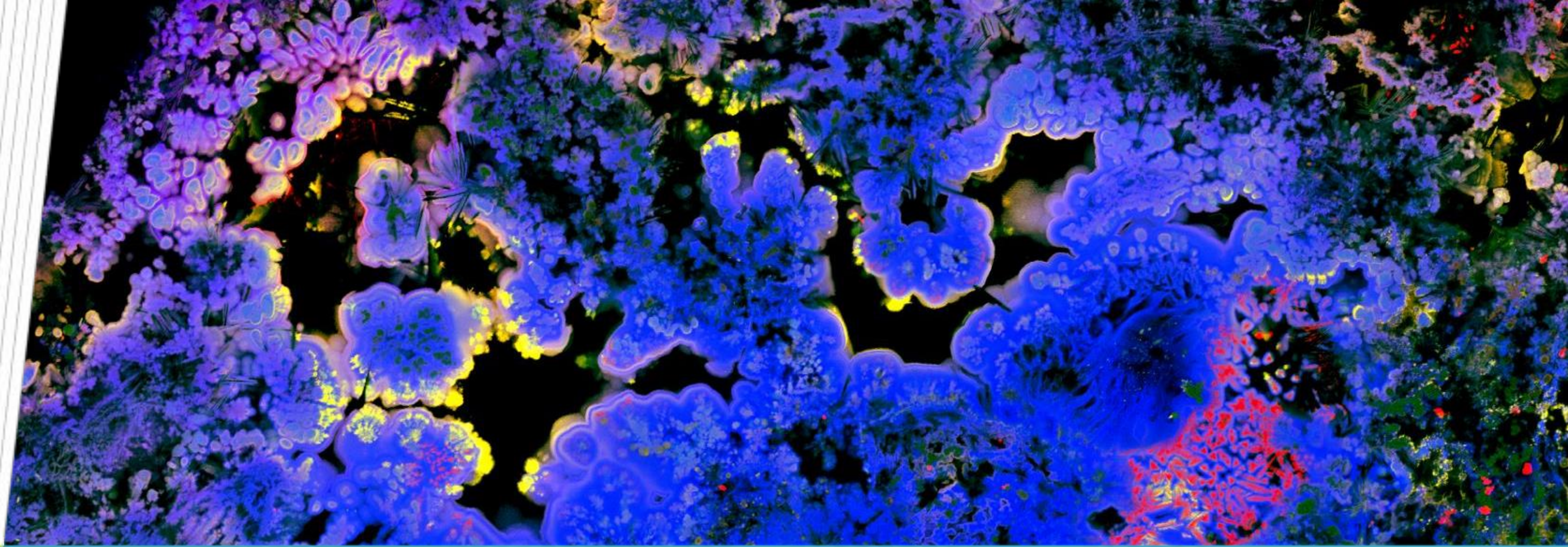
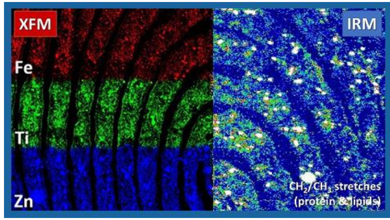


XRF analysis and imaging at XFM using GeoPIXE

Chris Ryan
CSIRO Mineral Resources
May 20, 2021



Virtual XFM & IRM Microscopy Workshop at the Australian Synchrotron

XFM Quantification in GeoPIXE

General approach

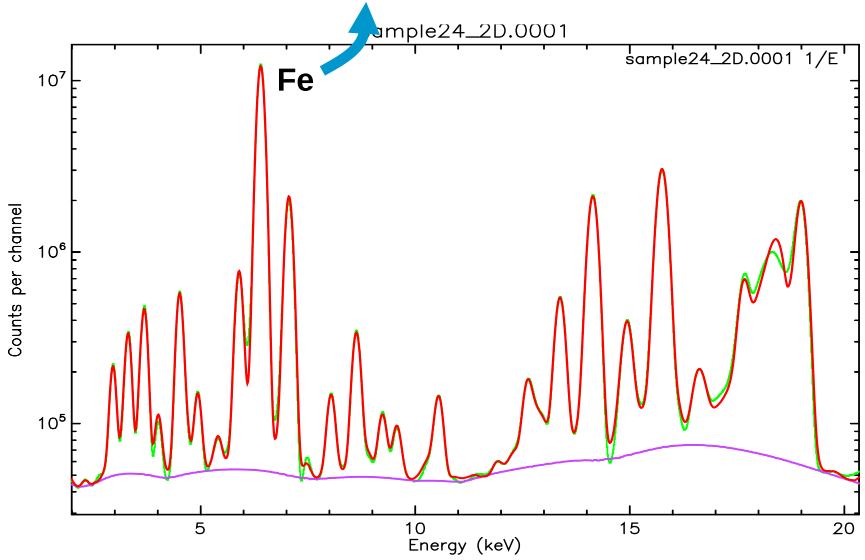
- **Standardless, fundamental parameters**
  - X-ray Yields calculated for a model sample
- **Need to know something about sample**
  - Thickness, main components
  - Undetected light elements
- **Extend this to imaging**
  - Using the ***Dynamic Analysis*** method
- **Combine all detectors in an array**
  - Model yields for each detector separately

1. Model X-ray yields Y_i (per unit flux Q)

3. Determine concentration C_i

$$C_i = N_i / (Q^* Y_i)$$

2. Measure counts N_i



XFM Quantification in GeoPIXE

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  - X-ray Yields calculated for a model sample
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- **Extend this to imaging**
  - Using the ***Dynamic Analysis*** method
- **Combine all detectors in an array**
  - Model yields for each detector separately

"Angular diversity" of a large array

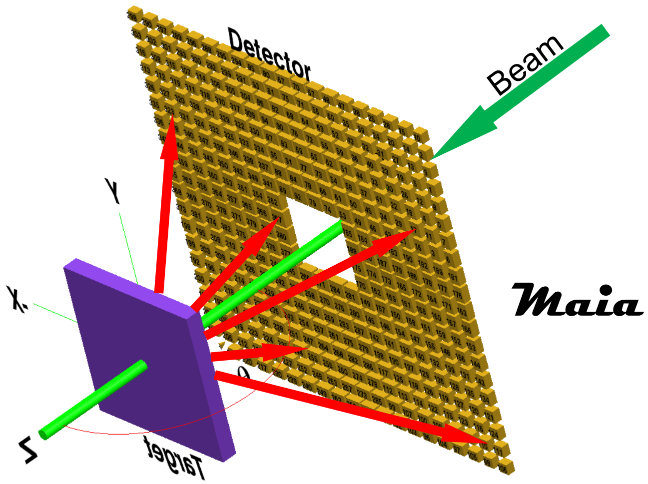
- Take-off angles to sample normal γ: 14° to 53°
  - Sensitivity to depth within sample
- Azimuthal angle (around beam) φ: 0 to 360°
  - Probe of internal structure in sample

1. Model X-ray yields Y_i (per unit flux Q)

3. Determine concentration C_i

$$C_i = N_i / (Q^*Y_i)$$

2. Measure counts N_i



Dynamic Analysis

“Event mode” spectral deconvolution

How to apply detailed spectrum fitting to imaging?

SXRF (PIXE) Spectrum - linear combination of element spectra.

Linear least squares fit of function f_i to data S_i
→ solve equations (for each j):

$$\underbrace{\sum_k \sum_i^{channels} w_i \left(\frac{\partial f_i}{\partial a_j}\right)\left(\frac{\partial f_i}{\partial a_k}\right)}_{\alpha_{jk}} a_k = \underbrace{\sum_i^{channels} w_i \left(\frac{\partial f_i}{\partial a_j}\right)}_{\beta_{ji}} S_i$$

for parameters a_k (X-ray peak areas …).

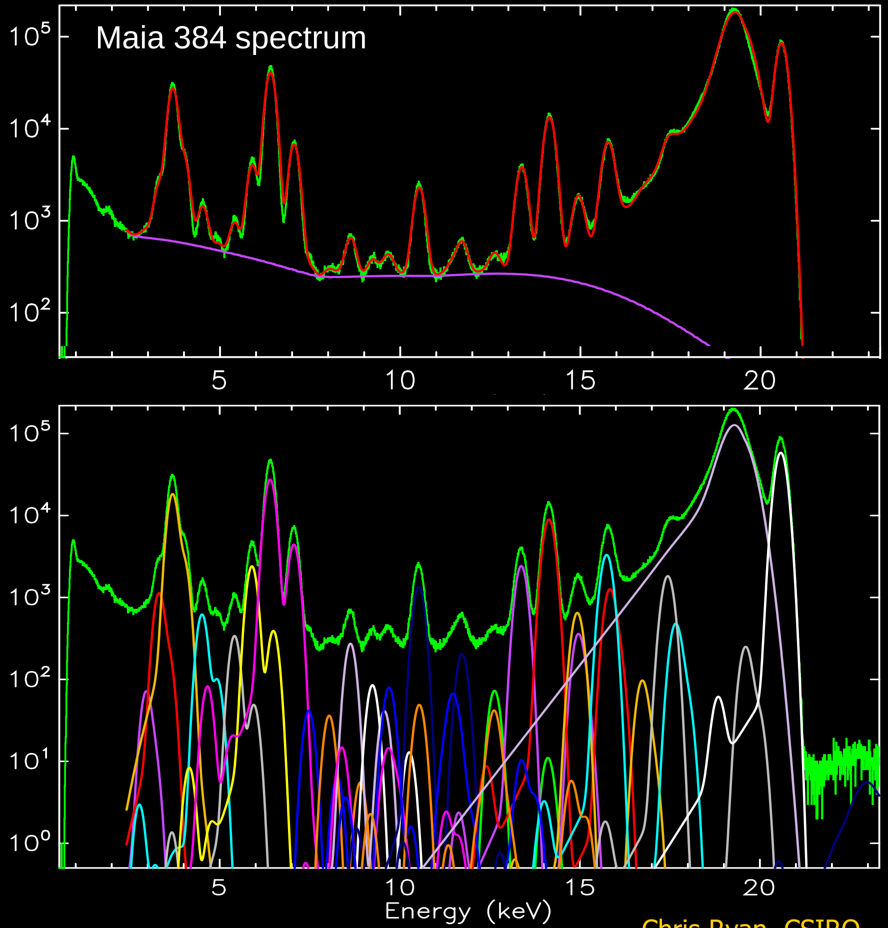
In matrix form:

$$\alpha \mathbf{a} = \beta \mathbf{S}$$

a matrix transform from spectrum vector $\mathbf{S}$ to peak area (and background) vector $\mathbf{a}$:

$$\mathbf{a} = (\alpha^{-1}\beta)\, \mathbf{S}$$

in terms of a matrix $\alpha^{-1}\beta$, which is built from '**shape**' functions.



Dynamic Analysis method

* Ryan, J. Imaging Sys. Tech. 11 (2000) 219
Ryan *et al.*, AIP Proc. 1221 (2010) 9

SXRF (PIXE) Spectrum - linear combination of element spectra.

Peak areas a_k are related to elemental concentration C_k by

$$a_k = (\Omega \varepsilon_k T_k Q).\ Y_k\ .\ C_k$$

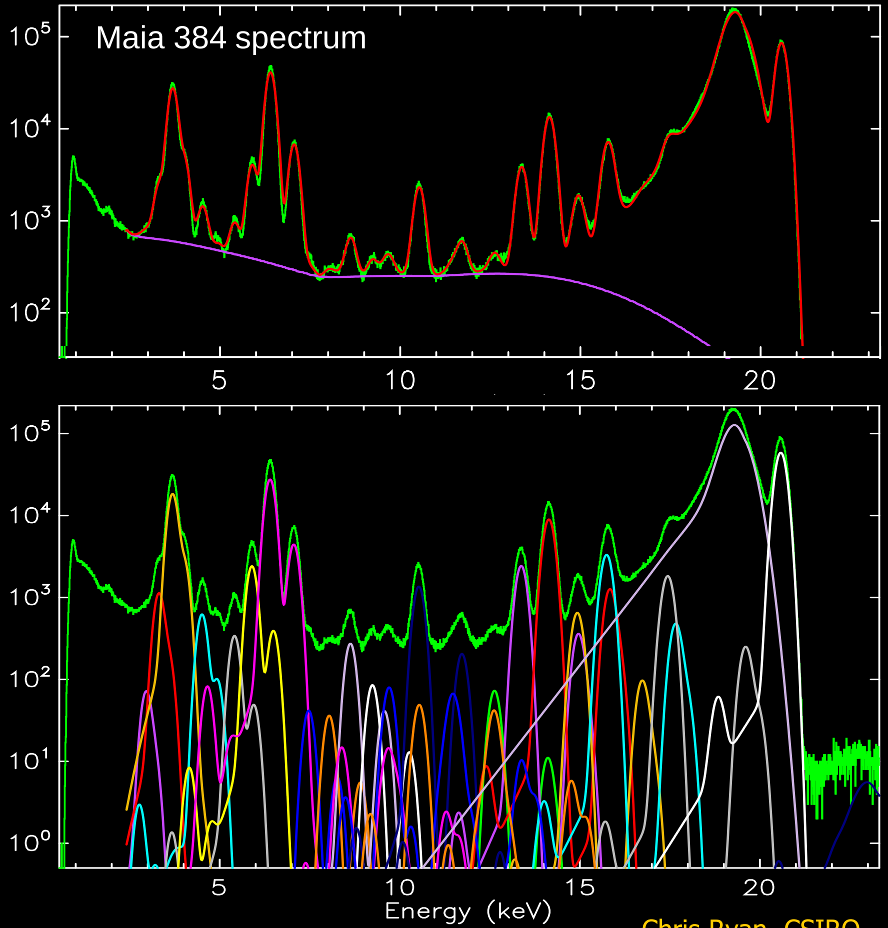
Ω	detector solid angle
ε_k	detector efficiency
T_k	filter transmission
Q	integrated beam charge/flux
Y_k	X-ray yields (**assume uniform composition**)

Therefore $\boldsymbol{a} = (\alpha^{-1}\beta)\boldsymbol{S}$ leads to a matrix transform from SXRF spectrum $\boldsymbol{S}$ to concentration vector $\boldsymbol{C}$:

$$\boldsymbol{C} = Q^{-1}\, \Gamma \boldsymbol{S}$$

where the matrix Γ is given by:

$$\Gamma_{ki} = (\Omega \varepsilon_k T_k Y_k)^{-1} \sum_j \alpha^{-1}_{kj}\, \beta_{ji}$$



Dynamic Analysis method

PIXE (SXRF) Spectrum - linear combination of element spectra.

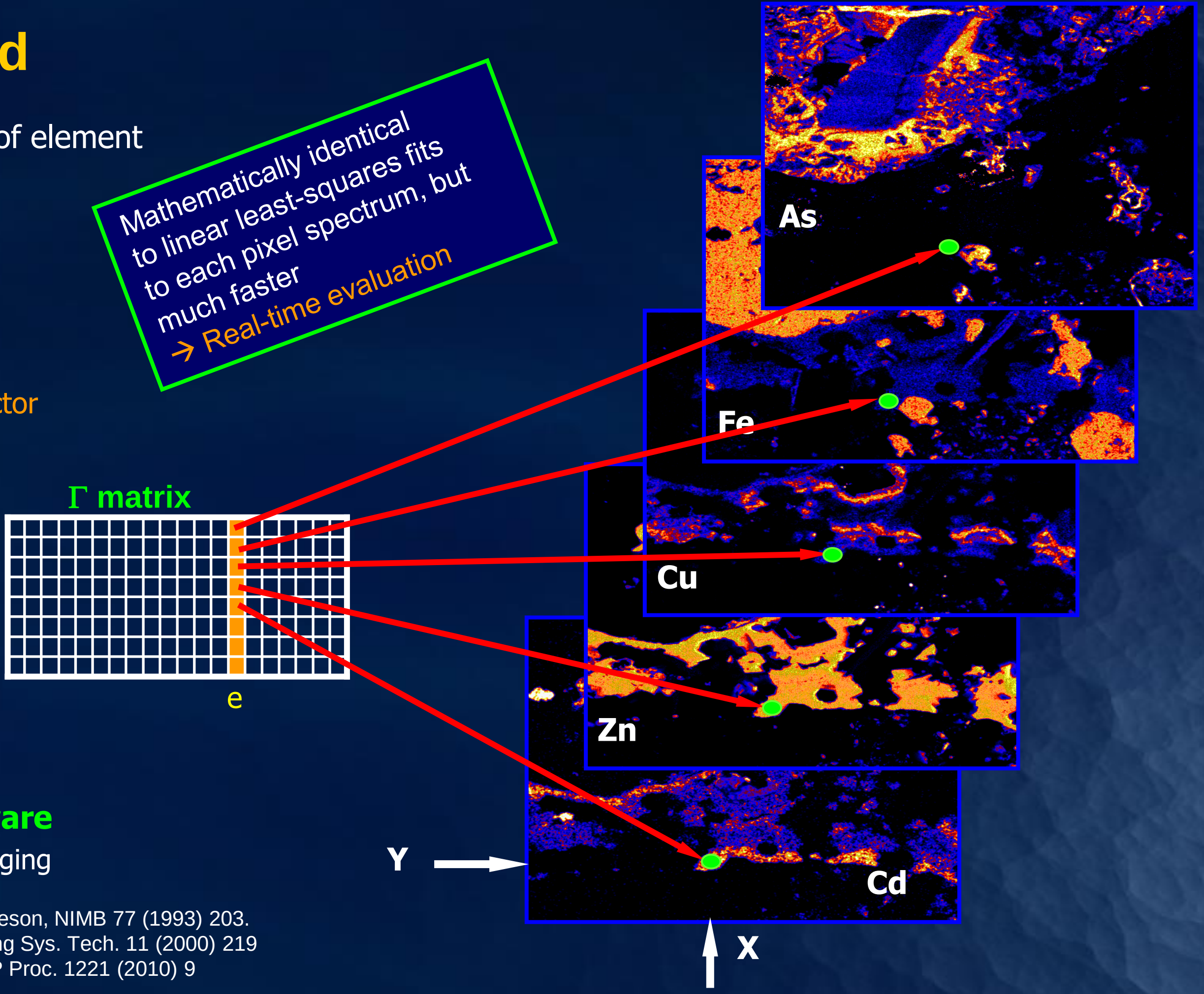
… cast as a matrix transformation:

$$C \quad = \quad Q^{-1}\,\Gamma\,\mathbf{S}$$

Concentration vector (C)

Transform matrix (Γ)

Spectrum vector (S)



PIXE and SXRF Imaging:

X-ray event: Energy 'e' Position 'x,y'

selects column of matrix Γ → increments to images at 'x,y'

GeoPIXE software

PIXE and SXRF imaging

- Ryan and Jamieson, NIMB 77 (1993) 203.
- Ryan, J. Imaging Sys. Tech. 11 (2000) 219
- Ryan *et al.*, AIP Proc. 1221 (2010) 9

XFM Quantification in GeoPIXE

General approach

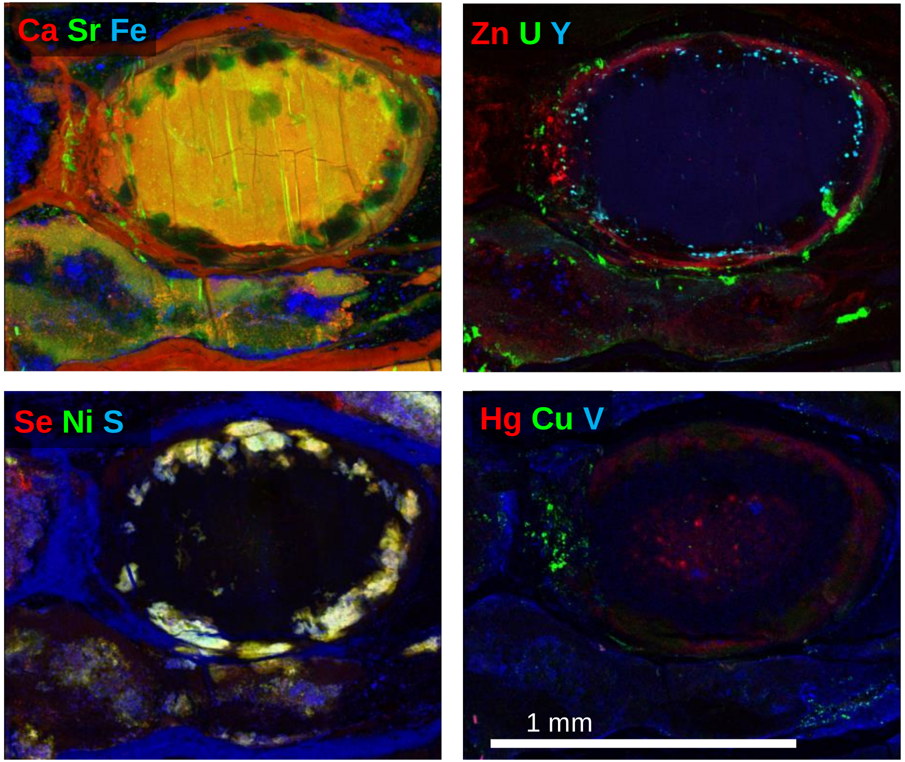
- Standardless, fundamental parameters
- Combine all detectors in an array

Apply to imaging → Dynamic Analysis

- Accumulate images “event by event”

Further issues

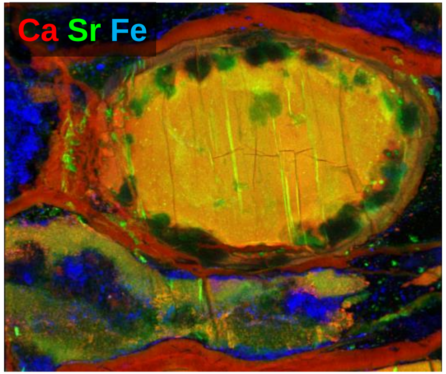
- Correct images for spatially varying sample composition (effects on model yields)
- Track changing beam energy E_b for XANES imaging (the model scatter peaks move)
- Exploit “angular diversity” of a large array

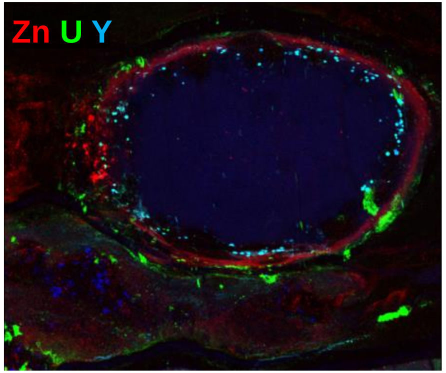


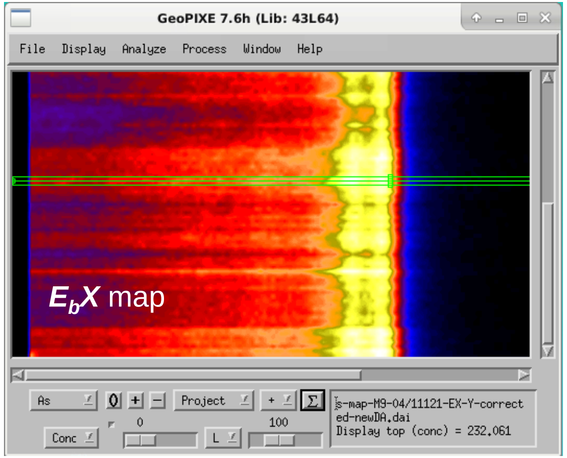
XFM imaging modes in GeoPIXE

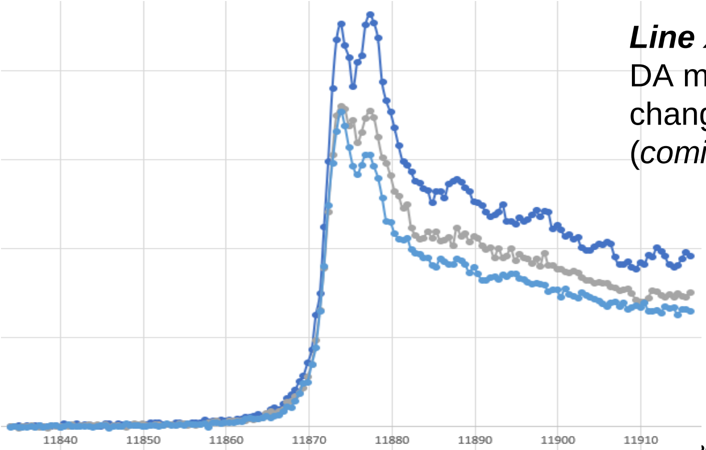
2D

- ***XY*** – full spectral event analysis using DA
    - Image for each element
- ***XE$_b$*** – Line XANES, many elements
    - Scan along line for each beam energy ***E$_b$***









Line XANES:
DA matrix model should follow changing beam energy ***E$_b$***
(*coming soon*)

Dynamic Analysis method - XANES

SXRF Spectrum - linear combination of element spectra.

… cast as a matrix transformation:

$$C = Q^{-1}\,\Gamma(E_b)\,\mathbf{S}$$

Concentration vector

Transform matrix

Spectrum vector

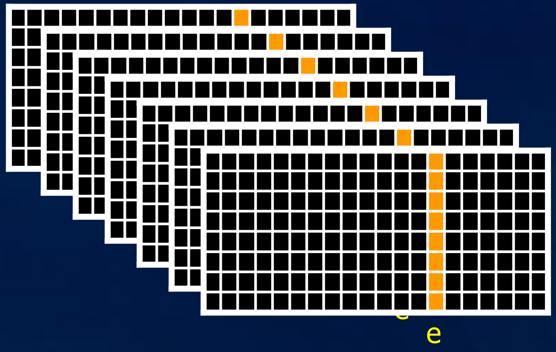
XANES Imaging:

X-ray event: Energy 'e'
Position 'x,y'
Beam energy 'E_b'

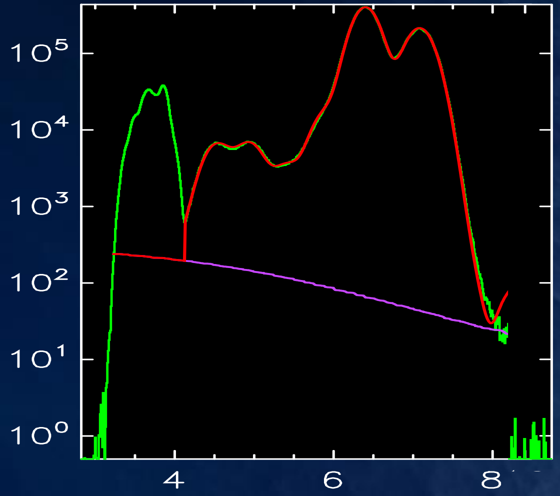
'E_b' selects matrix Γ in stack →

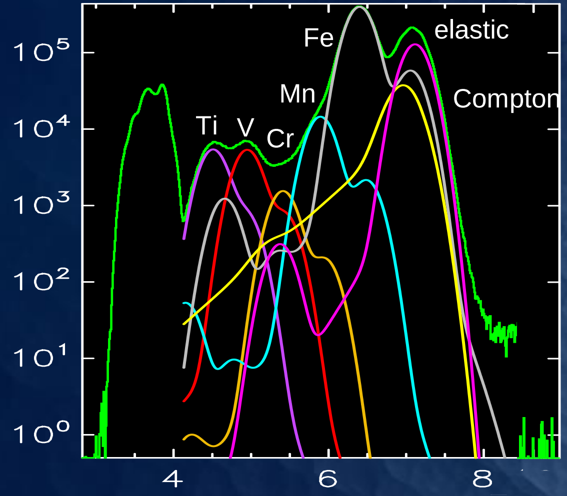
'e' selects column of matrix $\Gamma(E_b)$ → the increments to images at 'x,y'

Γ Matrix stack



one for each beam energy 'E_b'





XFM imaging modes in GeoPIXE

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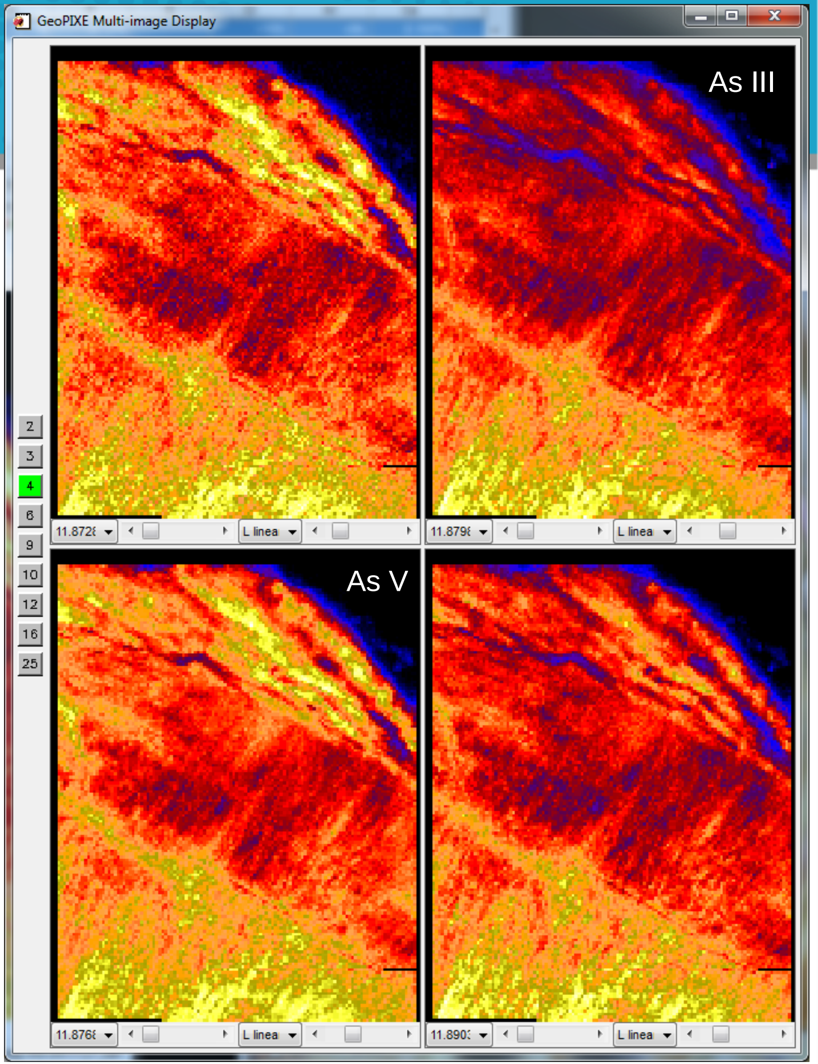
- ***XY*** – full spectral event analysis using DA
    - Image for each element
- ***XE$_b$*** – line XANES, many elements
    - Scan along line for each beam energy ***E$_b$***

3D

- ***XYθ*** – Fluorescence Tomography,
    - full XY frames at each θ
- ***XYE$_b$*** – XANES stack (for selected element)
    - XY image frames at each beam energy ***E$_b$***
- ***XE$_b$Y*** – XANES stack (for selected element)
    - ***E$_b$*** from undulator encoder as second fastest axis



XFM imaging modes in GeoPIXE

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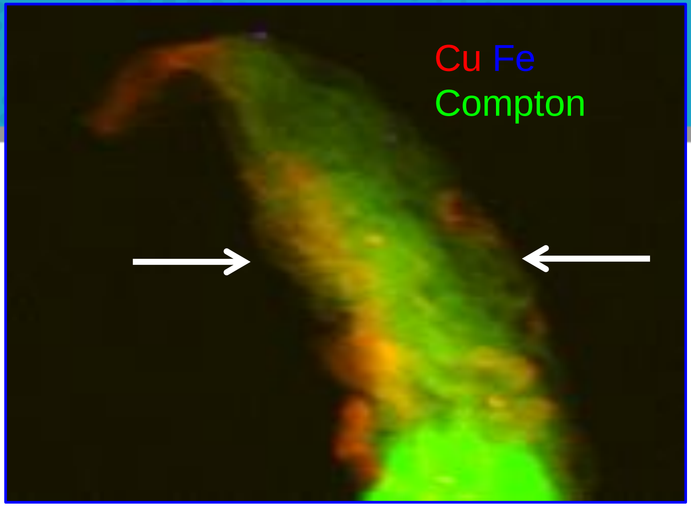
- ***XY*** – full spectral event analysis using DA
  - Image for each element
- ***XE$_b$*** – line XANES, many elements
  - Scan along line for each beam energy ***E$_b$***

3D

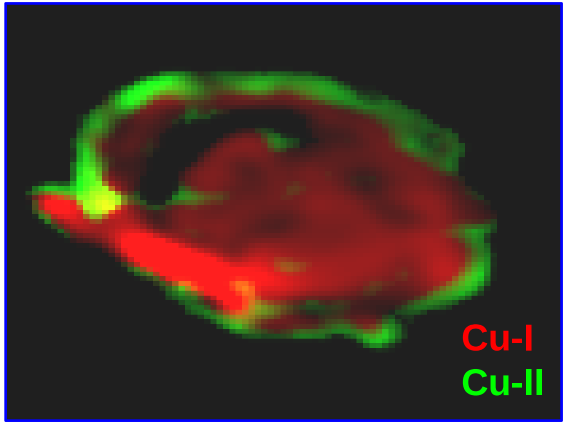
- ***XYθ*** – Fluorescence Tomography,
  - full XY frames at each θ
- ***XYE$_b$*** – XANES stack (for selected element)
  - XY image frames at each beam energy ***E$_b$***
- ***XE$_b$Y*** – XANES stack (for selected element)
  - ***E$_b$*** from undulator encoder as second fastest axis
- ***XθE$_b$*** – XANES Tomography
  - Xθ as fastest axes, stacked by ***E$_b$***

2D XFM



0.4 x 0.55 mm; 200 x 275 pixels, 16 min

XANES Tomography section

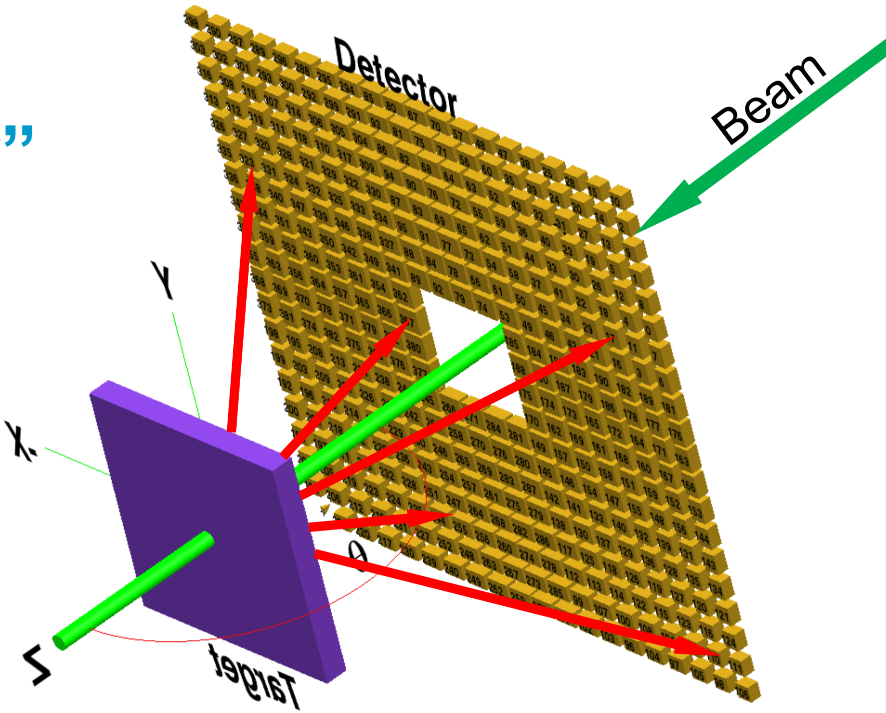


Cu speciation maintained in Drosophila…
James + de Jonge *et al.*

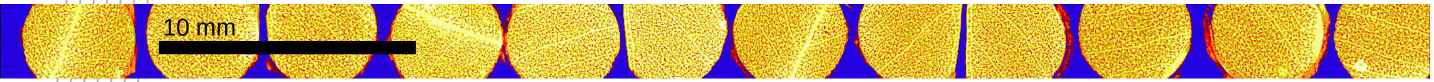
0.3 mm x 180°, 100 angles; 150 x 100 pixel sinogram, 4.7 minutes per energy x 80 energies

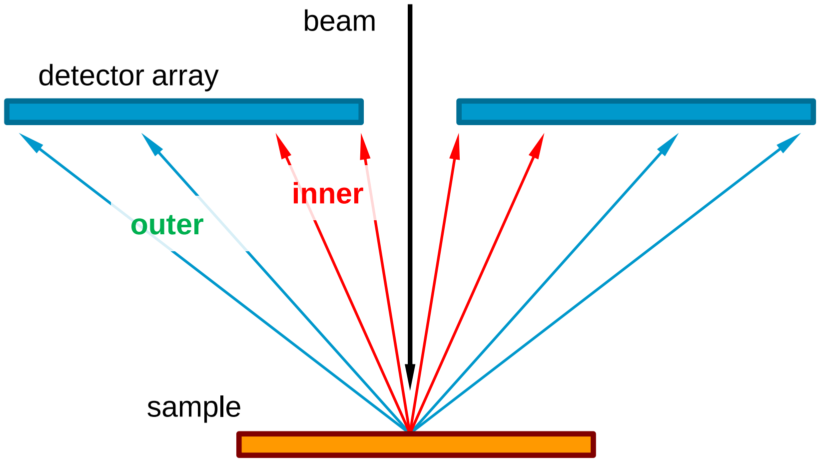
Maia detector array
“take-off angle diversity”

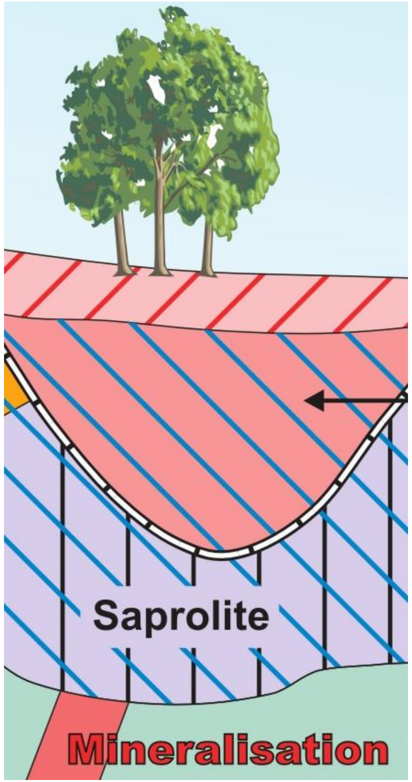
- Take-off angle range:- γ: 14° to 53°
- Azimuthal angle range:- φ: 0 to 360°



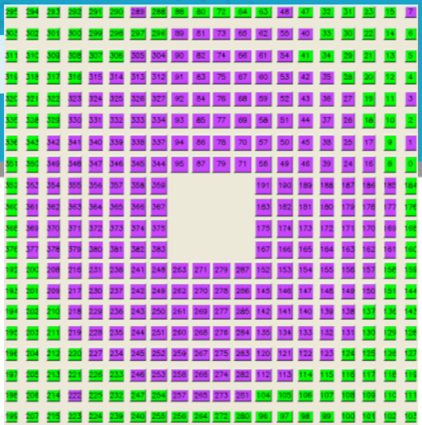
Depth mapping
Gold precipitates in leaves



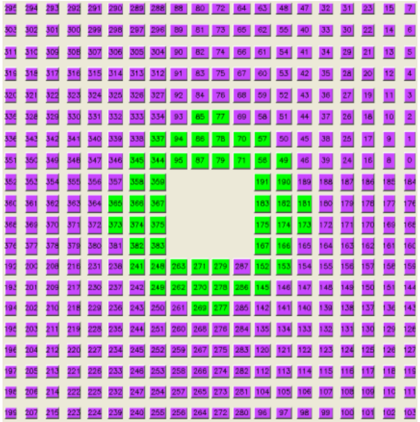




outer

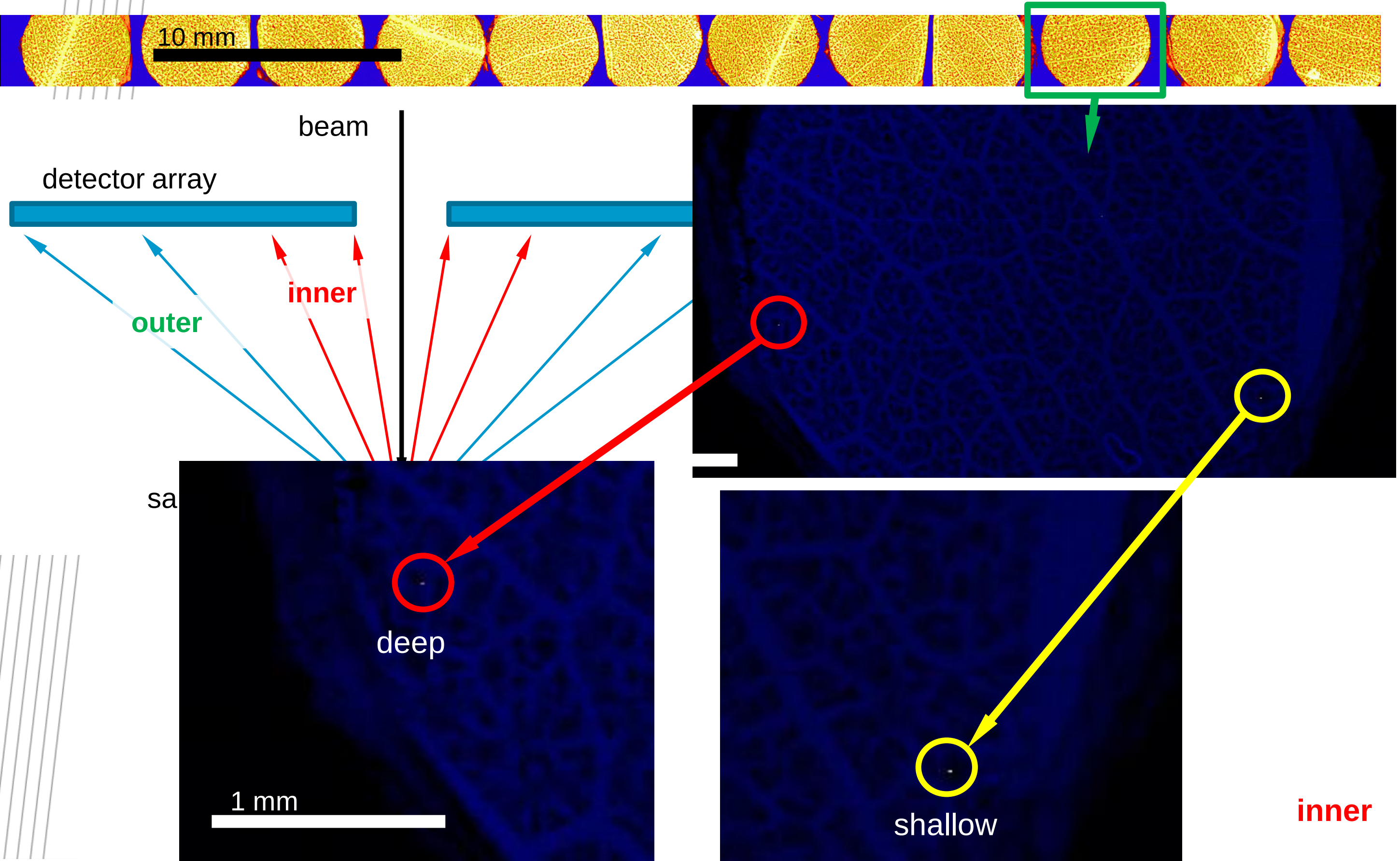


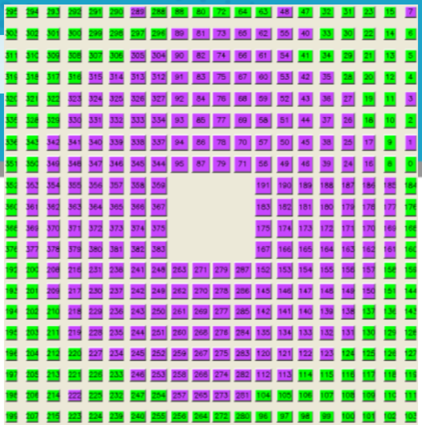
inner

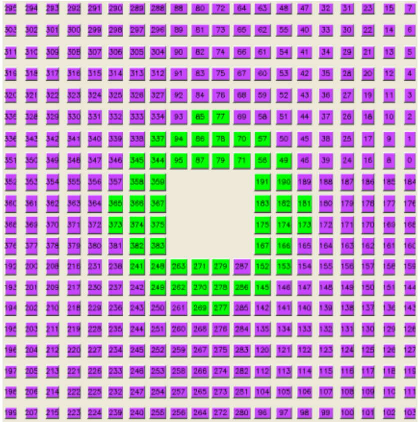


Lintern *et al.*, Nature Communications 4, 2274

Depth mapping
Gold precipitates in leaves

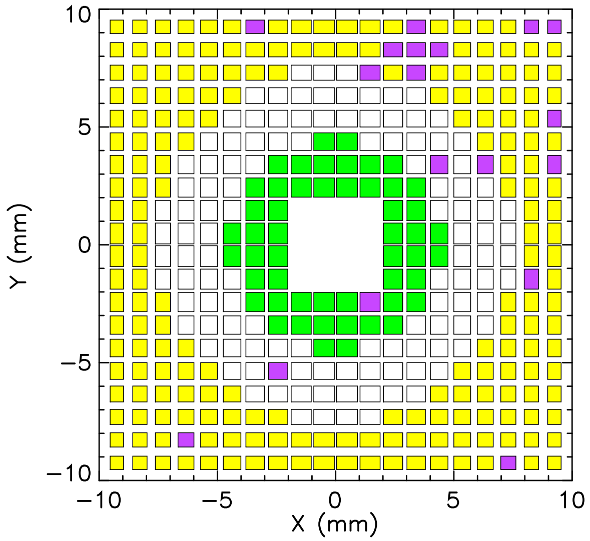


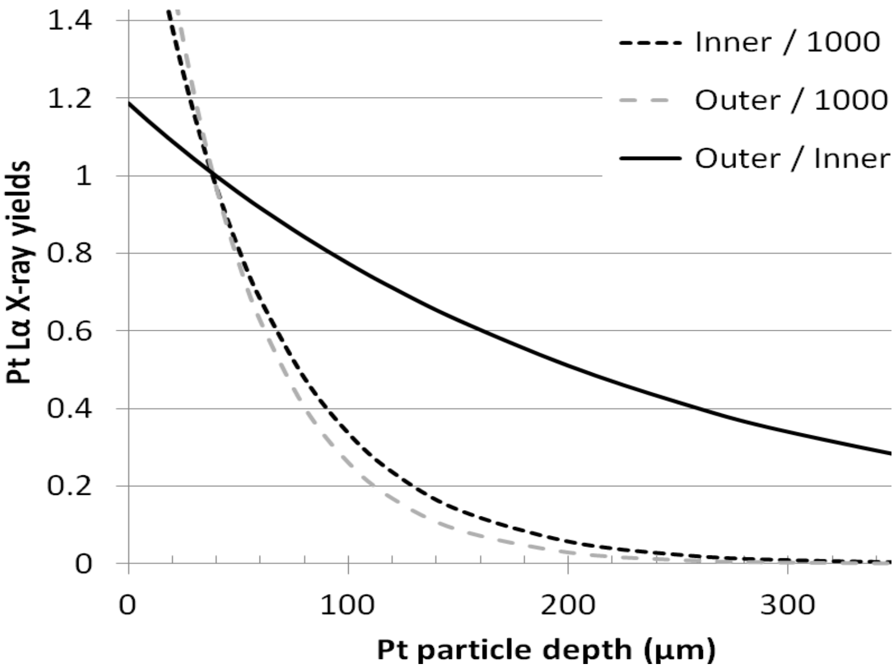




Maia 384 array:
Depth sensitivity and measurement

- **Depth sensitivity using large detector array**
  - ✓ Angles from normal range from 13.9 ° to 52.6°
  - ✓ Outer detectors "see" more self-absorption
  - ✓ Inner detectors "see" deeper particles
  - ✓ **Ratio "outer" / "inner" → depth measure**



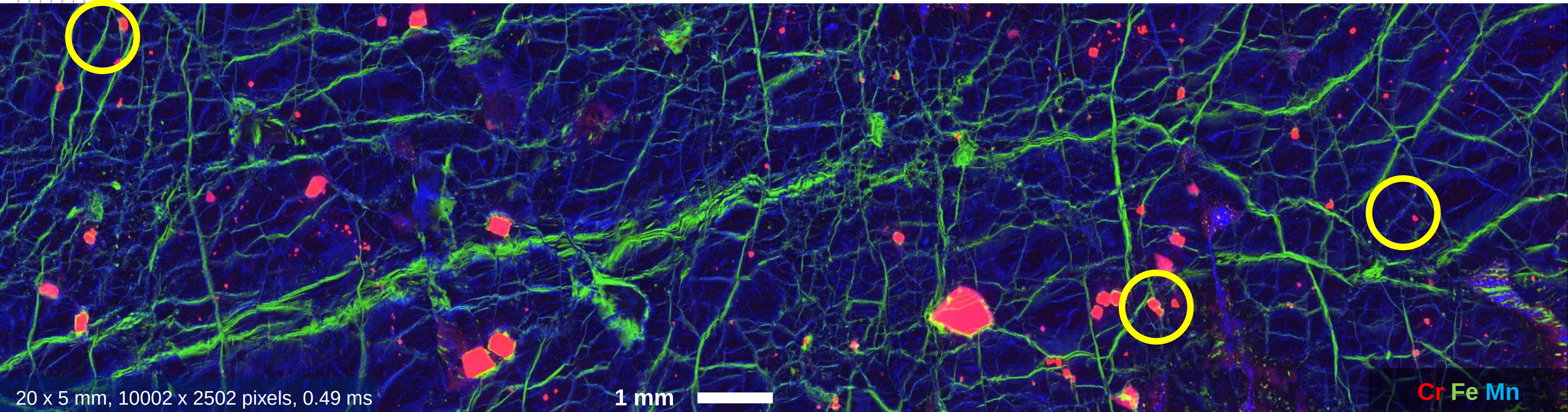


Pt Lα yields, "outer"/"inner" ratio for Pt particle in olivine at 18.5 keV beam energy

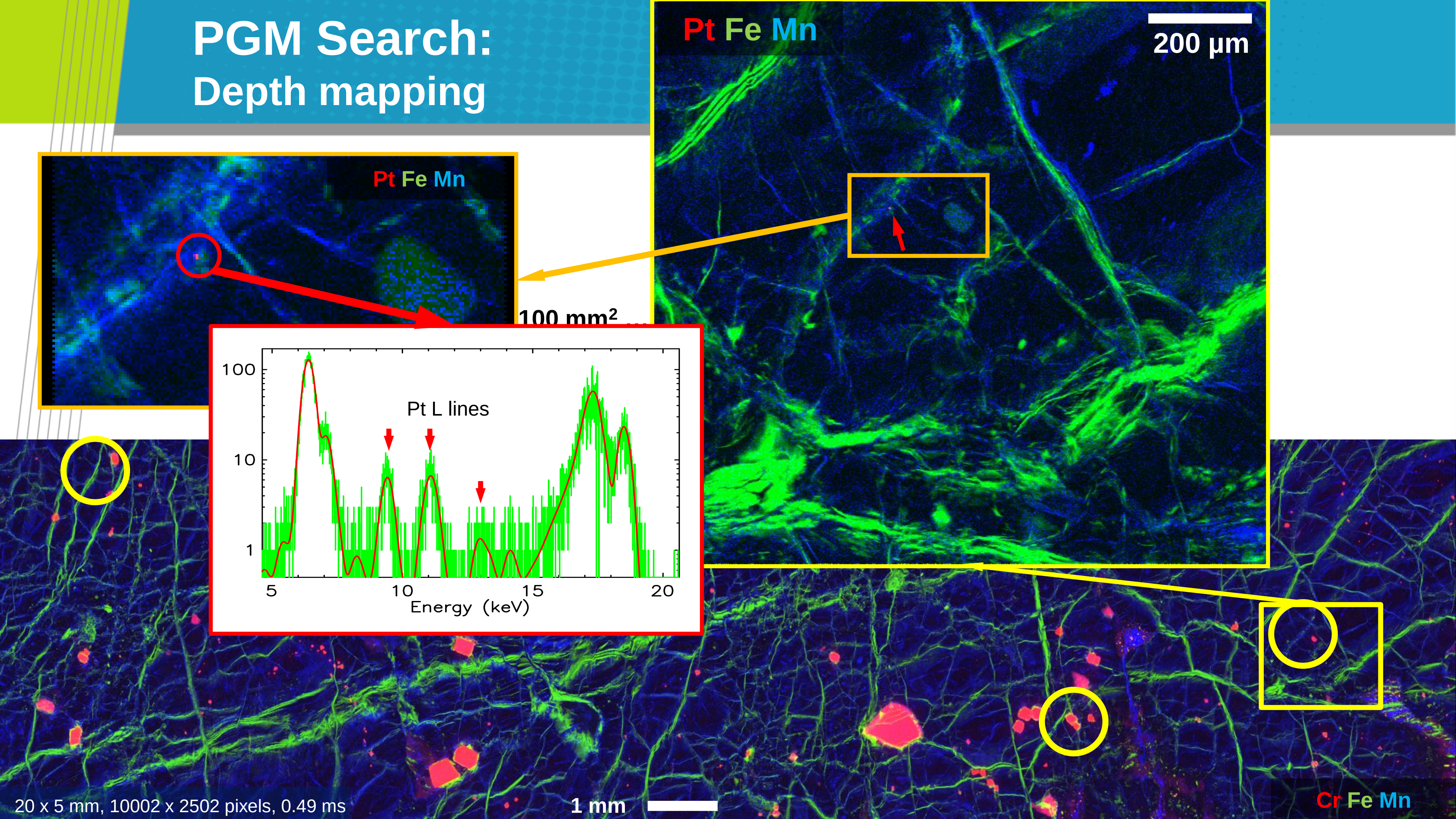
PGM Search:
Depth mapping

Three groups of PGMs found in 100 mm^2 …

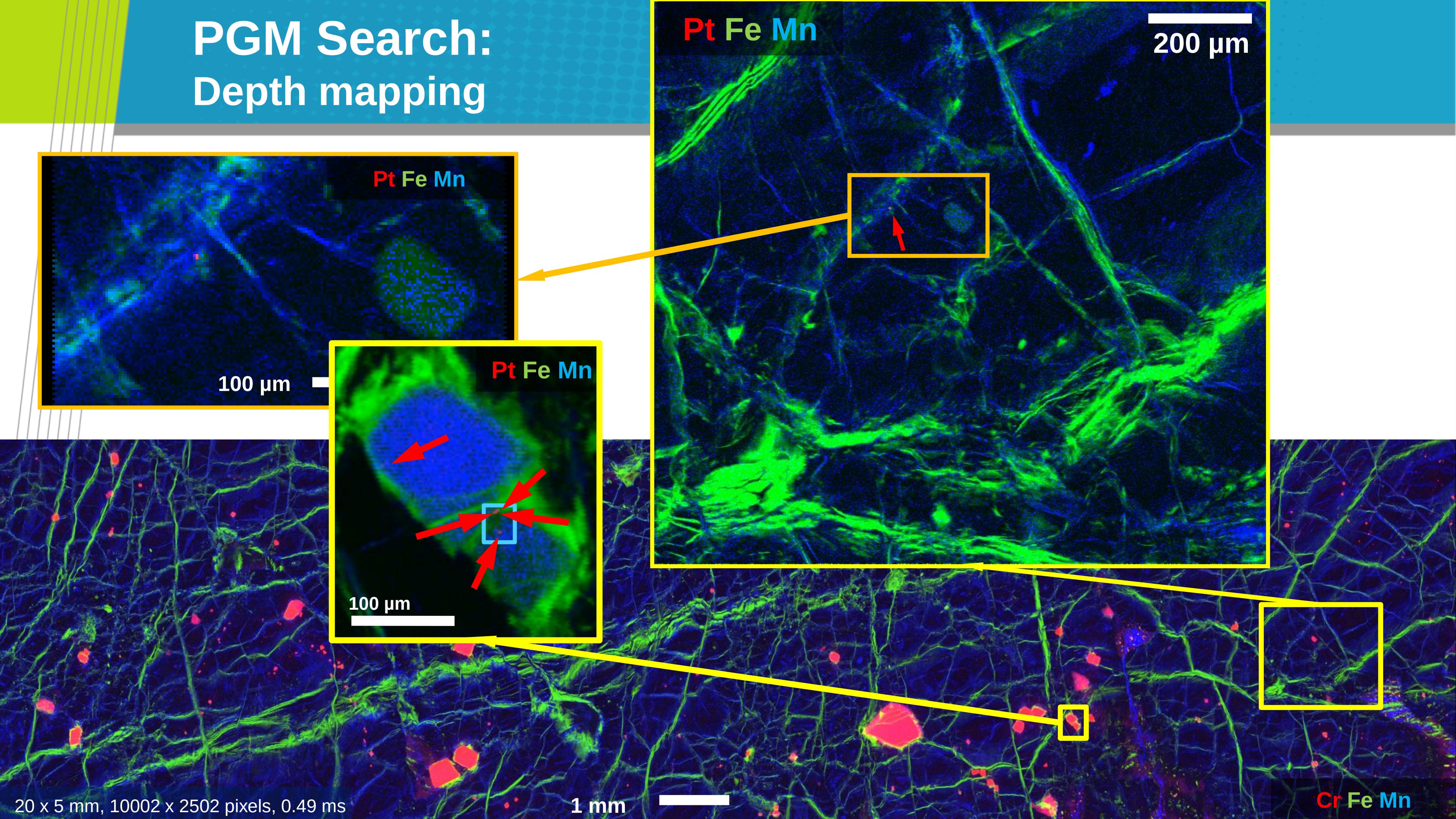
Dunite polished section from Muang Pha intrusion Laos (Godel *et al*., CSIRO)



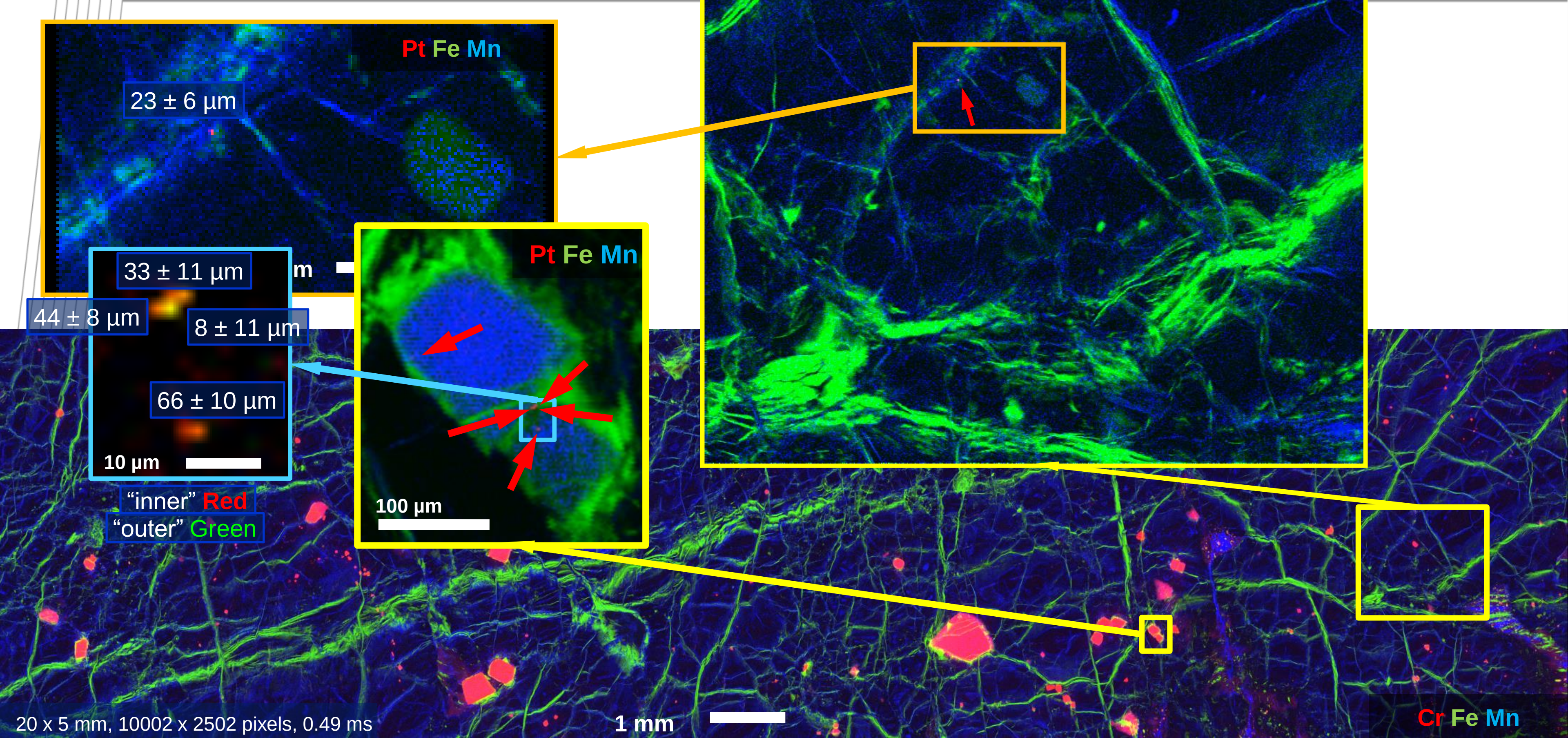
PGM Search:
Depth mapping

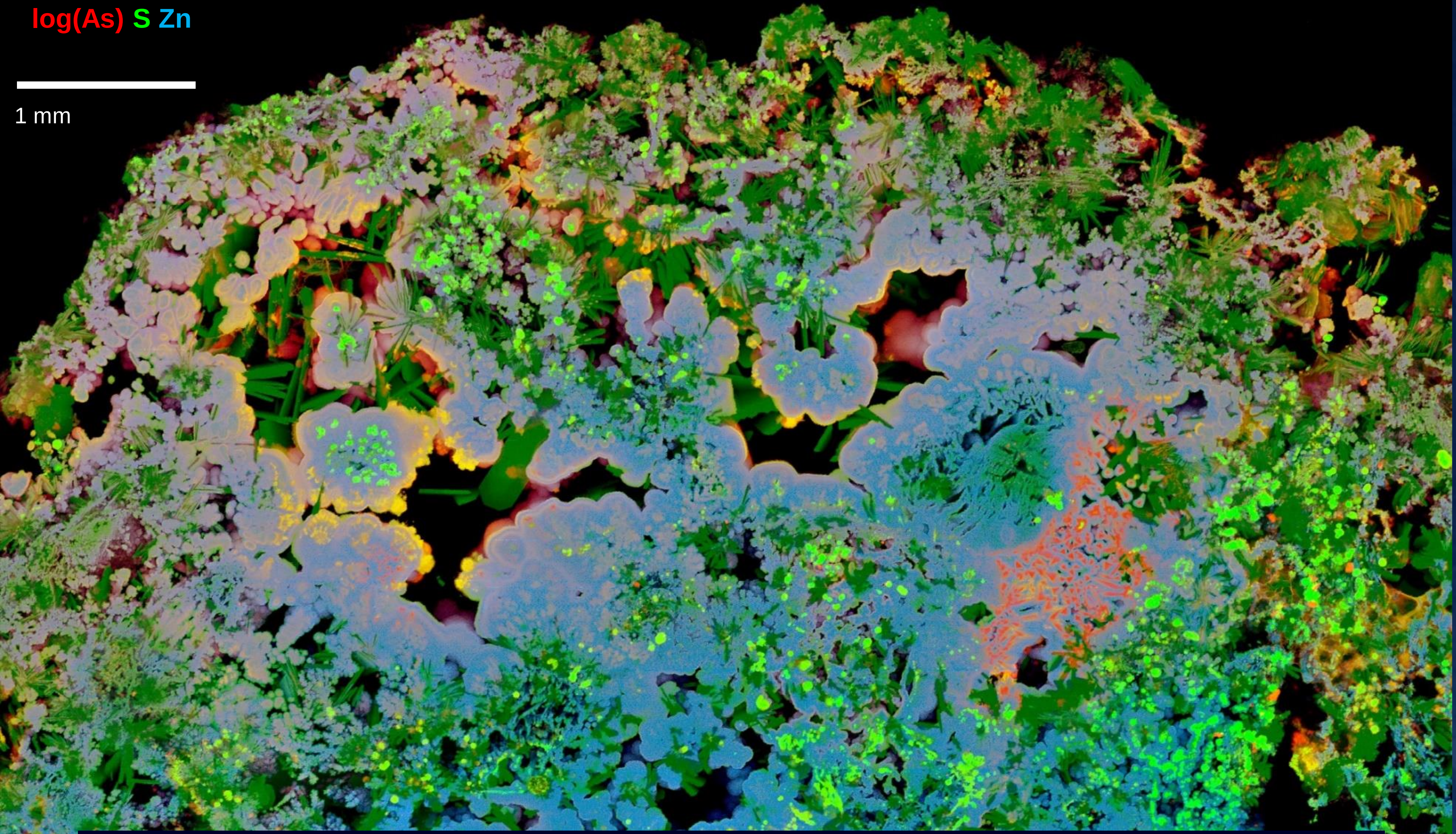


PGM Search:
Depth mapping



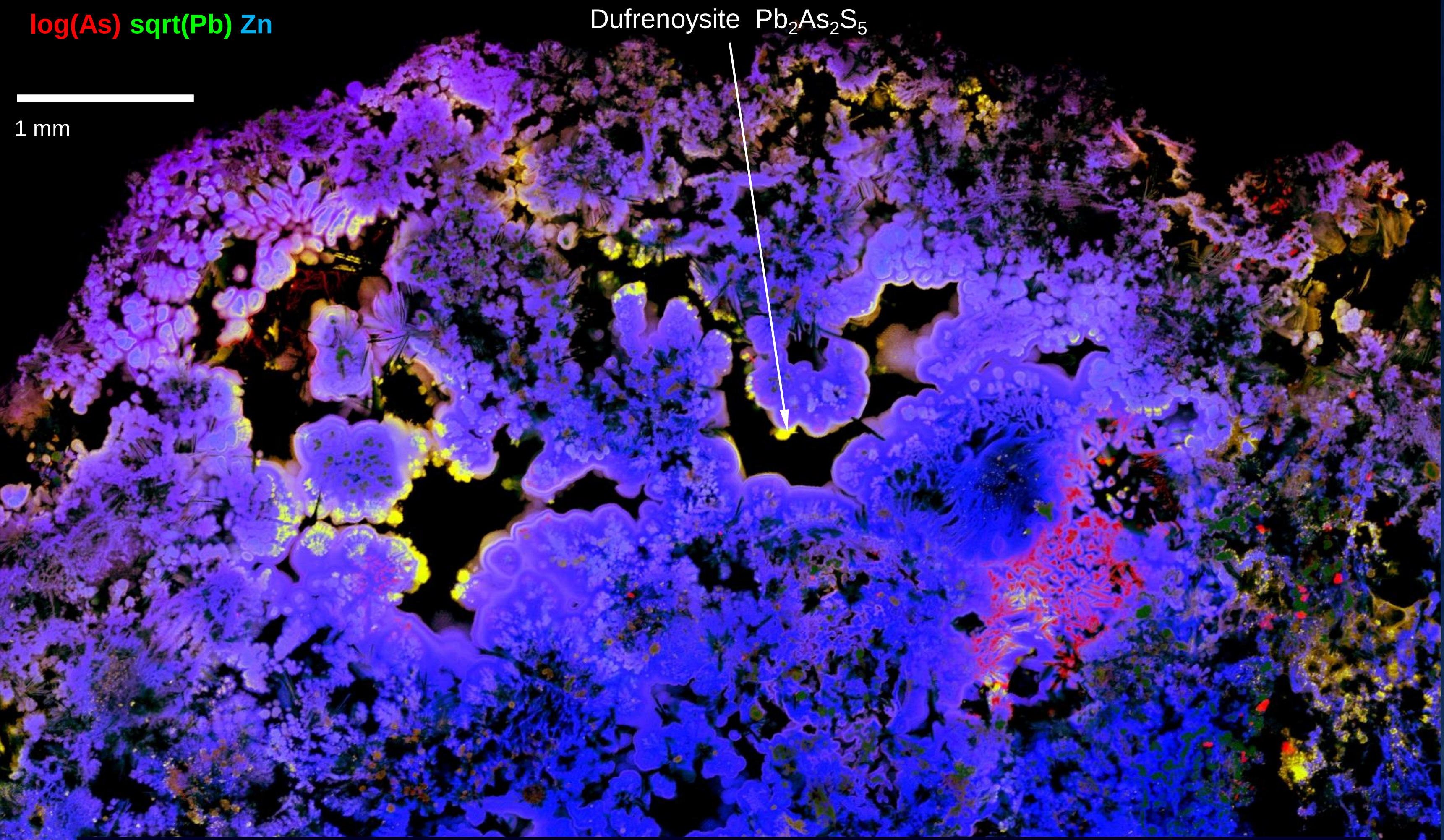
PGM Search:
Depth mapping





Black smoker chimney conduit thin-section, PACMANUS seafloor hydrothermal field, study by Siyu Hu *et al*., CSIRO Maia-PIXE images (#664): **3500 x 2197 pixels** @ 8 ms; 7.0 x 5.0 mm^2, 3 MeV protons, 122 µC, (see Laird *et al*., NIMB 449 (2019) 11-16)

Ryan, CSIRO



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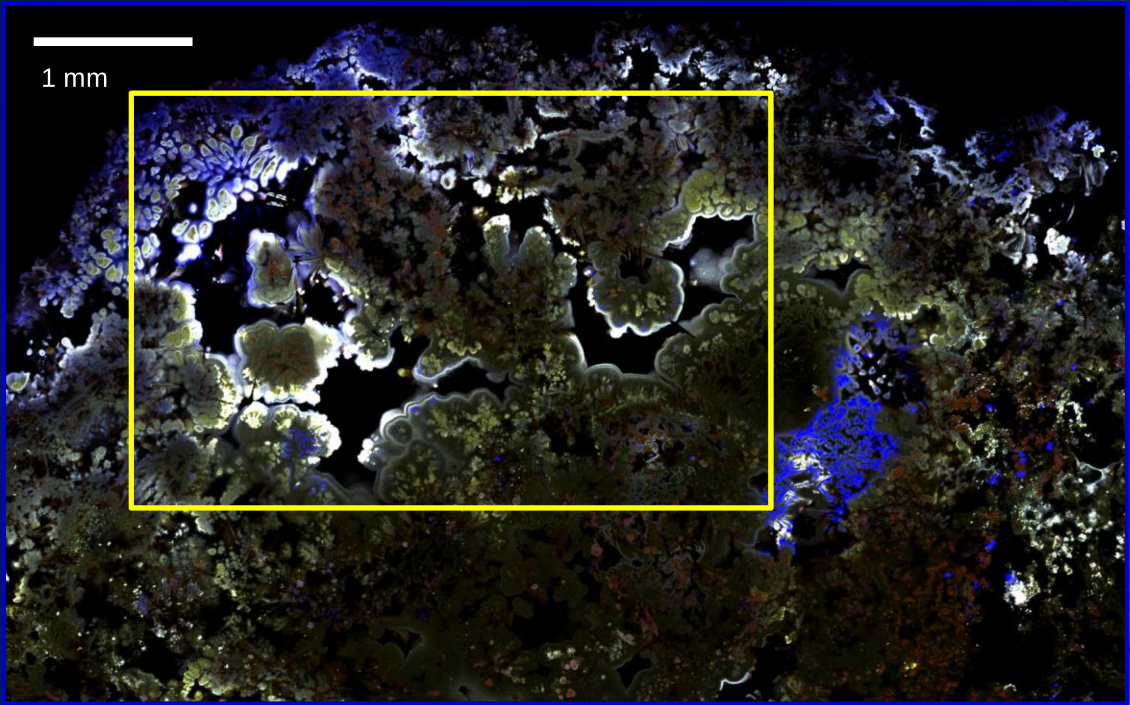
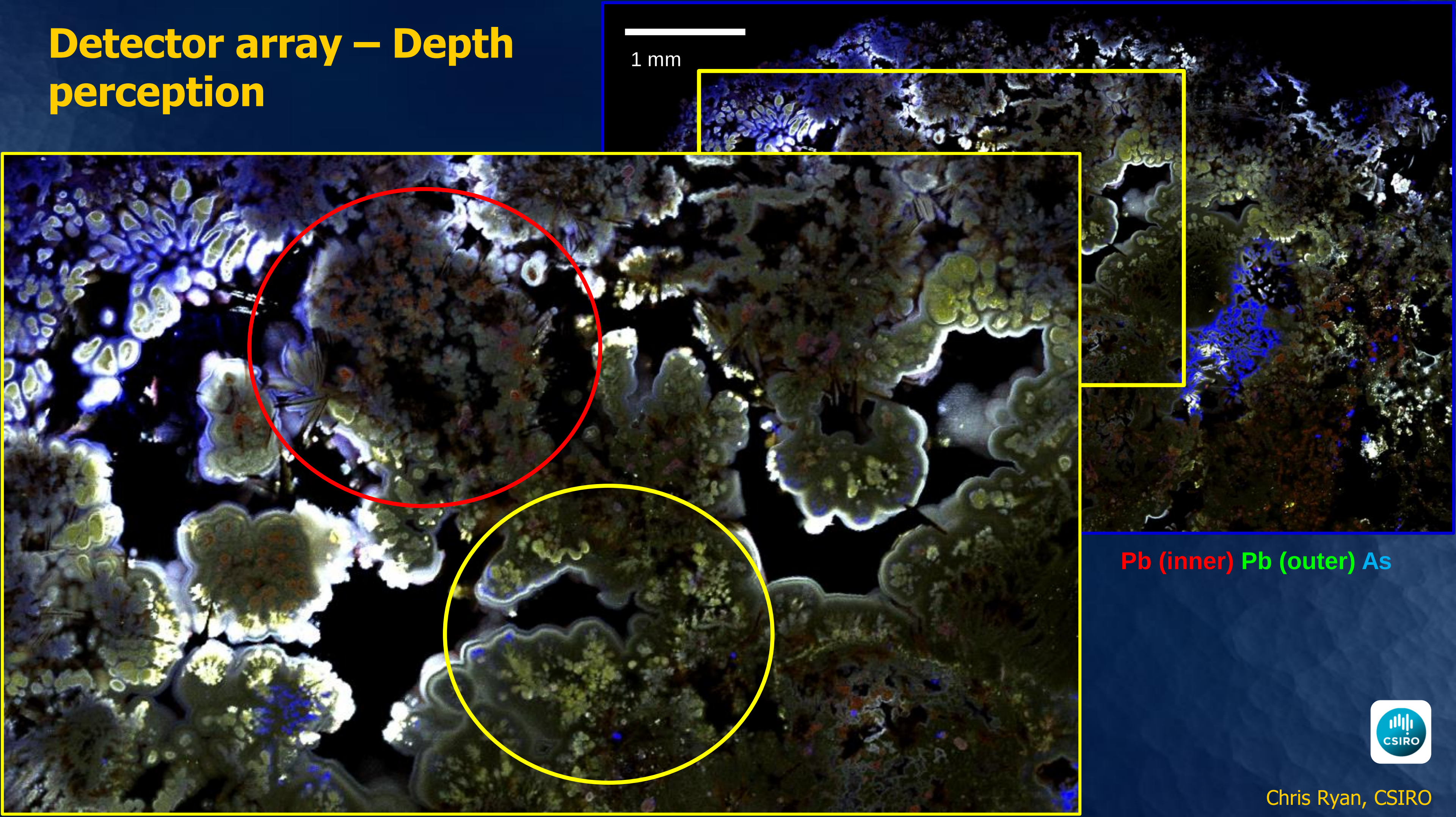
yan, CSIRO

Detector array – Depth perception



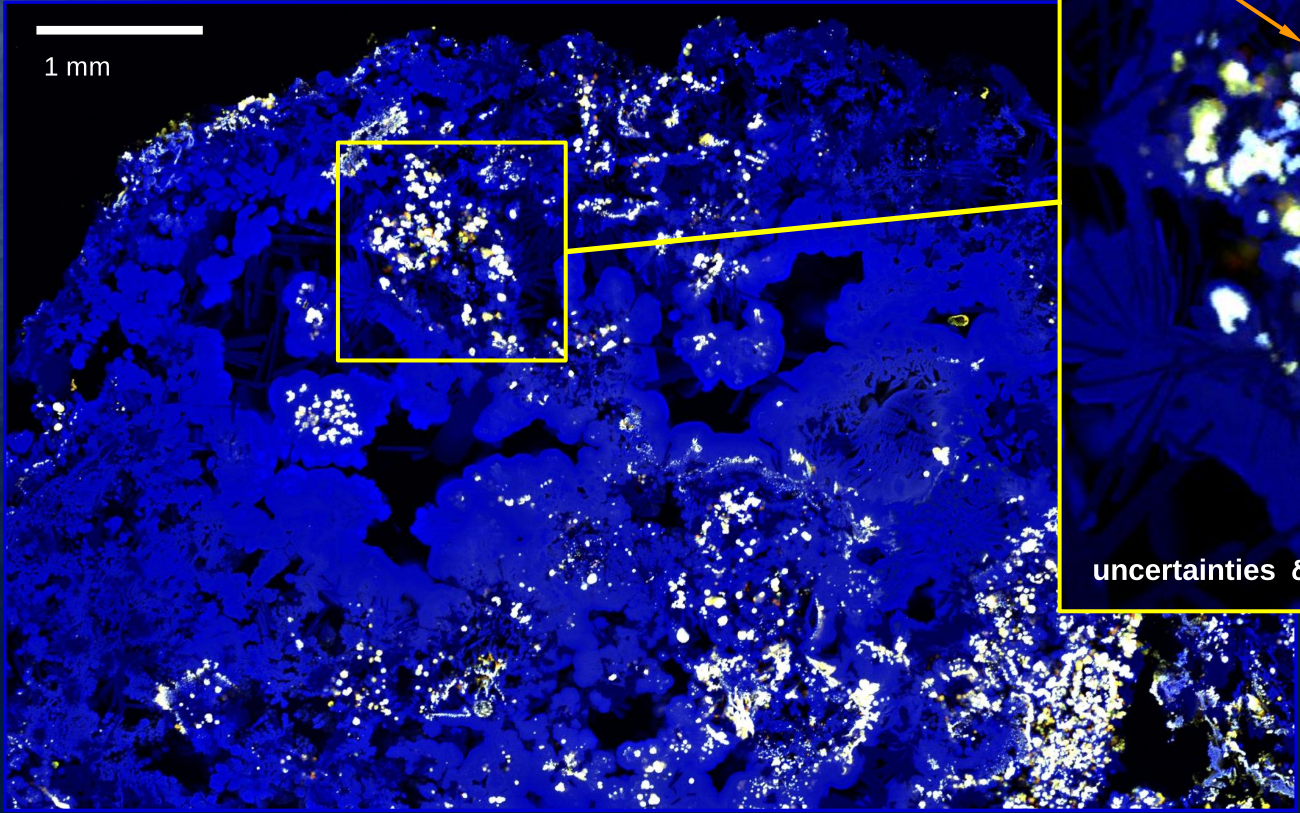
Pb (inner) Pb (outer) As

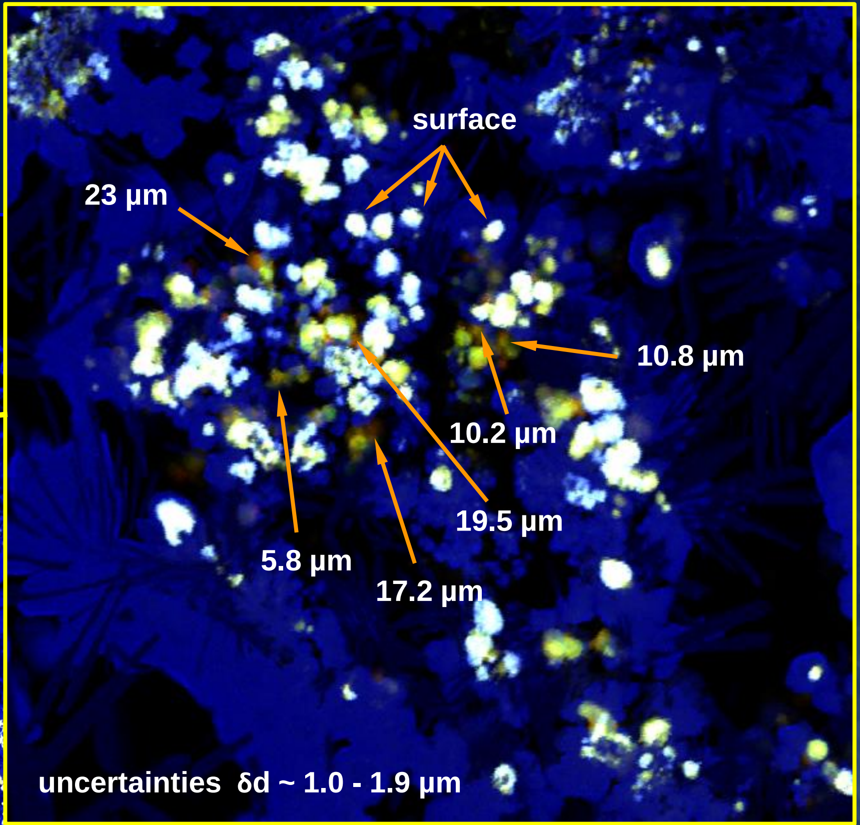
Detector array – Depth perception



Chris Ryan, CSIRO

Detector array – Depth perception

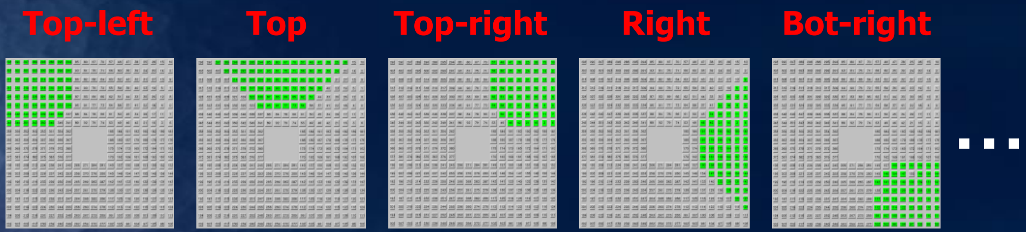




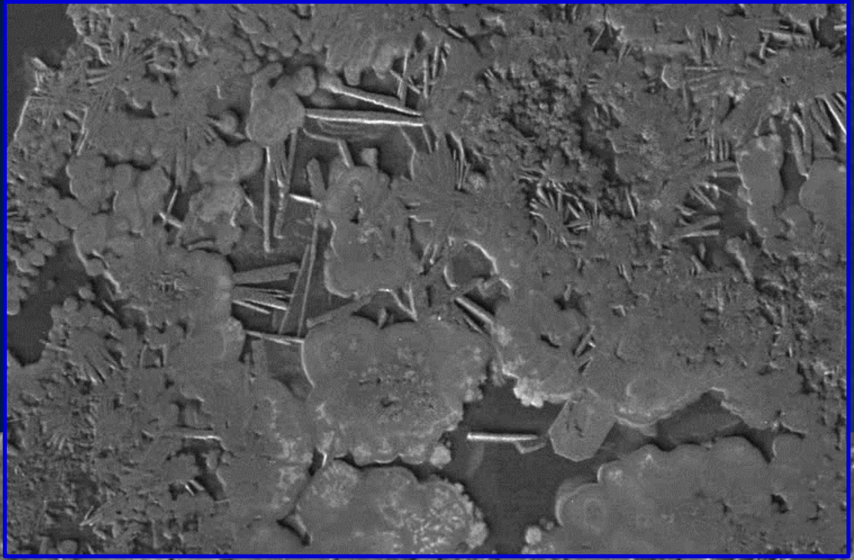
Fe (inner) Fe (outer) S

Chris Ryan, CSIRO

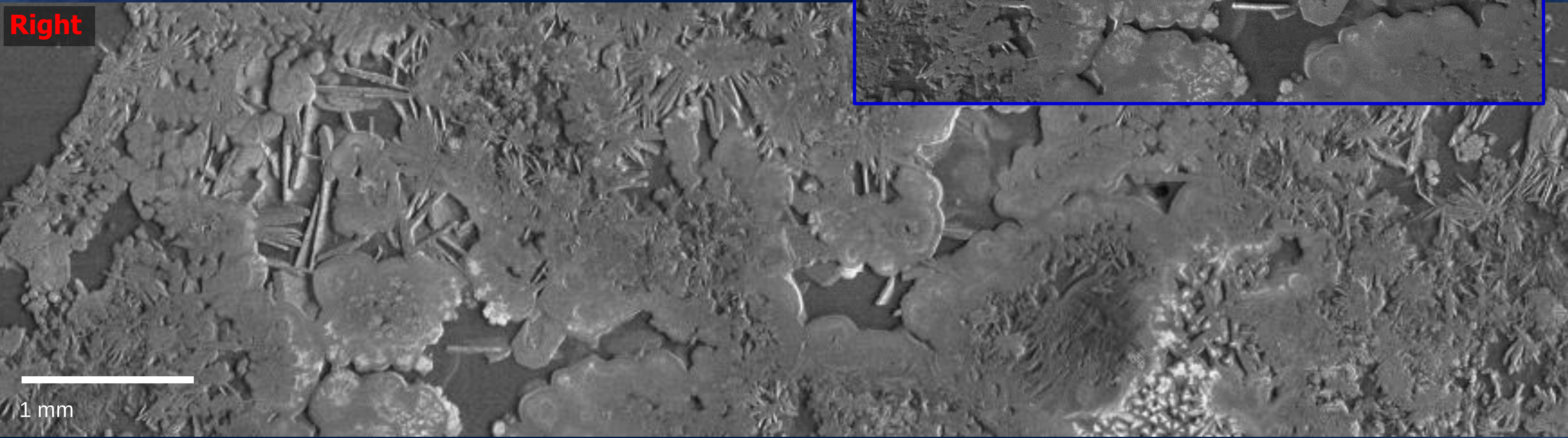
Detector array: Take-off angle perspectives

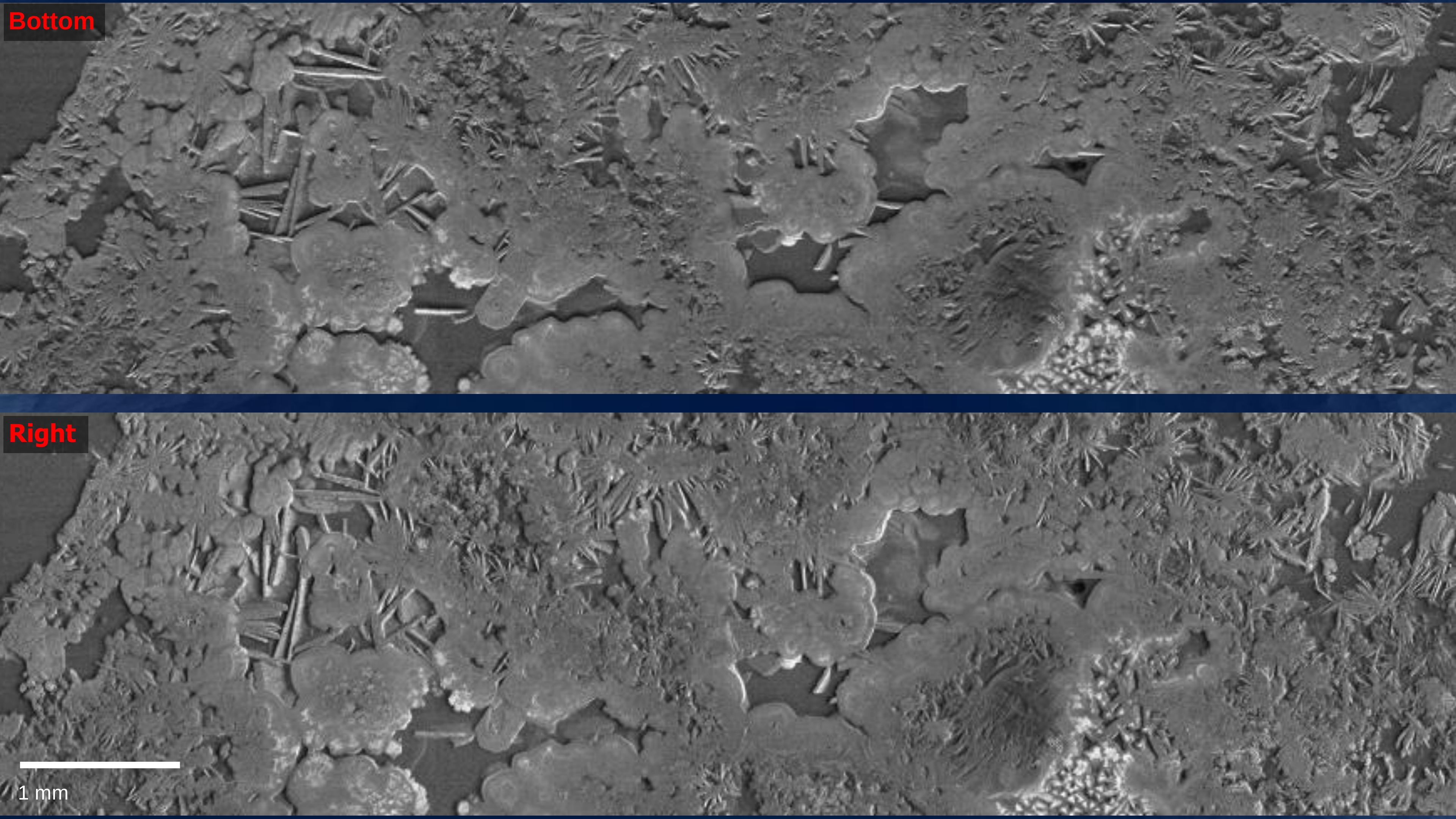


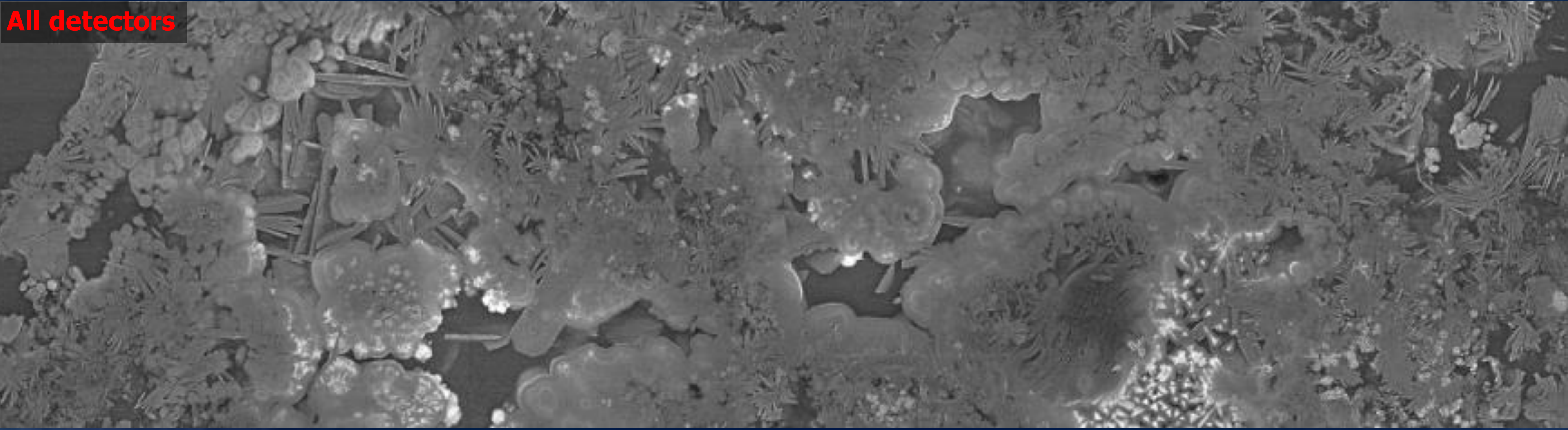
Group detectors by azimuthal angle around array …

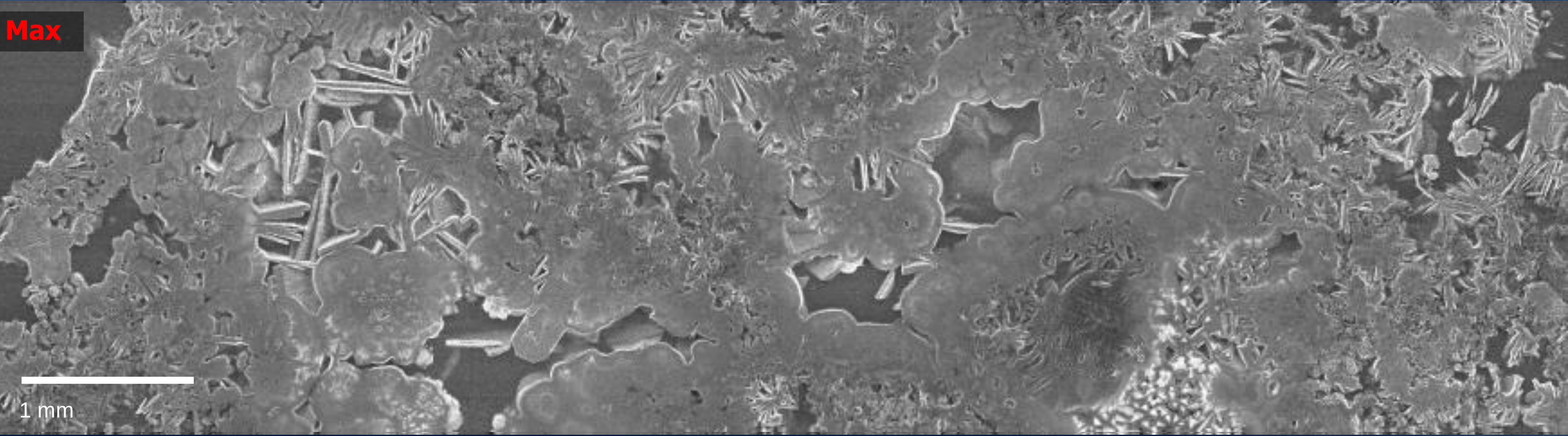


Bremsstrahlung background intensity




Bottom
Right
1 mm

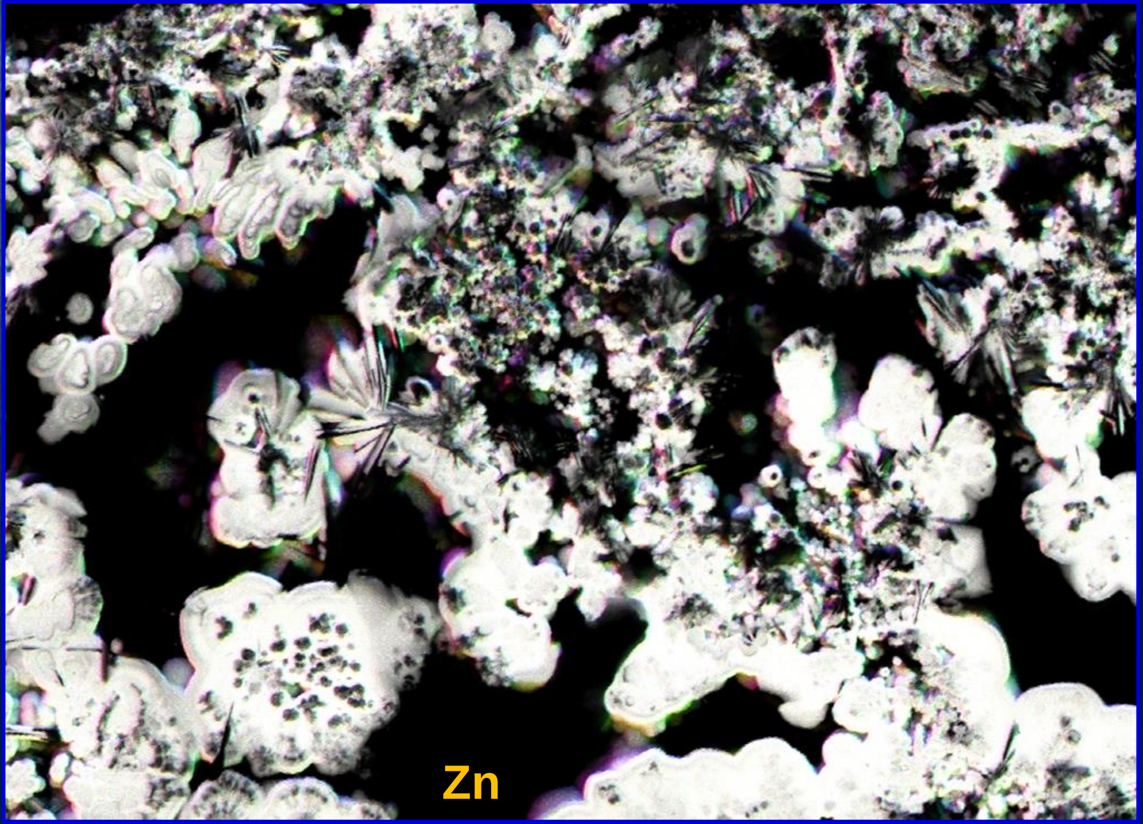

All detectors

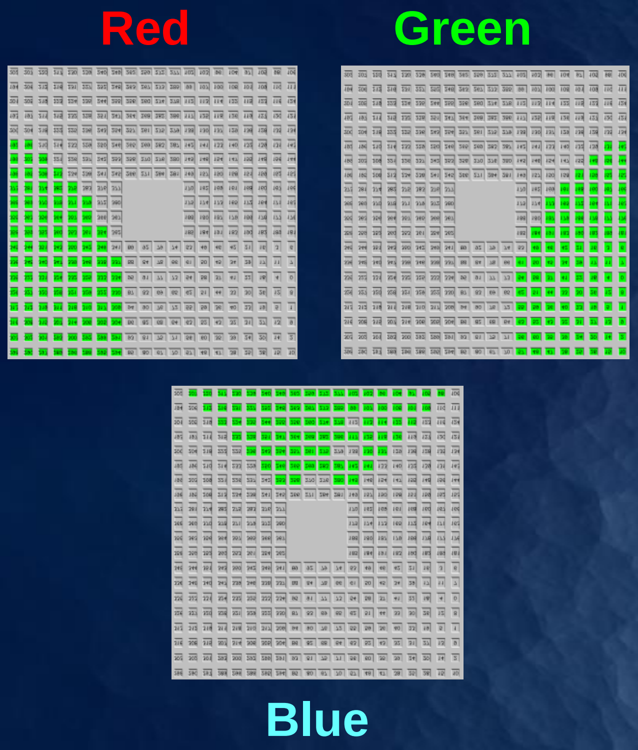

Max
1 mm

Detector array: Take-off angle perspectives

3 angle perspectives

Bottom-left Bottom-right Top

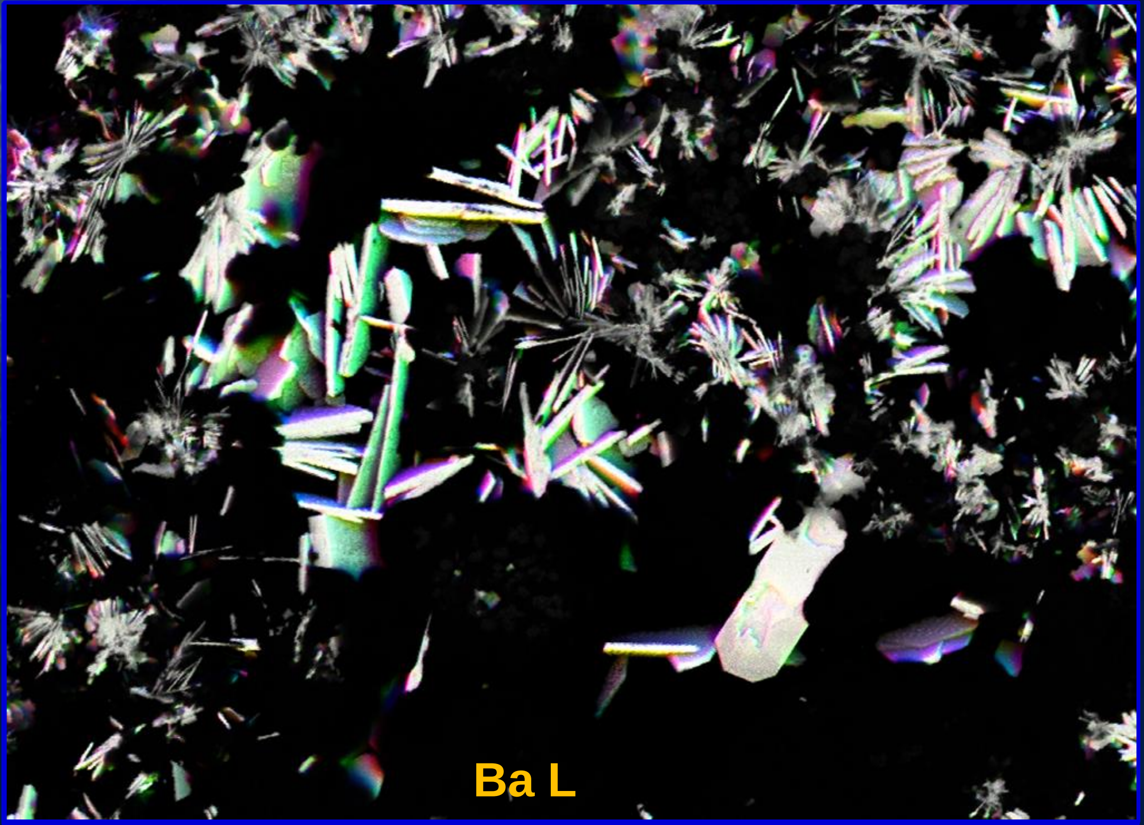




Chris Ryan, CSIRO

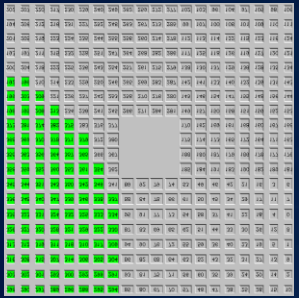
Detector array: Take-off angle perspectives

Bottom-left Bottom-right Top

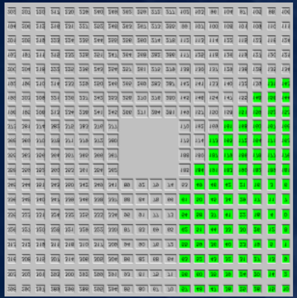


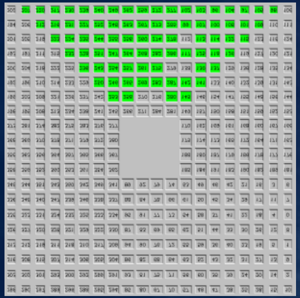
3 angle perspectives

Red



Green





Blue

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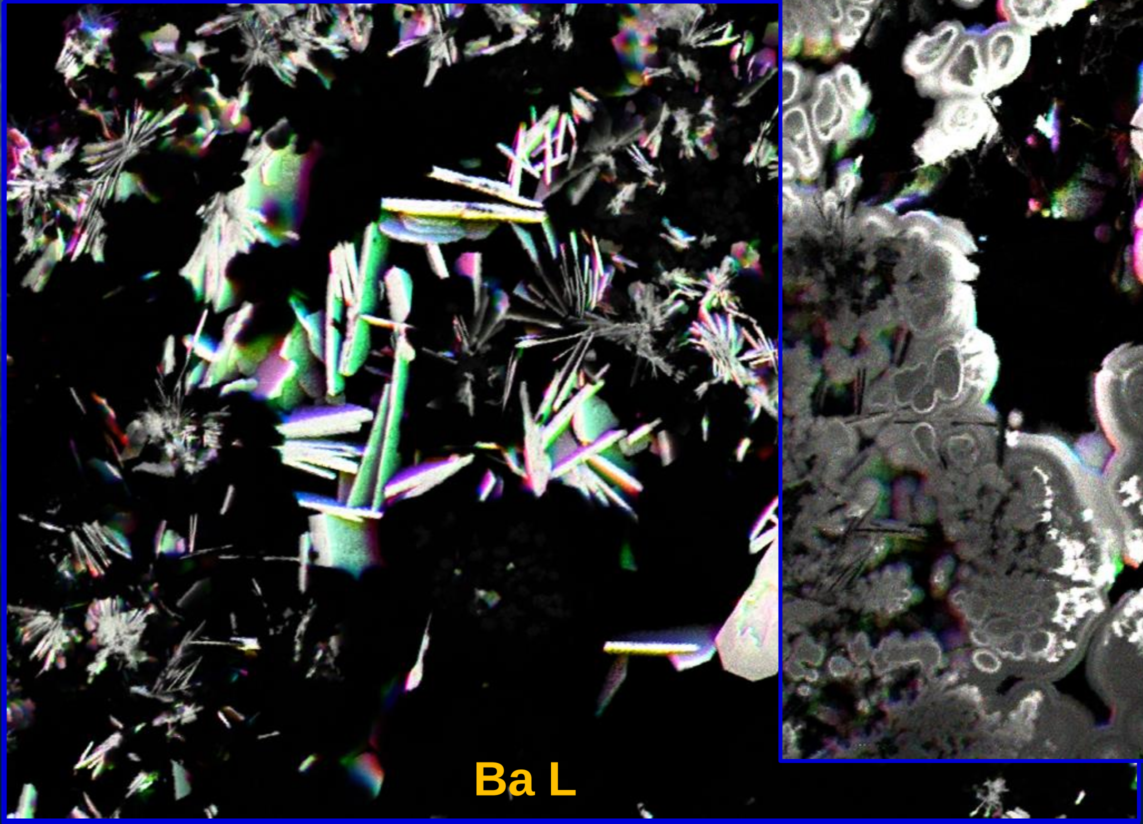
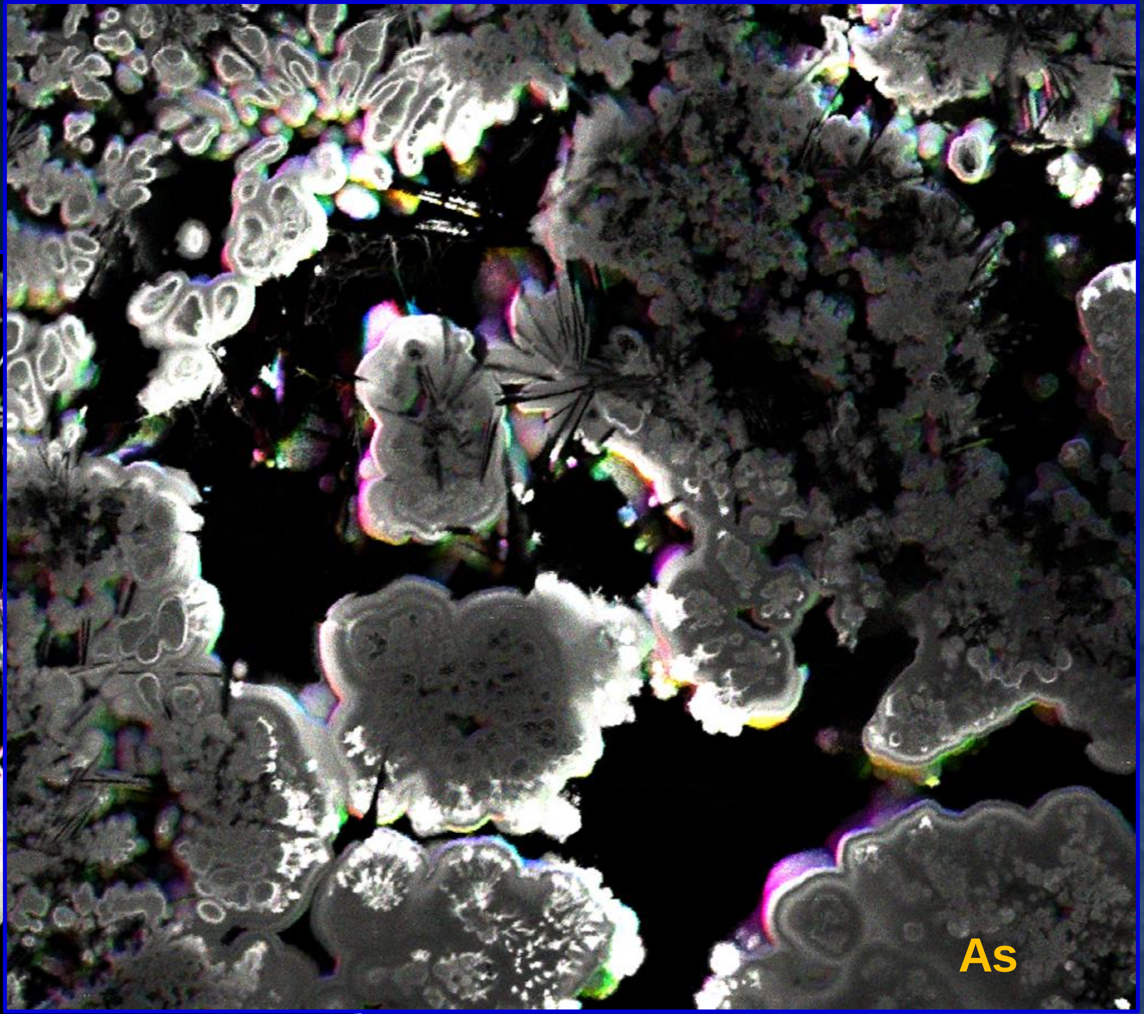
Detector array: Take-off angle perspectives

Bottom-left Bottom-right Top



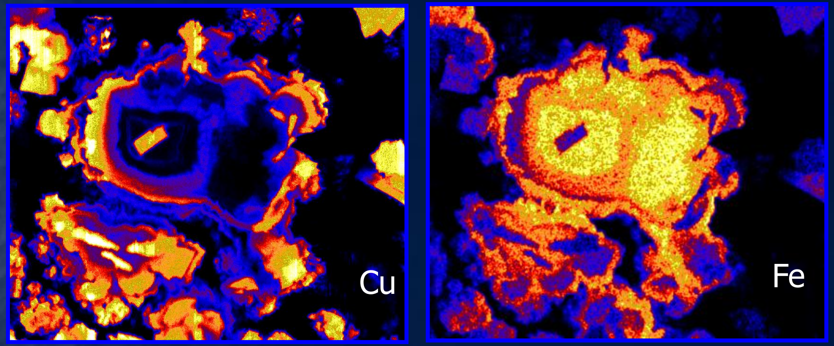


Chris Ryan, CSIRO

Matrix correction of images

Correct images for spatially changing composition

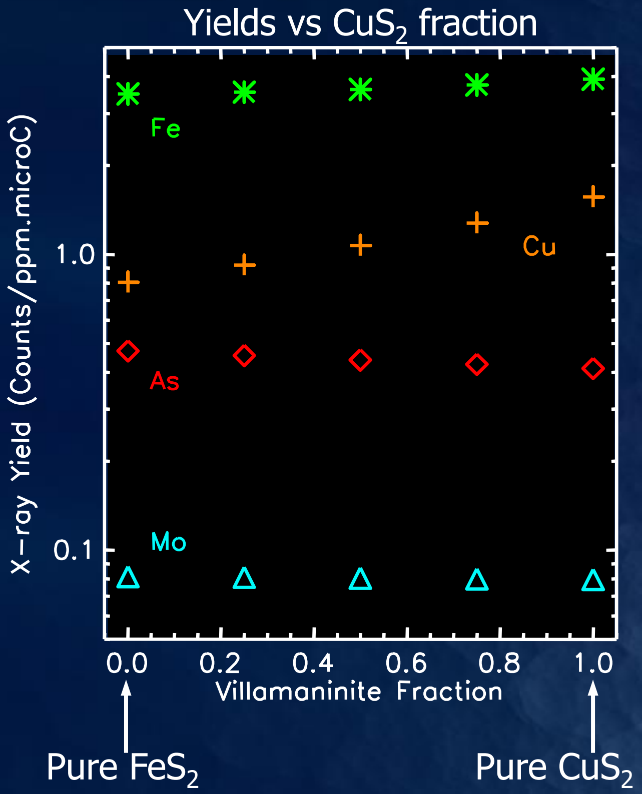
Yield Correction of Images



Huge contrasts in major element composition:

Uniform yields no longer valid.

- Can we estimate yields in terms of a mixture of 'end-member' terms?



Yield Correction of Images

C_k is a mix of end-member j compositions P_{jk}:

$$C_k = \sum_j r_j P_{jk}$$

where r_j is the fraction of end-member phase j.

Hence, form end-member images by transforming:

$$\mathbf{r} = \mathbf{C}\,\mathbf{P}^{-1}$$

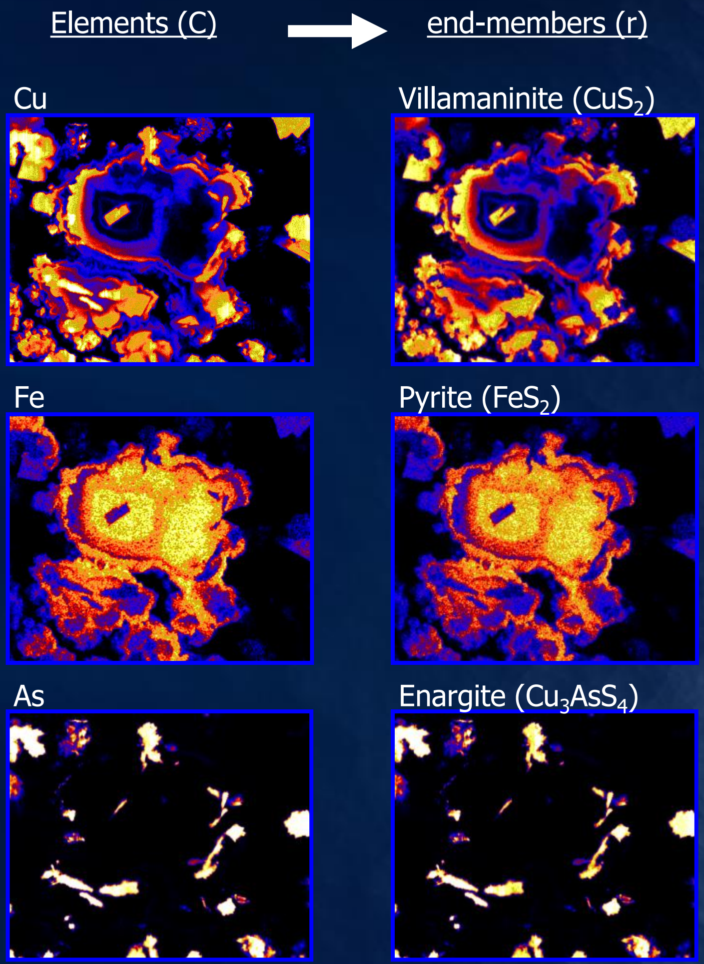
Self-absorption dominates XRF/PIXE X-ray yields Y_k
→ they vary ~inversely with mass absorption.

Therefore, can approximate yields for a mixture by:

$$(Y_k^{mixture})^{-1} \cong \sum_j r_j (Y_{jk}^{phase})^{-1}$$

in terms of the yields Y_{jk}^{phase} calculated for the end-members j.

- Ryan, J. Imaging Sys. Tech. 11 (2000) 219



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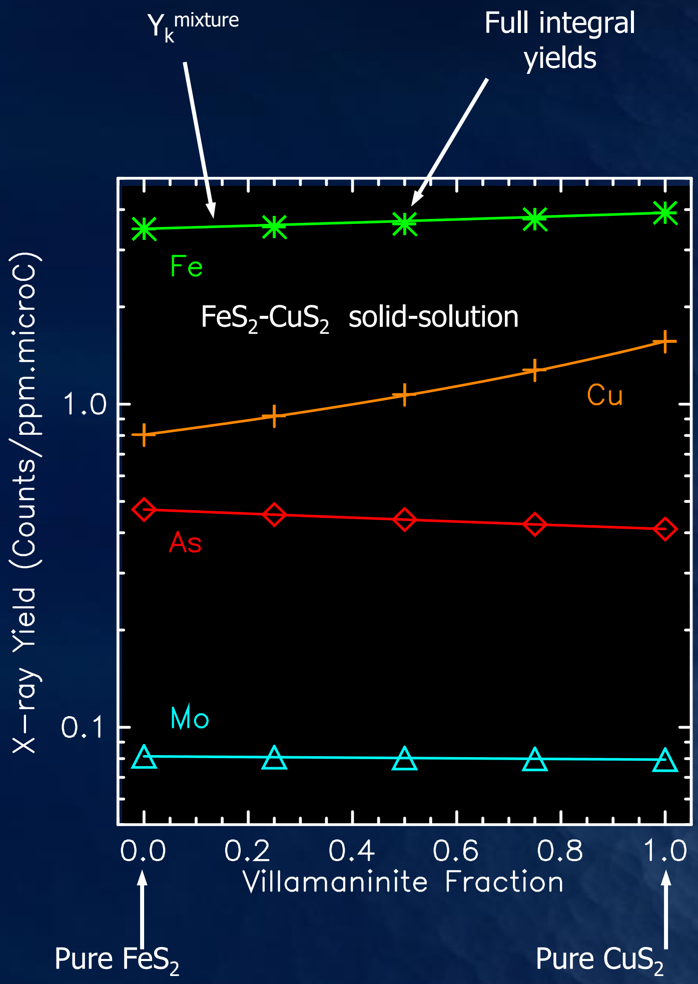
Hence, correct images (pixel by pixel) by:

$$Y_k^{original} \,/\, Y_k^{mixture}$$



Yield Correction of Images

C_k is a mix of end-member j compositions P_{jk}:

$$C_k = \Sigma_j \; r_j \, P_{jk}$$

where r_j is the fraction of end-member phase j.

Hence, form end-member images by transforming:

$$\mathbf{r} = \mathbf{C} \, \mathbf{P}^{-1}$$

Self-absorption dominates XRF/PIXE X-ray yields Y_k
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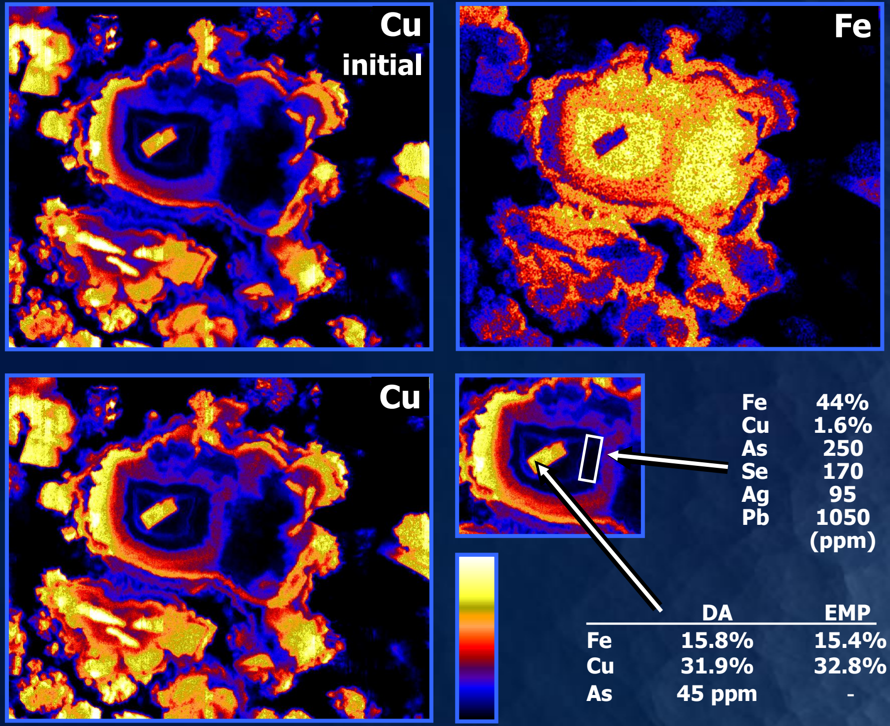


- Ryan, J. Imaging Sys. Tech. 11 (2000) 219

Matrix correction of images

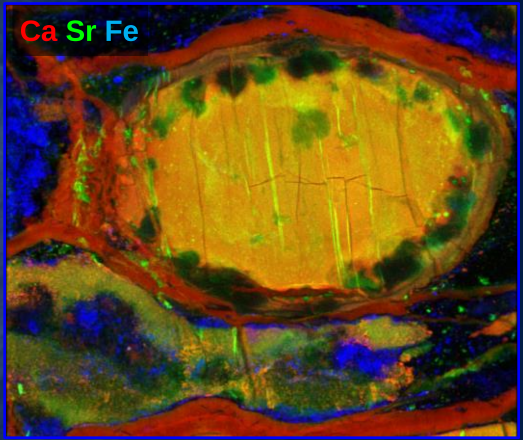
A new approach …

Can we correct for spatial variation in:

- Sample composition?
- X-ray relative intensities?
- Background?

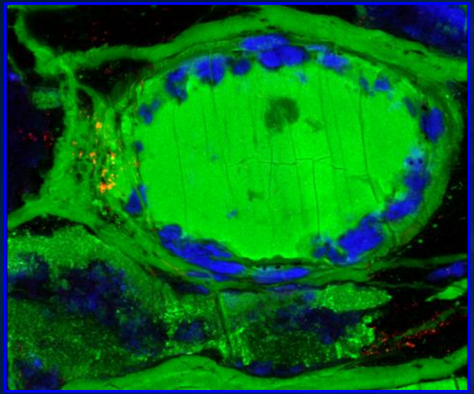
Dynamic Analysis method → Multi-Phase (MPDA)

Can fit isolated phases → build MPDA from linear combination of phase terms

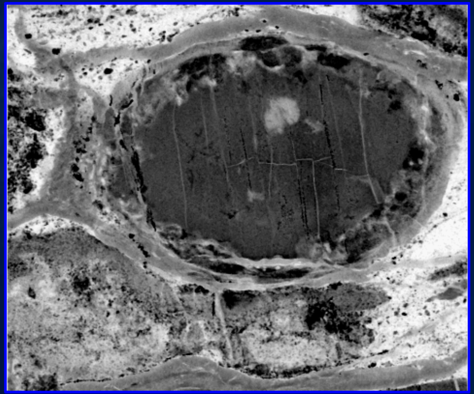


Approach:

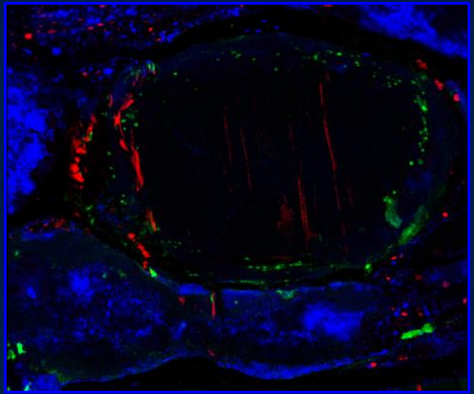
- Project phase maps
- Extract spectra for representative end-members
- Fit spectra to build a DA matrix for each phase.
- **Can we combine these to better re-process data?**



cov coll mill



silicate



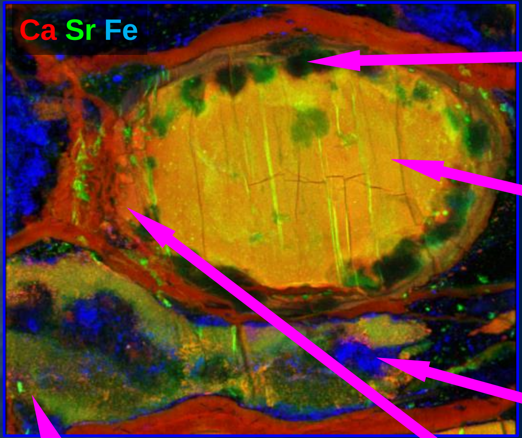
bar uran py

Use per phase:

- ✓ Correct composition → SXRF yields
- ✓ Correct X-ray line relative intensities
- ✓ Correct background shape
- ✓ These flow into DA matrices

Dynamic Analysis method → Multi-Phase (MPDA)

Can fit isolated phases → build MPDA from linear combination of phase terms



Approach:

- Project phase maps
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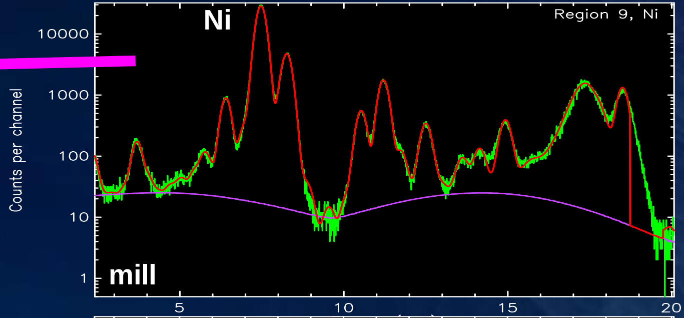
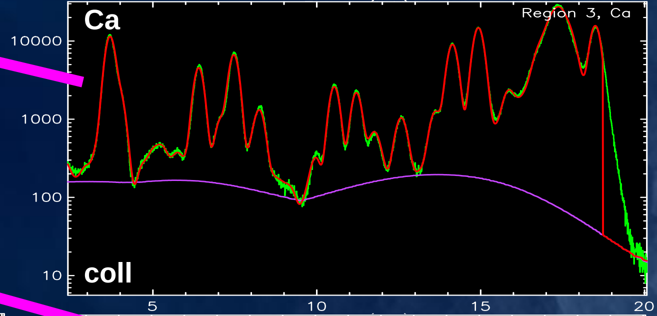
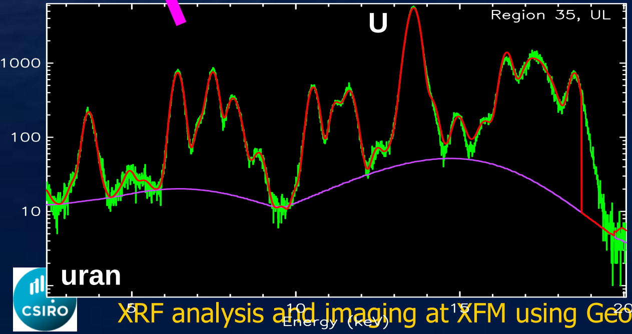
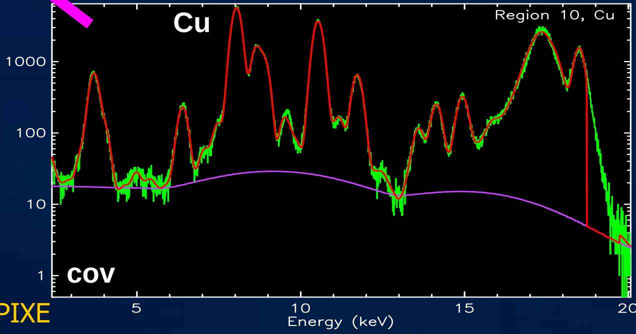
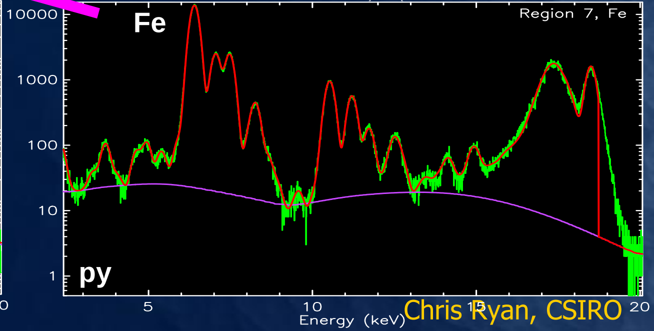




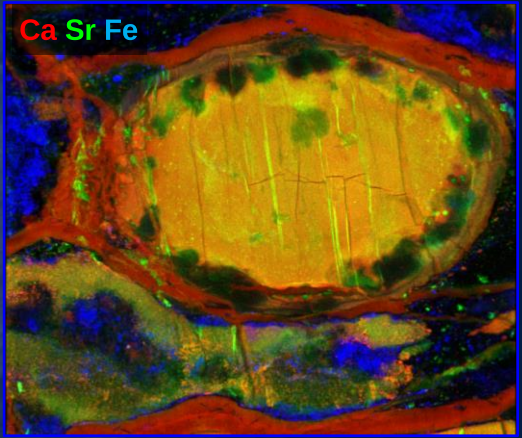






Dynamic Analysis method → Multi-Phase (MPDA)

Can fit isolated phases → build MPDA from linear combination of phase terms

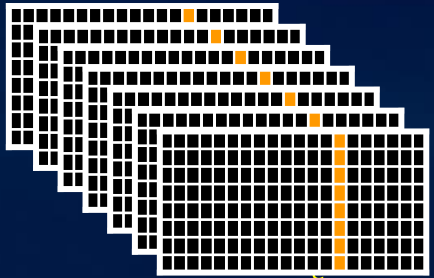


Approach:

- Project phase maps
- Extract spectra for representative end-members
- Fit spectra to build a DA matrix for each phase.
- Combine these to better re-process data

Γ∝1/Y. Hence, this is analogous to the phase weighted inverse yields.

Γ Matrix stack



one for each 'phase' *j*

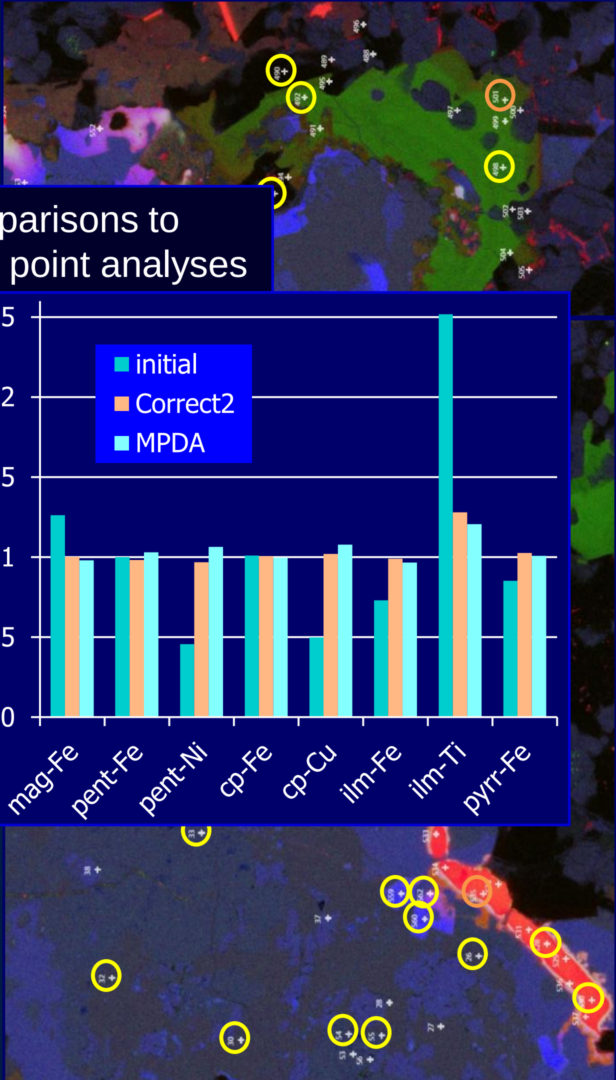
Build Images

For each element *k image*, accumulate for each event (*exy*):

$$\delta C_k = \frac{\sum_j \Gamma_{kj}(e).phase_j(xy)}{\sum_j phase_j(xy)}$$

with each DA matrix *Γ* for phase *j* weighted by 'phase' fraction.

Comparisons to EMP point analyses



Le Vaillant *et al.*, CSIRO

Dynamic Analysis method → Multi-Phase (MPDA)

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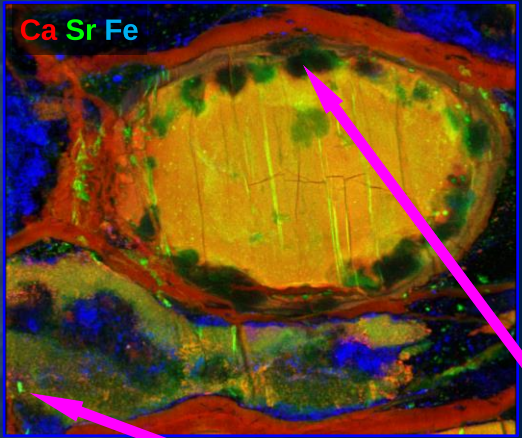


Approach:

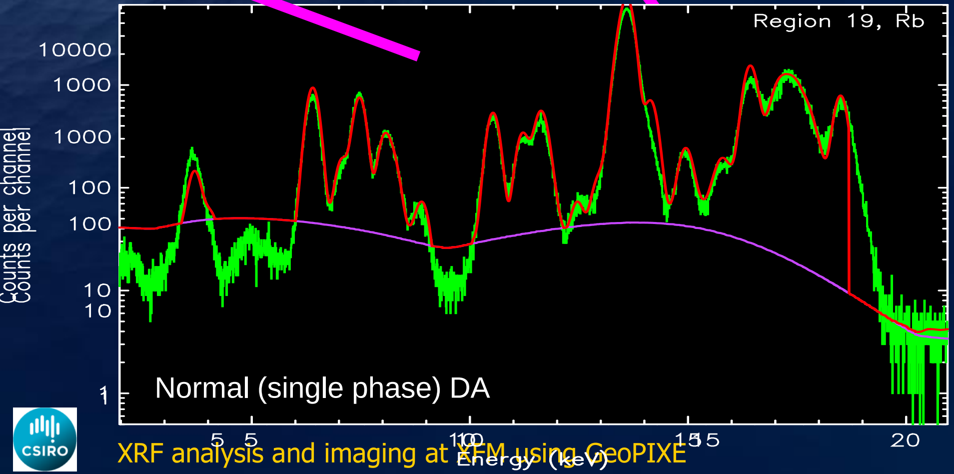
- Project phase maps
- Extract spectra for representative end-members
- Fit spectra to build a DA matrix for each phase.
- Combine these to re-process data
- Reconstruct spectra from phase terms

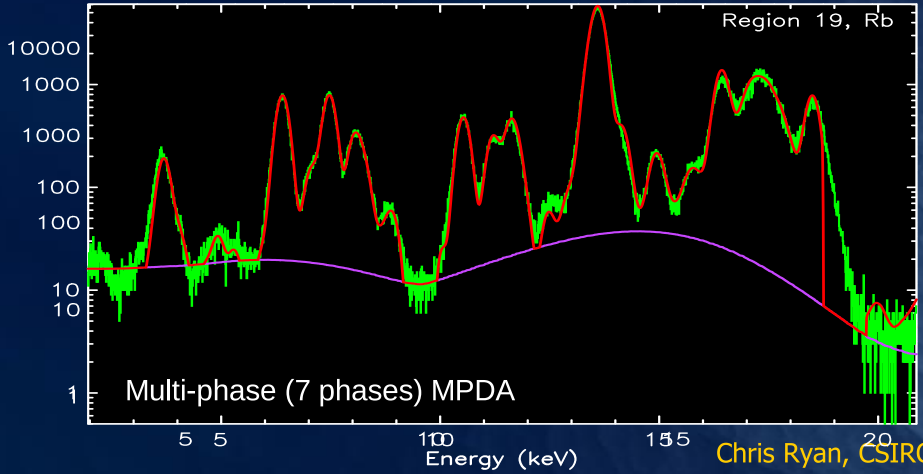
Reconstruct spectrum overlay

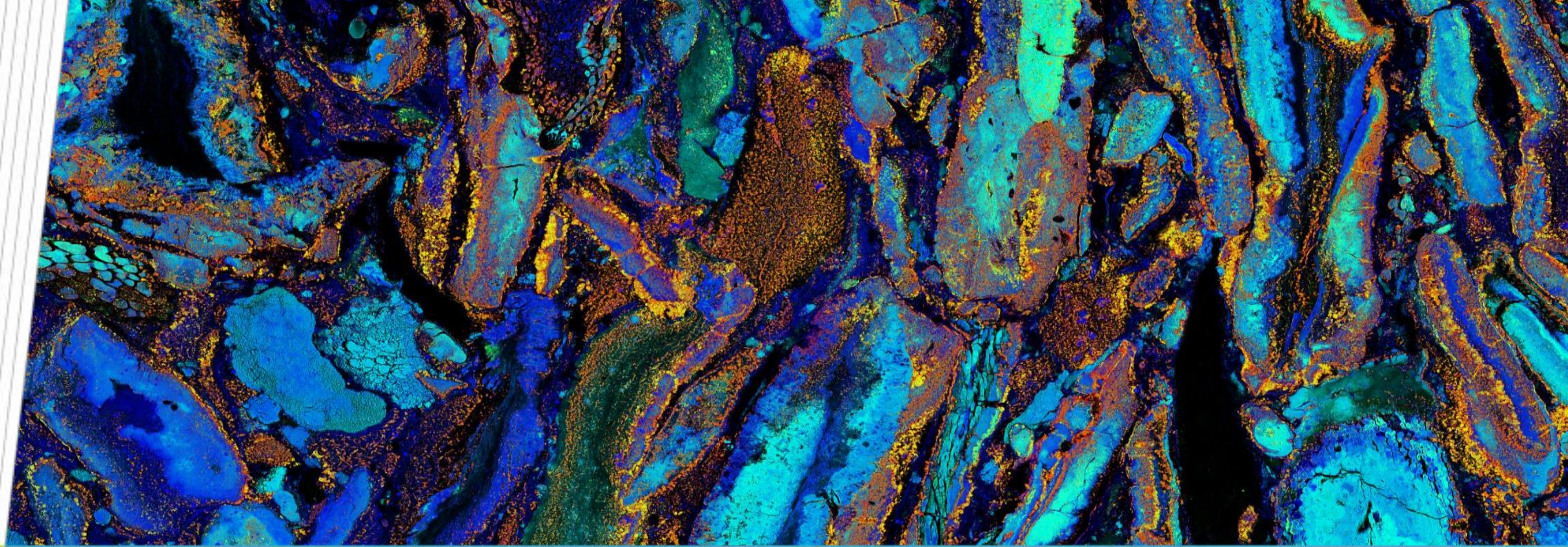
Terms:

- region 'conc' C_k
- 'pure' element spectra
- phase averaged yields $<Y>_k$

$$\frac{Q.\sum_{kj} f_k.<Y>_k C_k.pure_{kj}.phase_j(region)}{\sum_j phase_j(region)}$$







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Thank you

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Chris Ryan
CSIRO Mineral Resources

Explore GeoPIXE *demo data* and “worked examples” on ASCI …

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