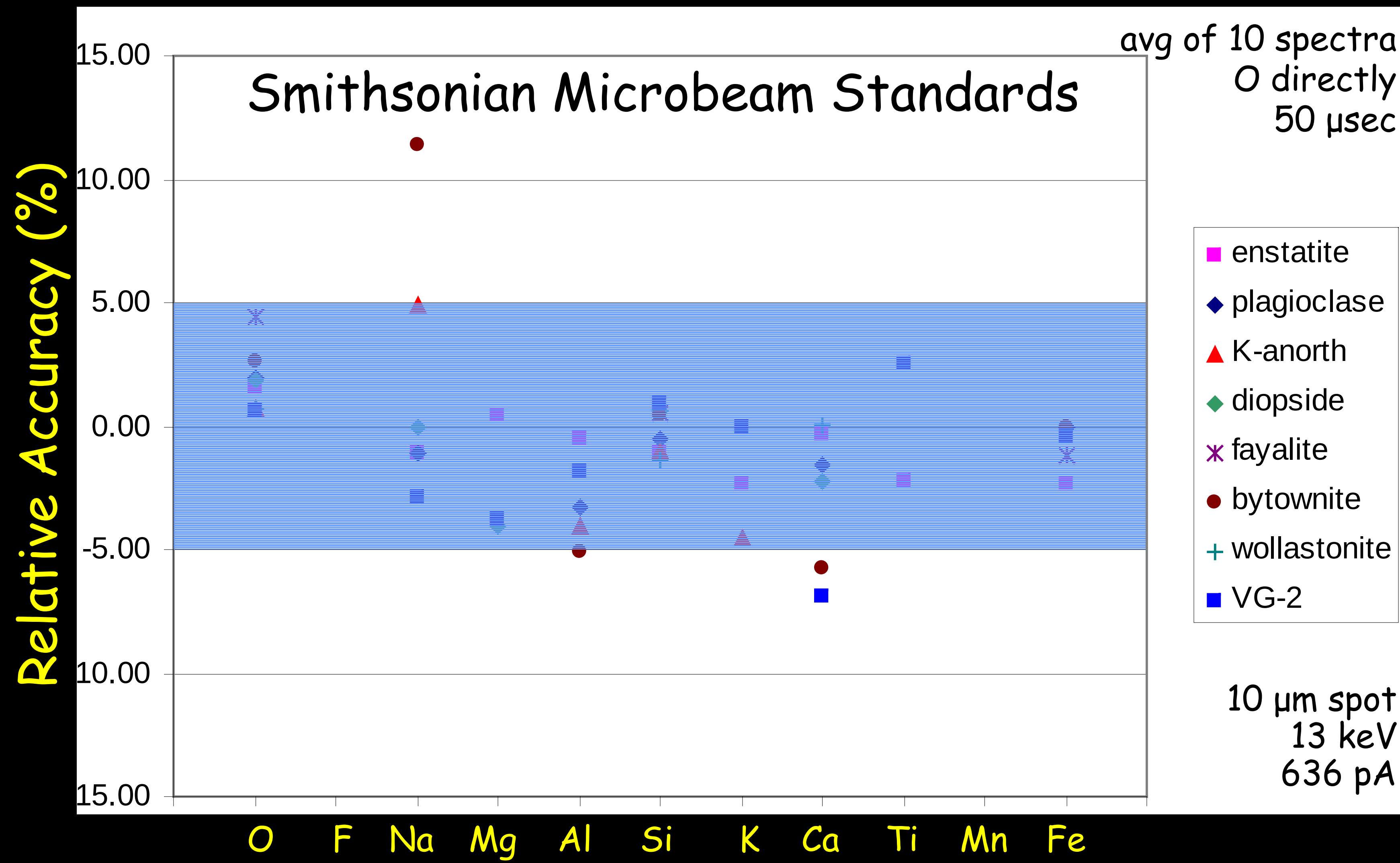
Good 1st pass for Spectral Imaging…

☑ all elements, including surprises

☒ anhydrous compositions

Quantification: Standards-based EDS:

K-hornblende as primary std



Parícutin Volcano

Mineralogical-Geological Glossary

Mineral name	End-member formulae
plagioclase	$NaAlSi_3O_8$ – $CaAl_2Si_2O_8$
olivine	Mg_2SiO_4 - Fe_2SiO_4
orthopyroxene	$MgSiO_3$ – $FeSiO_3$

term	definition
scoria	Rapidly cooled vesicular volcanic rock, darker than pumice.
ash	Particles of crystals and glass ejected into the atmosphere $<$ 2 mm in diameter.

The Extraordinary Story of Parícutin Volcano

- In Feb. 1943 the volcano was born in the presence of several Tarascan indians, erupted for 9 years
- RARE event!
- Lava flows covered 25 km^2 burying 2 villages, killing 4500 cattle, 550 horses, and forcing the evacuation of several thousand people.
- Smithsonian has a special connection to the eruption as William Foshag, curator of mineralogy was in Mexico studying ore deposits when the birth occurred and documented the first 2.5 years of the volcano's life
- Foshag was an avid photographer and took lots of 16 mm footage

Play video with
Overly Dramatic Soundtrack: 1943 Newsreel

Play video of man rolling a recently solidified rock off lava flow…

used to cook dinner by Smithsonian scientist

The Specimens

Scoria

May 1943

108135

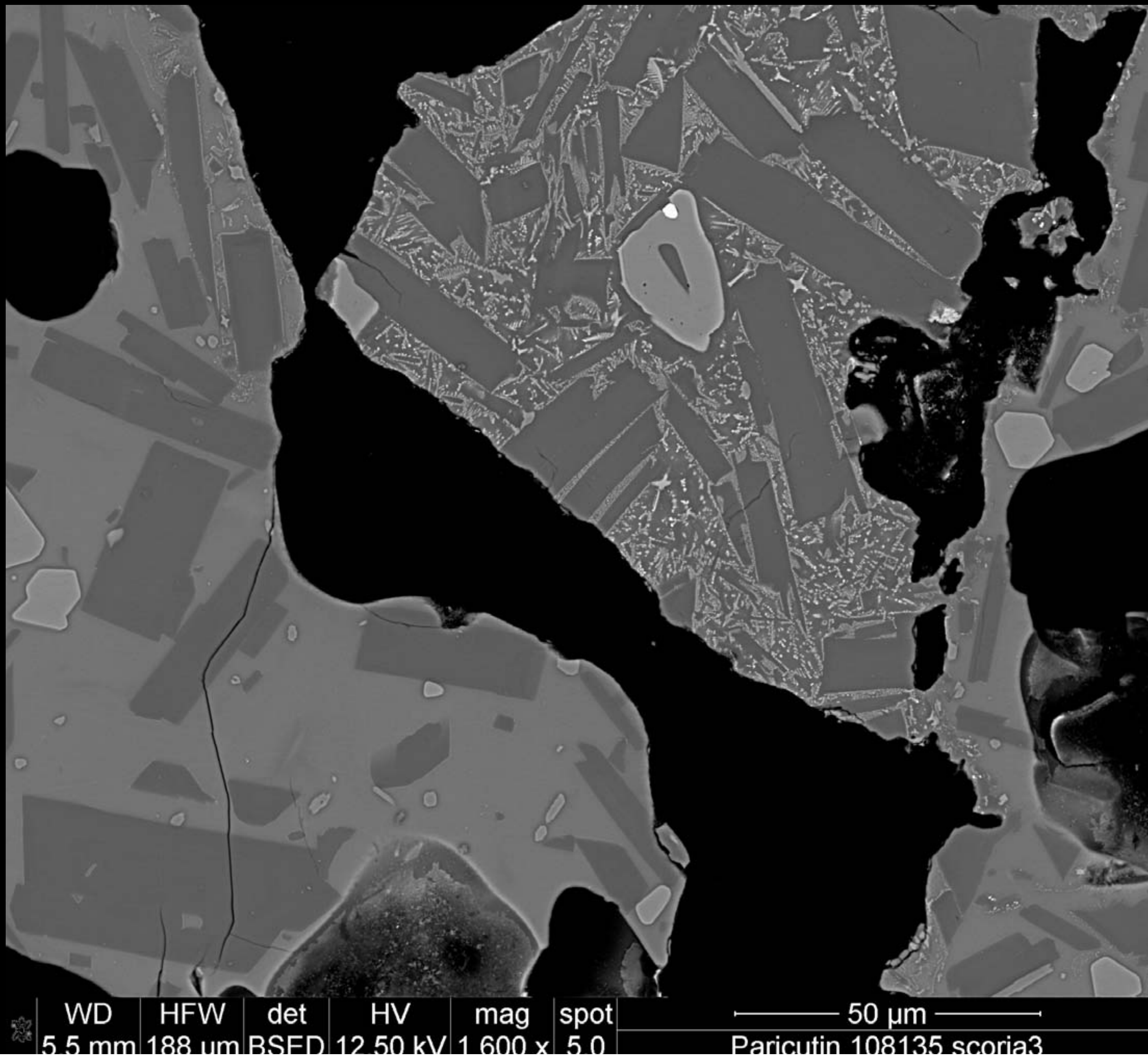
Ash

March 1948

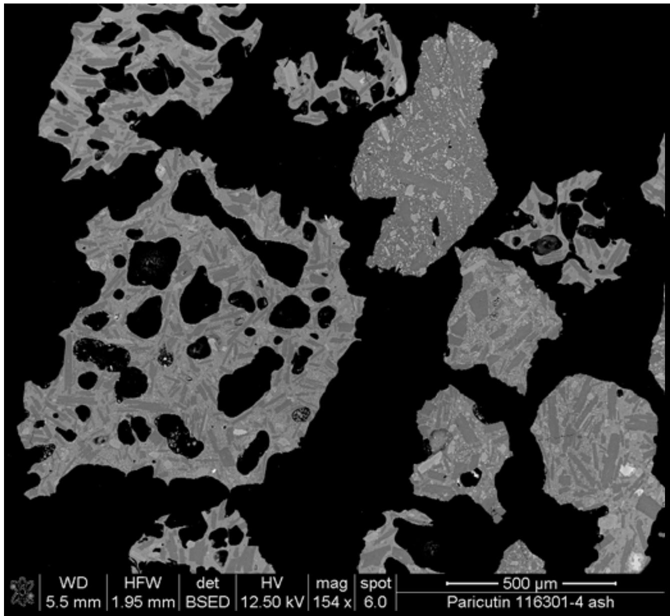
116301-4

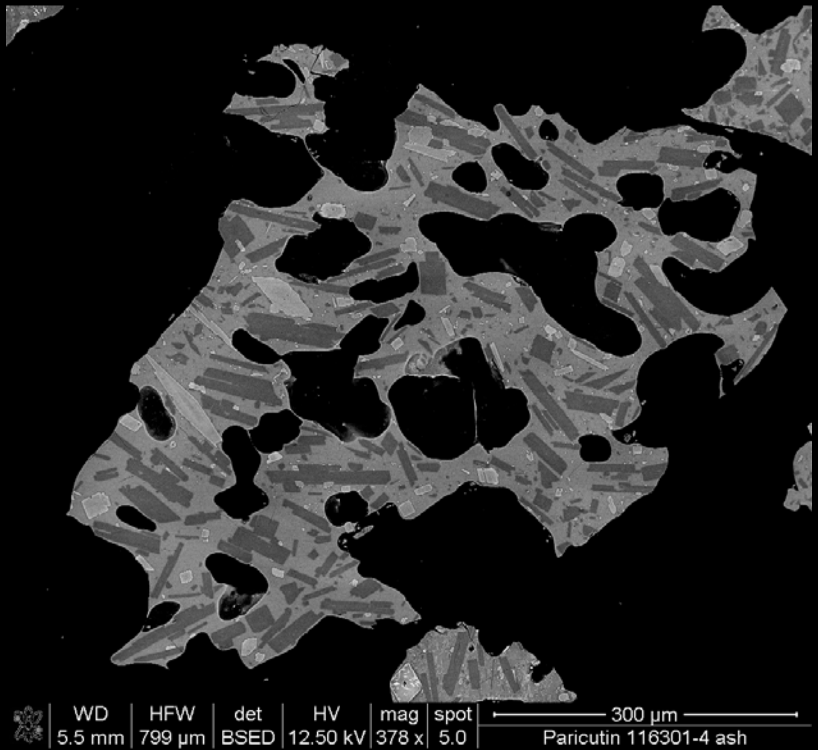
Note nearly bi-modal distribution of black and brown particles…magma mixing? Subtle compositional differences?

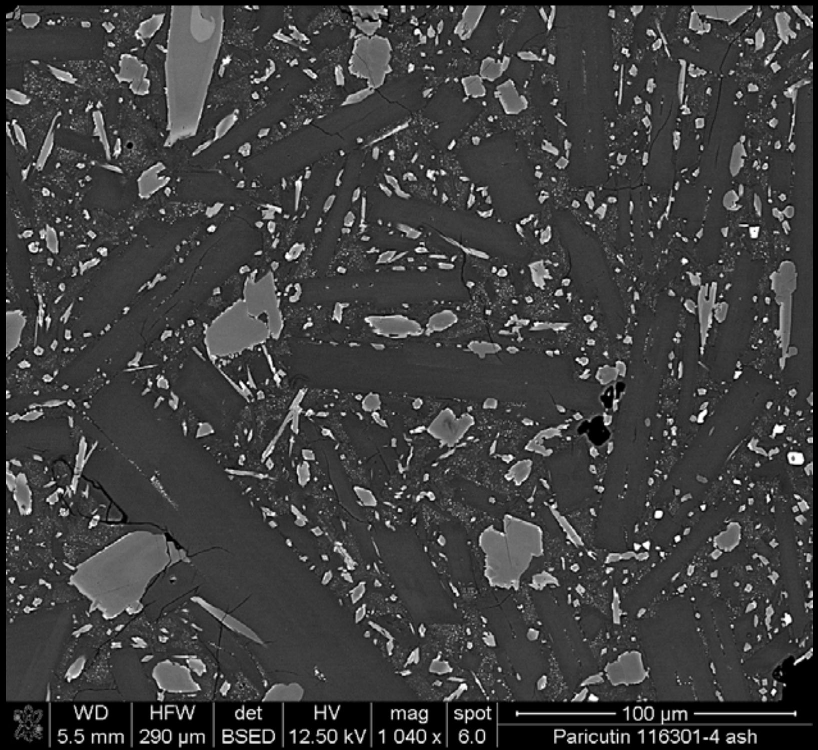
Scoriae Particles



Ash Particles

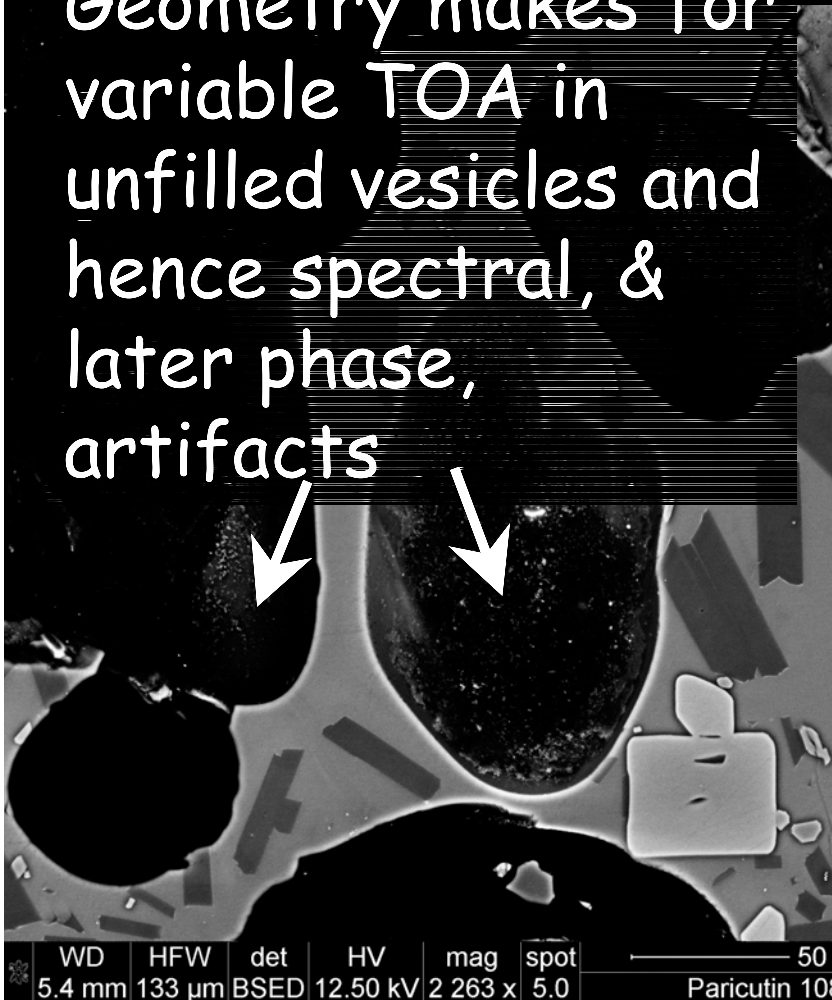




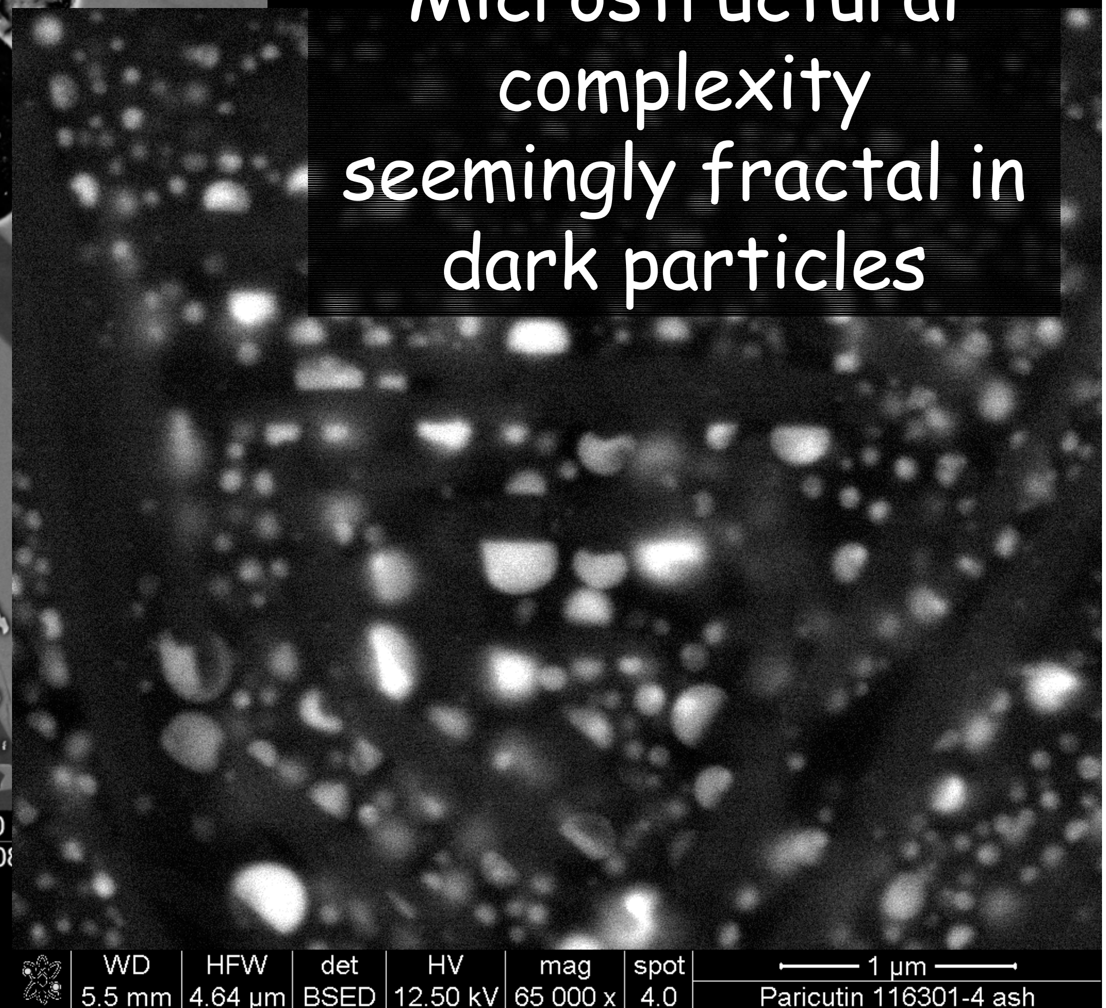


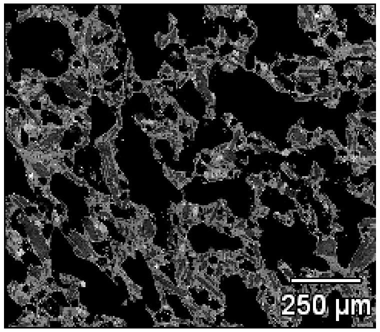
Complicating factors

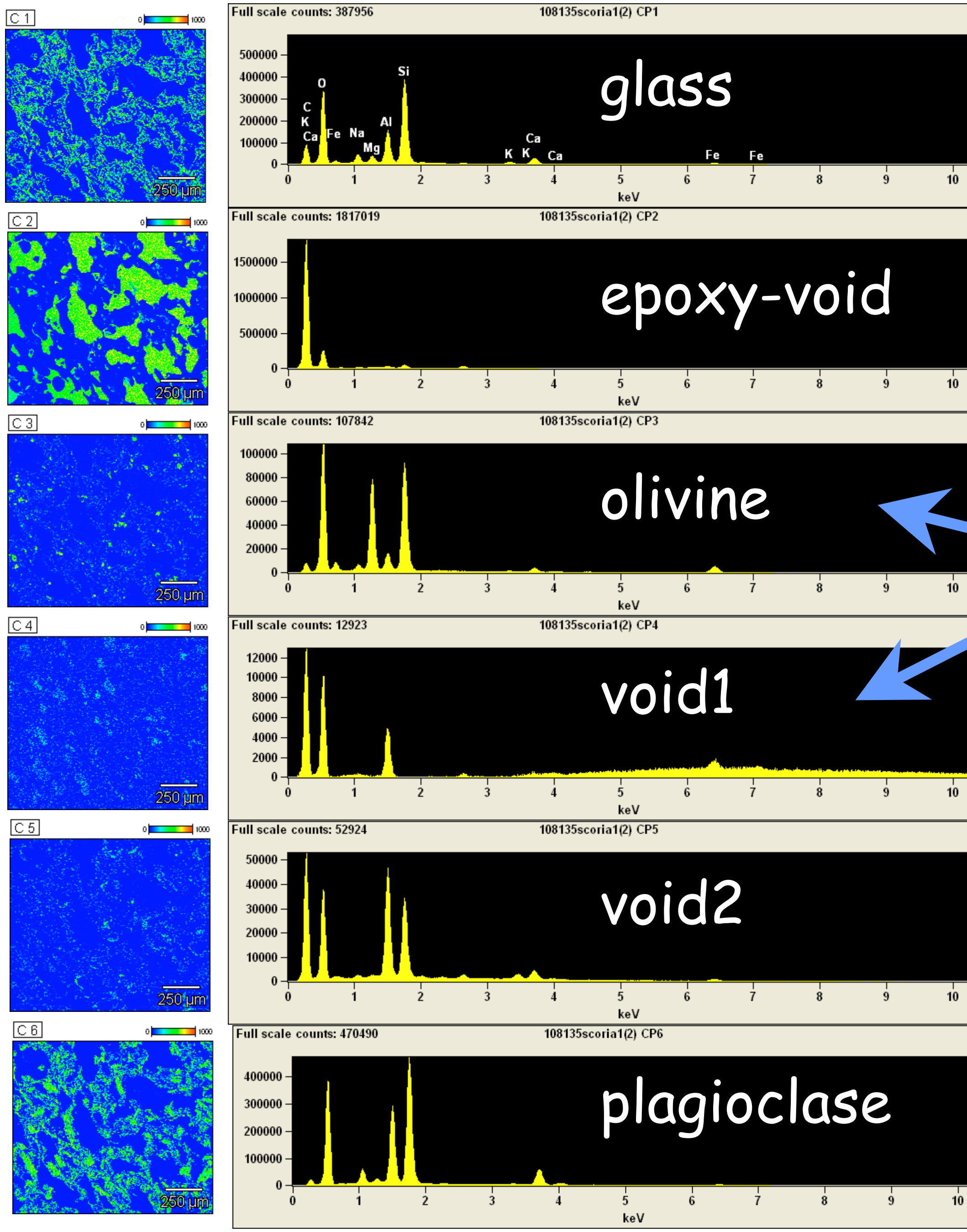
Geometry makes for variable TOA in unfilled vesicles and hence spectral, & later phase, artifacts



Microstructural complexity seemingly fractal in dark particles







Compass Results:

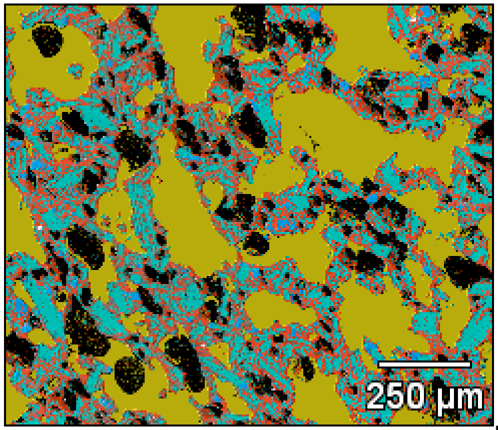
Scoria Pure Components

resemble real spectra but math solution

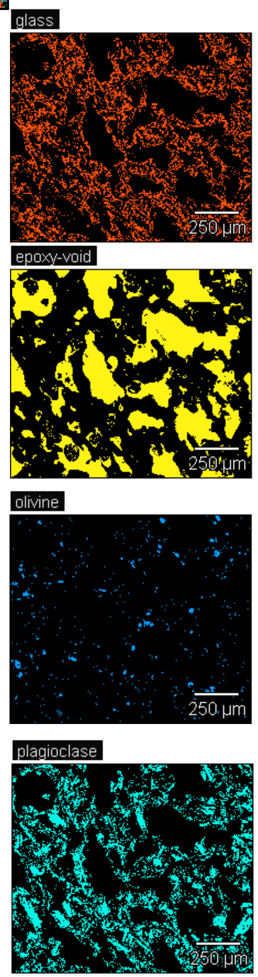
Note: Component images are 16 bits deep

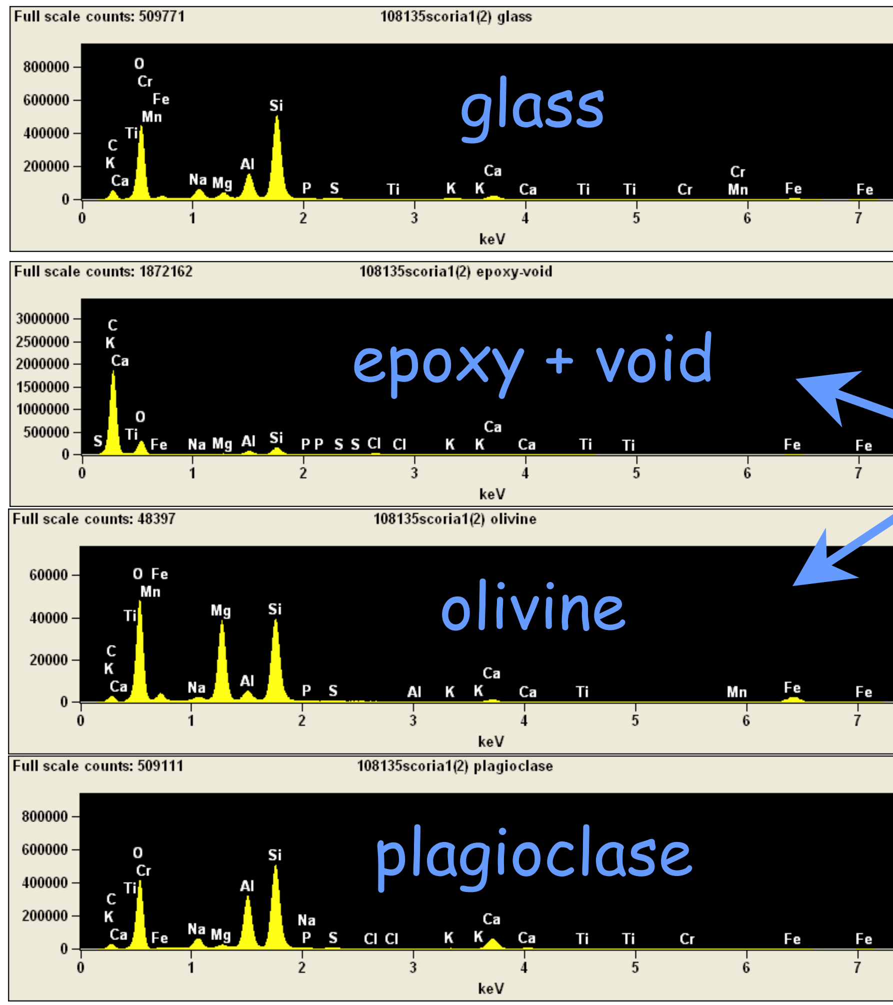
X Phase Results:

Scoria



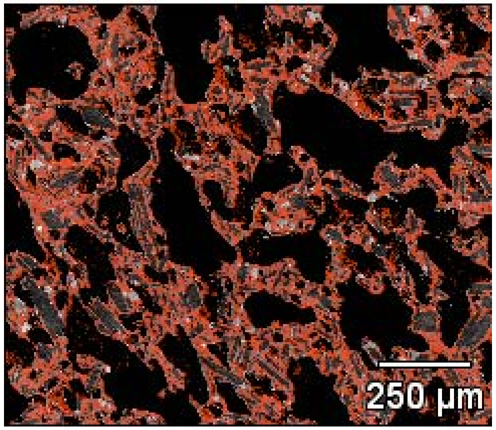
Composite phase overlay onto BSE





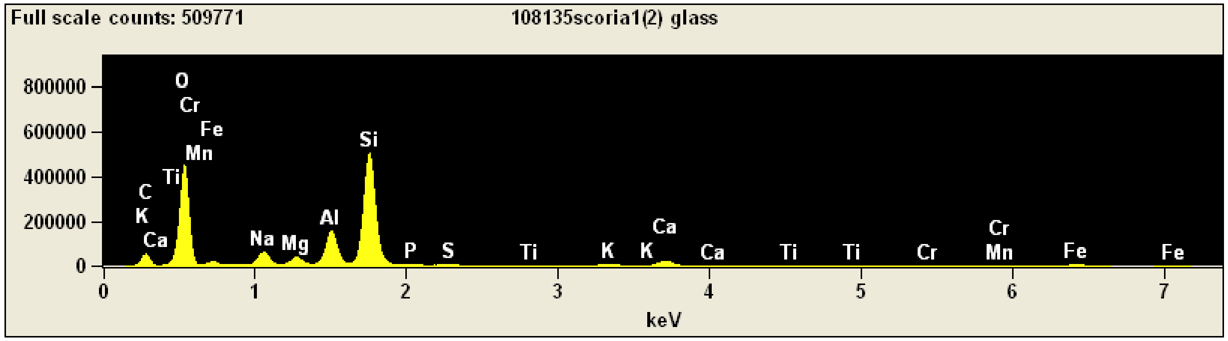
genuine data

These images are binary masks, eg the phase is either there or not



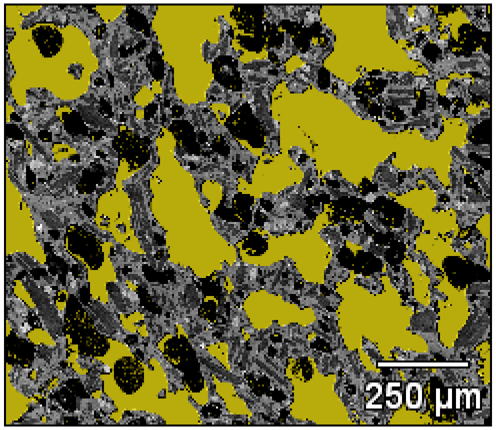
Area = 22.7%

Glass



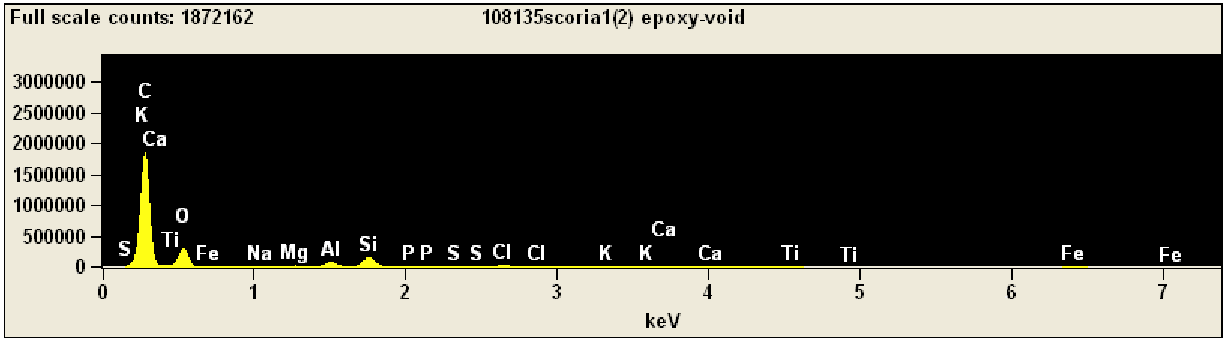
Element Line	Weight %	Atom %	Compnd %
O K	46.4S	62.4	---
Na K	3.3	3.1	4.4
Mg K	1.7	1.5	2.9
Al K	7.1	5.7	13.5
Si K	27.4	20.9	58.6
P K	0.4	0.3	0.9
S K	0.3	0.2	0.8
K K	1.2	0.6	1.4
Ca K	3.2	1.7	4.5
Ti K	1.1	0.5	1.9
Cr K	0.1	0.0	0.1
Mn K	0.2	0.1	0.2
Fe K	7.5	2.9	10.8
Total	100.0	100.0	100.0

Element Line	Weight %	Atom %
O K	46.8	62.7
Na K	3.3	3.1
Mg K	1.7	1.5
Al K	7.1	5.6
Si K	27.2	20.8
P K	0.4	0.3
S K	0.3	0.2
K K	1.2	0.6
Ca K	3.2	1.7
Ti K	1.1	0.5
Cr K	0.1	0.0
Mn K	0.2	0.1
Fe K	7.5	2.9
Total	100.0	100.0

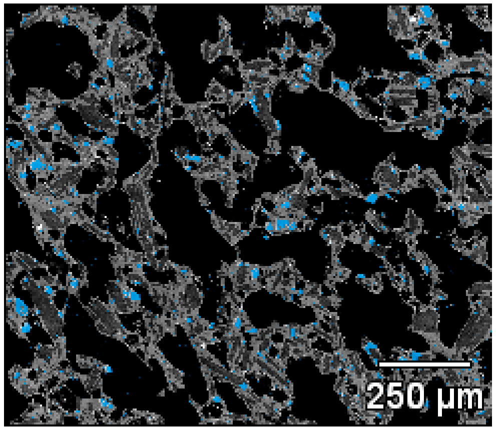


Area = 50.9%

Epoxy + Void

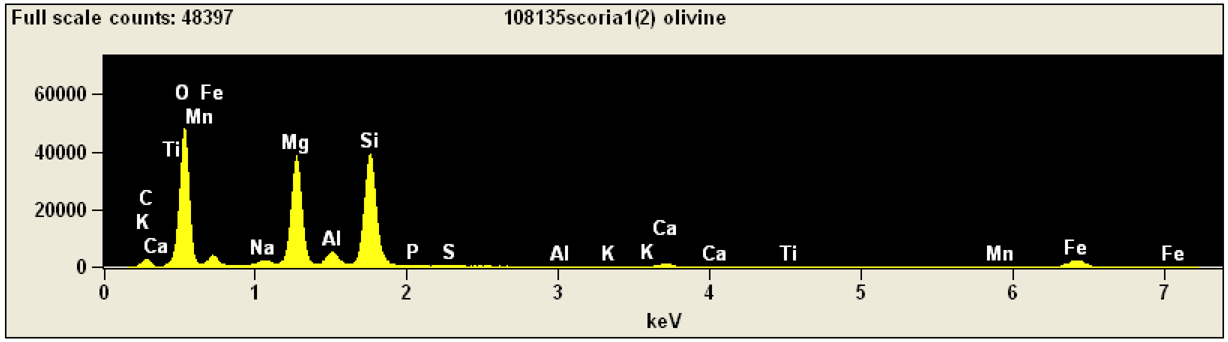


Not a POI



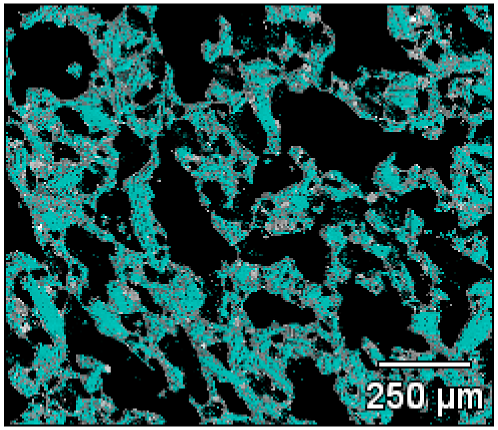
Area = 2.4%

Olivine



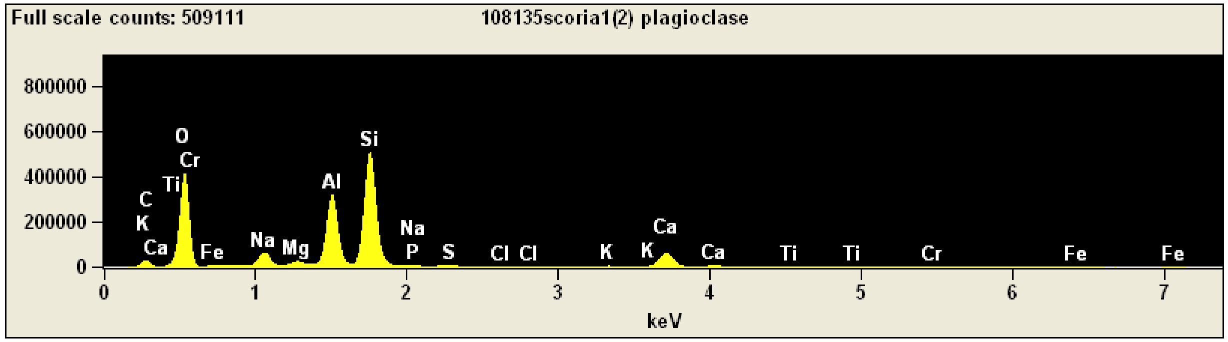
Element Line	Weight %	Atom %	Compnd %
O K	43.2S	59.6	---
Na K	0.8	0.8	1.1
Mg K	17.1	15.5	28.4
Al K	2.0	1.6	3.7
Si K	19.5	15.3	41.8
P K	0.1	0.1	0.3
S K	0.1	0.1	0.4
K K	0.2	0.1	0.3
Ca K	1.0	0.6	1.4
Ti K	0.3	0.1	0.5
Mn K	0.4	0.2	0.5
Fe K	15.2	6.0	21.7
Total	100.0	100.0	100.0

Element Line	Weight %	Atom %
O K	40.4	56.7
Na K	0.9	0.8
Mg K	17.9	16.5
Al K	2.1	1.7
Si K	20.6	16.5
P K	0.1	0.1
S K	0.1	0.1
K K	0.2	0.1
Ca K	1.1	0.6
Ti K	0.3	0.1
Mn K	0.4	0.2
Fe K	15.9	6.4
Total	100.0	100.0



Plagioclase

Area = 24.0%



Element Line	Weight %	Atom %	Compnd %
O K	46.7S	61.7	---
Na K	3.0	2.8	4.1
Mg K	0.8	0.7	1.3
Al K	13.2	10.3	24.9
Si K	24.8	18.7	53.1
P K	0.2	0.1	0.5
S K	0.2	0.2	0.6
Cl K	0.0	0.0	0.0
K K	0.4	0.2	0.4
Ca K	7.9	4.2	11.1
Ti K	0.3	0.1	0.5
Cr K	0.1	0.0	0.1
Fe K	2.5	0.9	3.5
Total	100.0	100.0	100.0

Element Line	Weight %	Atom %
O K	44.7	59.8
Na K	3.1	2.9
Mg K	0.8	0.7
Al K	13.6	10.8
Si K	25.8	19.7
P K	0.2	0.2
S K	0.2	0.2
Cl K	0.0	0.0
K K	0.4	0.2
Ca K	8.2	4.4
Ti K	0.3	0.1
Cr K	0.1	0.0
Fe K	2.6	1.0
Total	100.0	100.0