X-ray Fluorescence Analysis

David Paterson, Principal Scientist
X-ray Fluorescence Microscopy and
X-ray Absorption Spectroscopy

Outline of Lecture

X-ray fluorescence analysis

Chiba University
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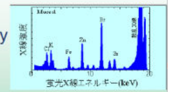

Introduction to X-ray fluorescence (XRF)

- Interaction of X-rays with matter
- Principle of X-ray fluorescence analysis
- Applications and examples

Synchrotron radiation and XRF analysis

- High brilliance: exceptional sensitivity
- Parallel beam, low divergence: microprobe => microscopy
- Energy tunability: elemental selectivity, XAS and microspectroscopy

X-ray fluorescence microscopy (XFM) and 3D techniques

- Detector advances: Maia detector &event mode acquisition
- Megapixel imaging, what does it enable?
- 3D techniques, tomography, XANES imaging, examples

Conclusions and future directions

- Summary: pros and cons of XRF
- Future directions: e.g. 3D XANES imaging

X-ray fluorescence analysis

Tokyo University of Science
Department of Applied Chemistry

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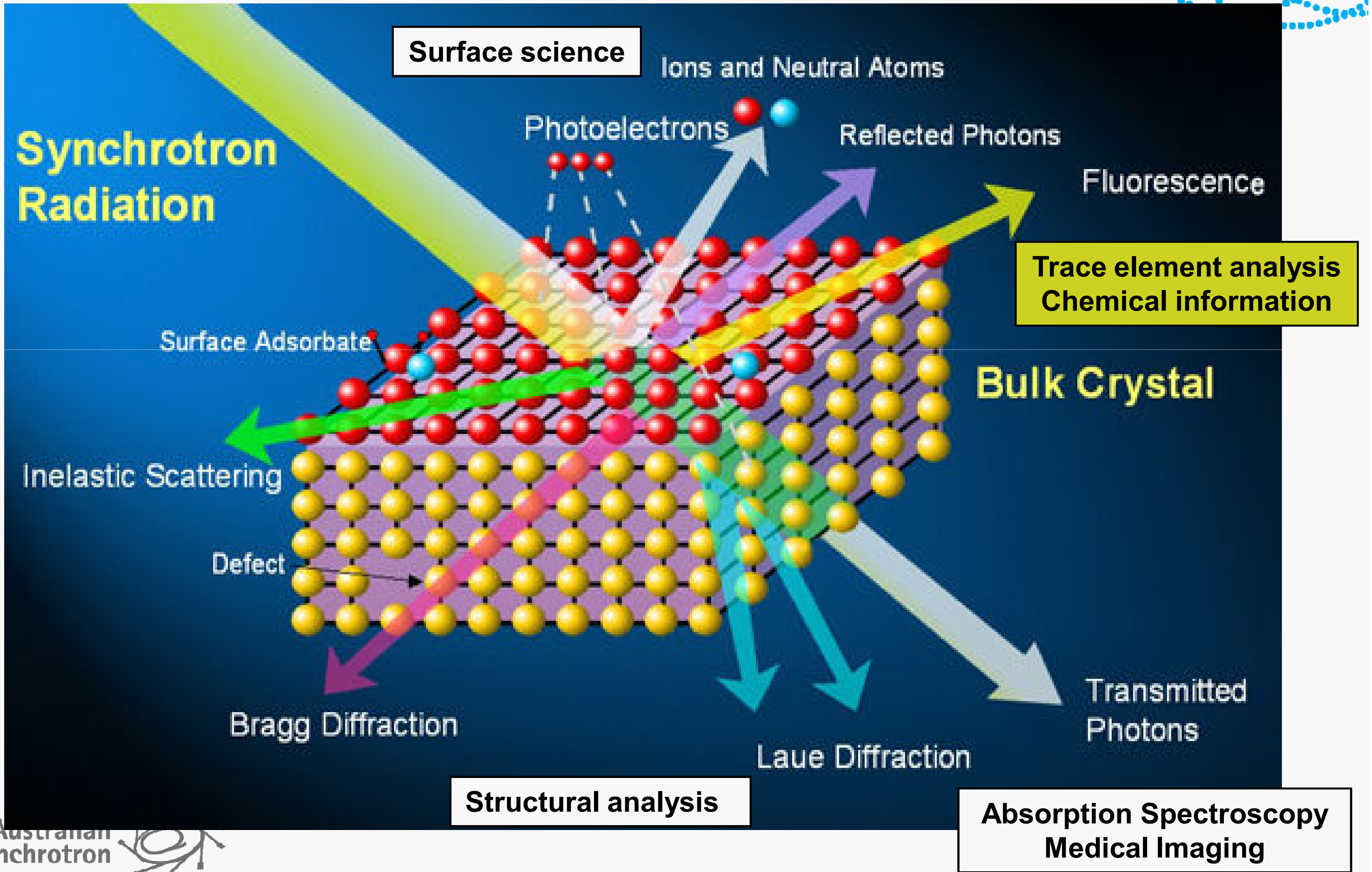
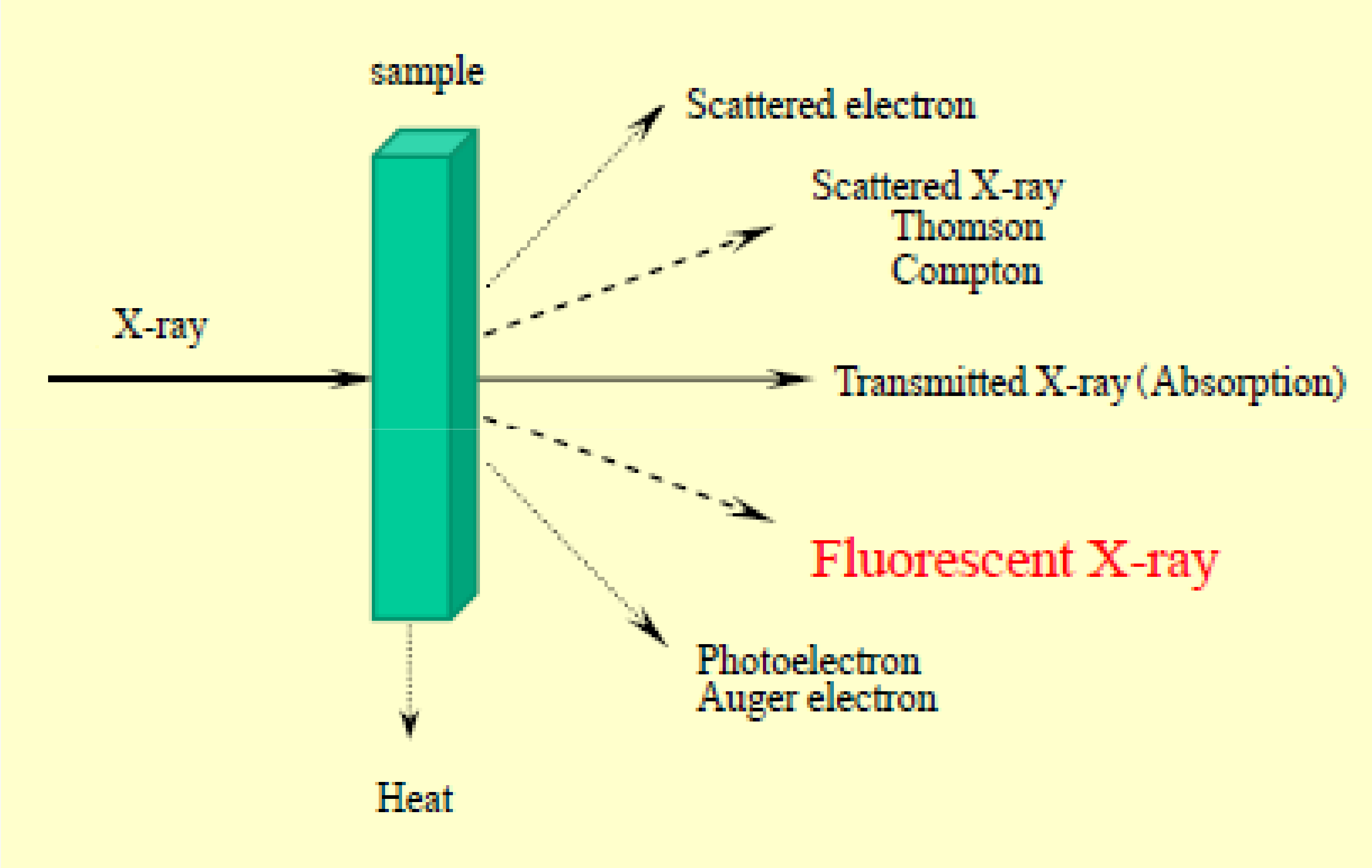
Interaction of X-rays with matter

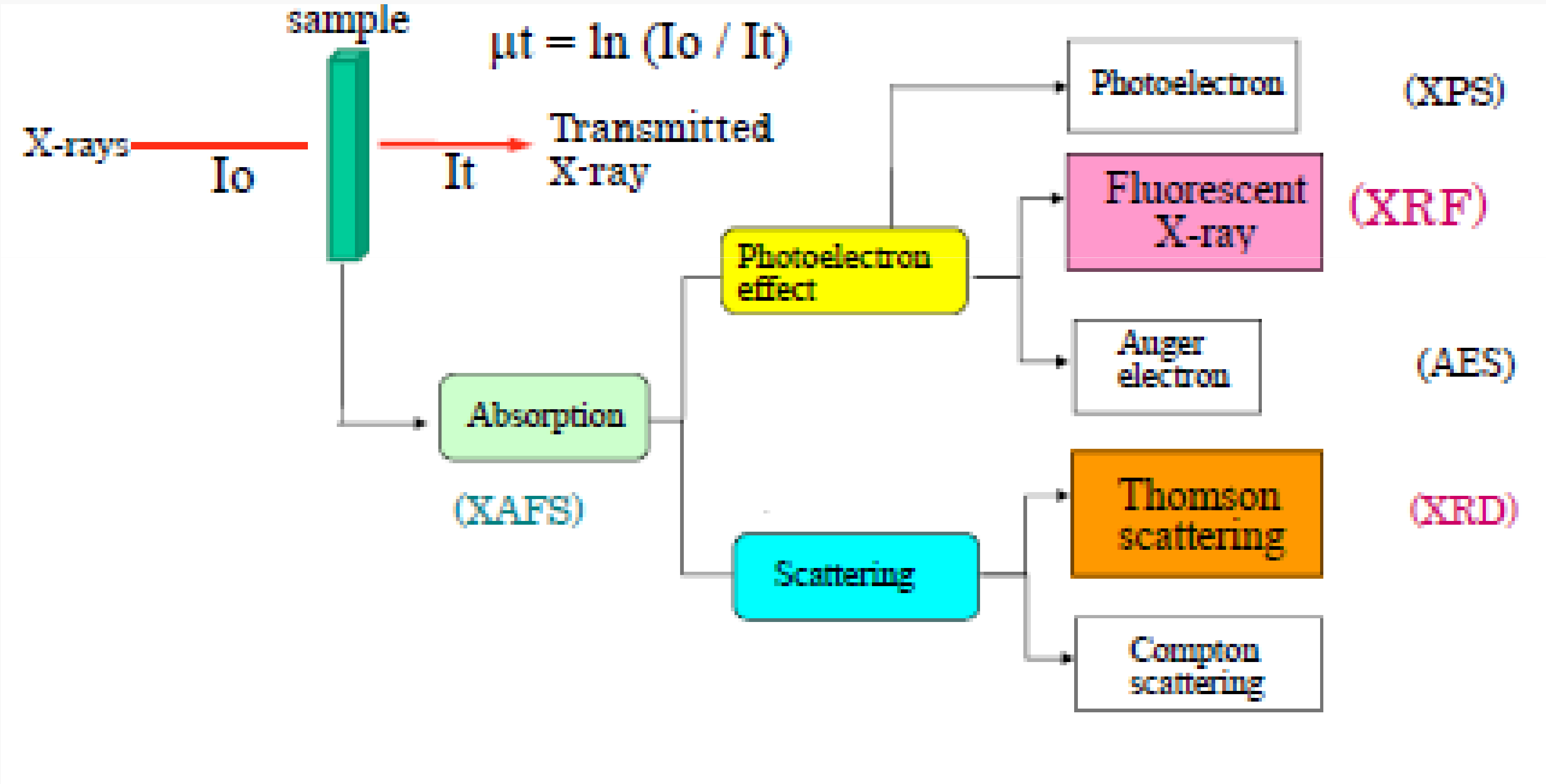


Courtesy SRRC, Taiwan

Interaction of X-rays with matter



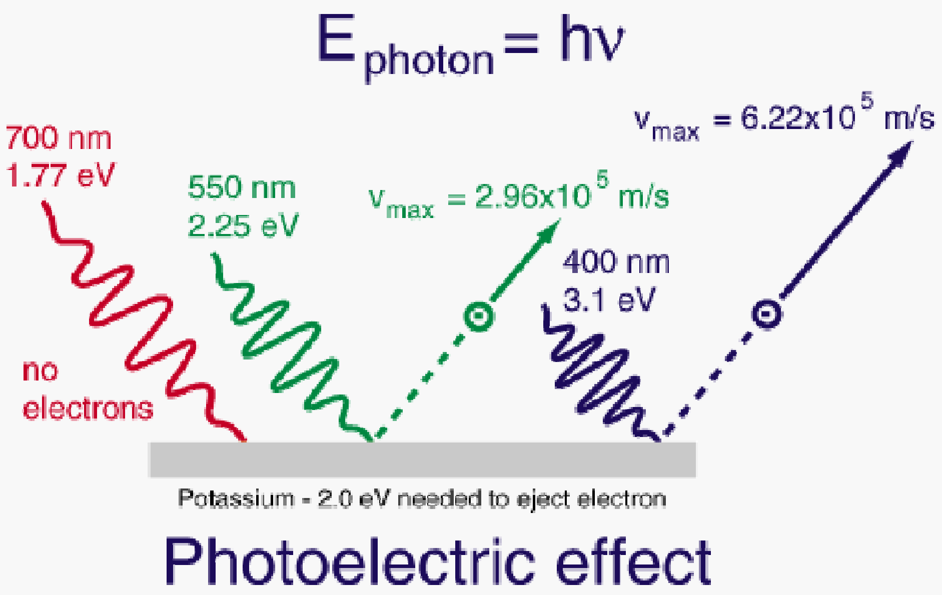
Interaction of X-rays with matter

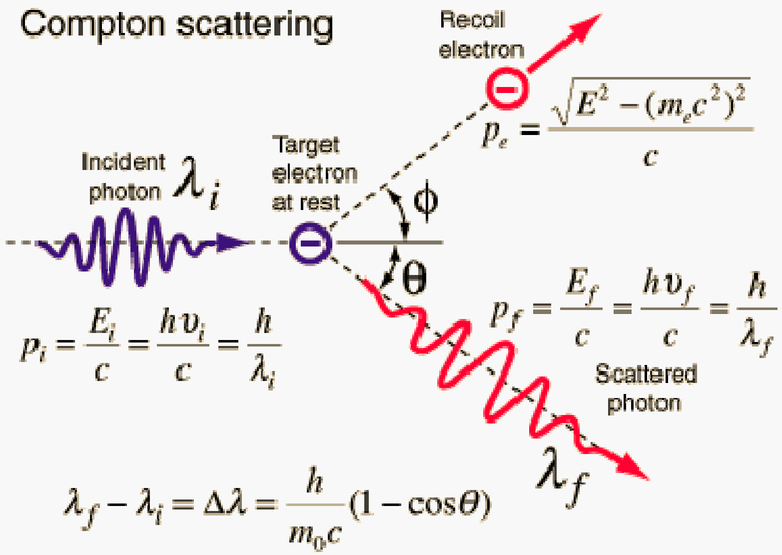


What is light?

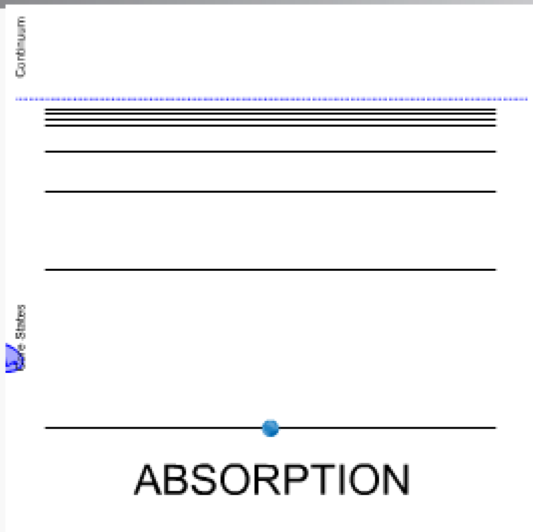
2 models

- Particle (photon)





Electron – x-ray interactions



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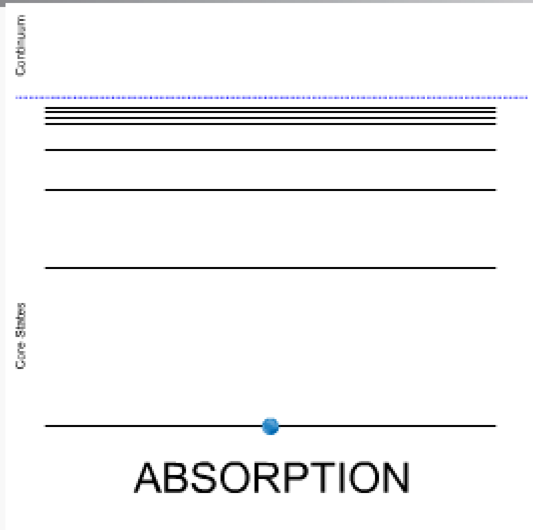

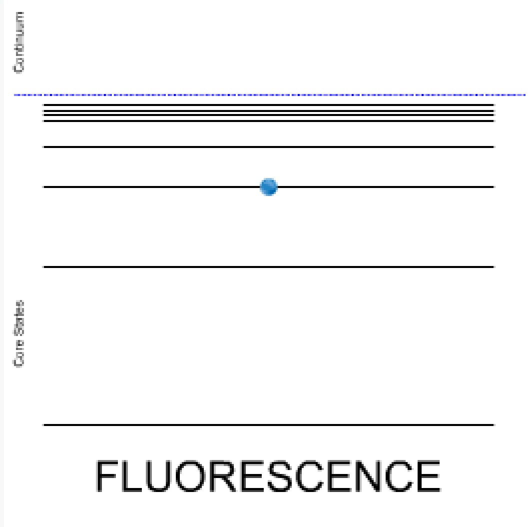

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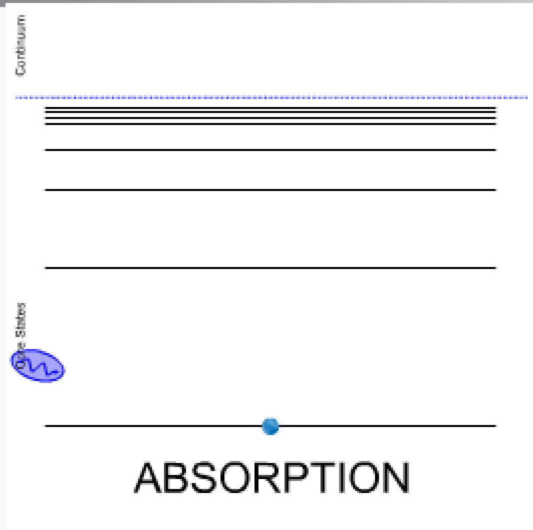

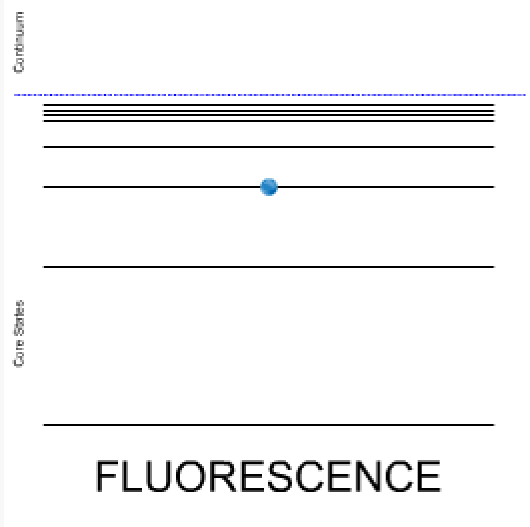

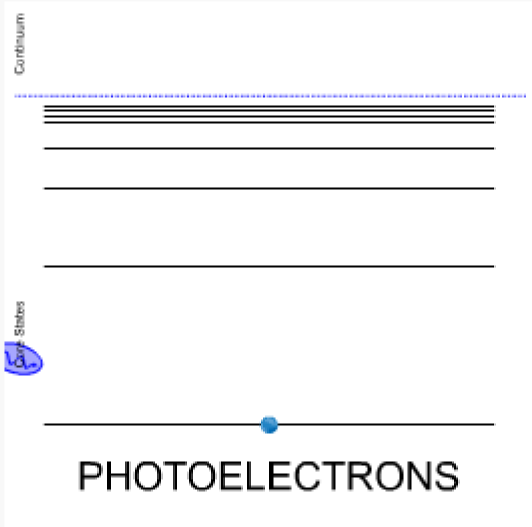

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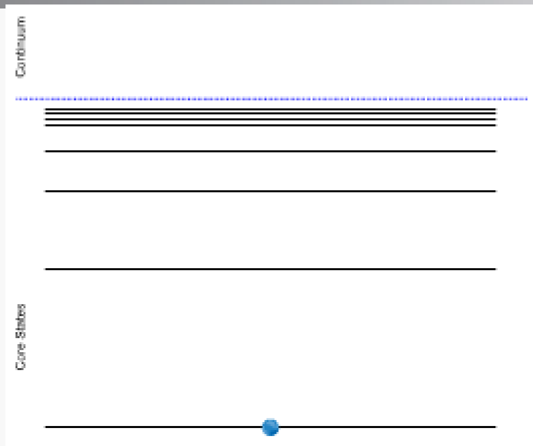
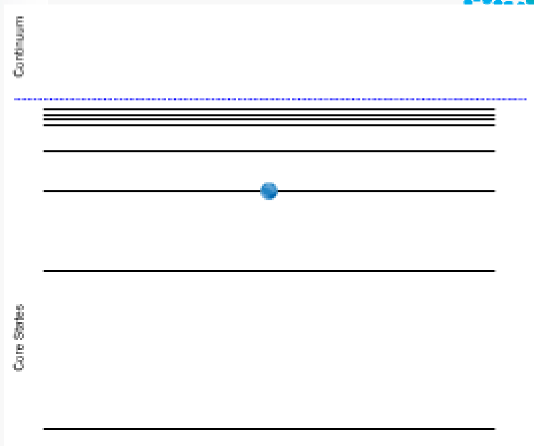
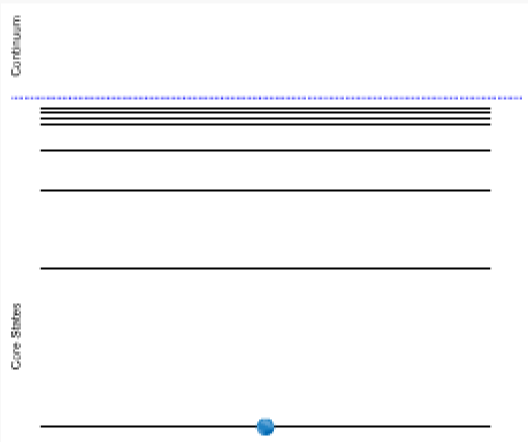


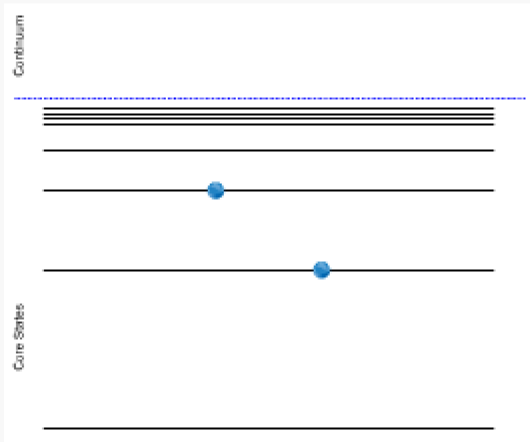
ABSORPTION



FLUORESCENCE



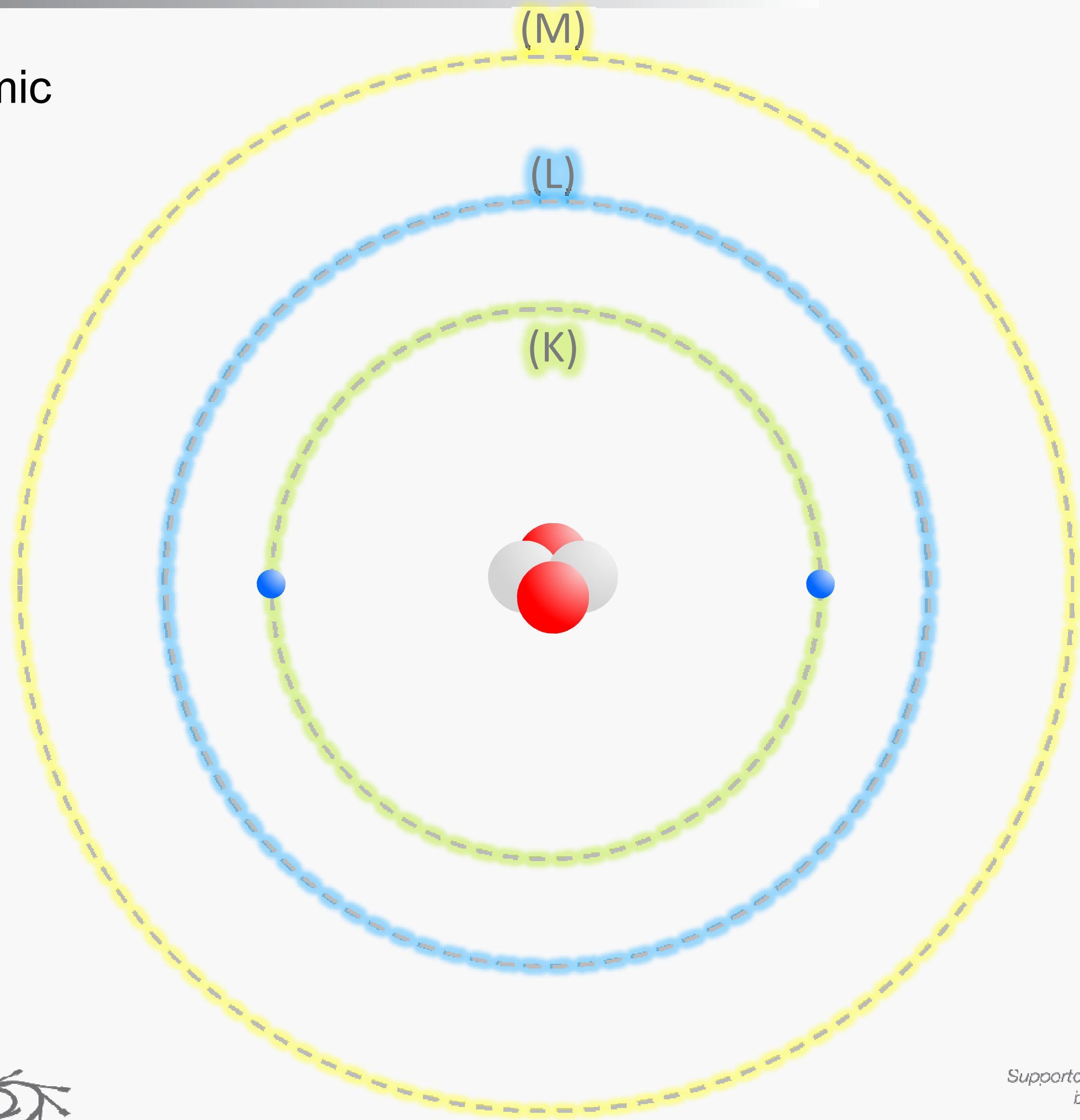
PHOTOELECTRONS



AUGER PROCESS

Atomic Edges

Simplified atomic model



Each also has sub shells known as s, p, d, f etc.

Electrons are free to move between these shells provided they obey some simple rules.

X-ray fluorescence

- A method for determining elemental composition

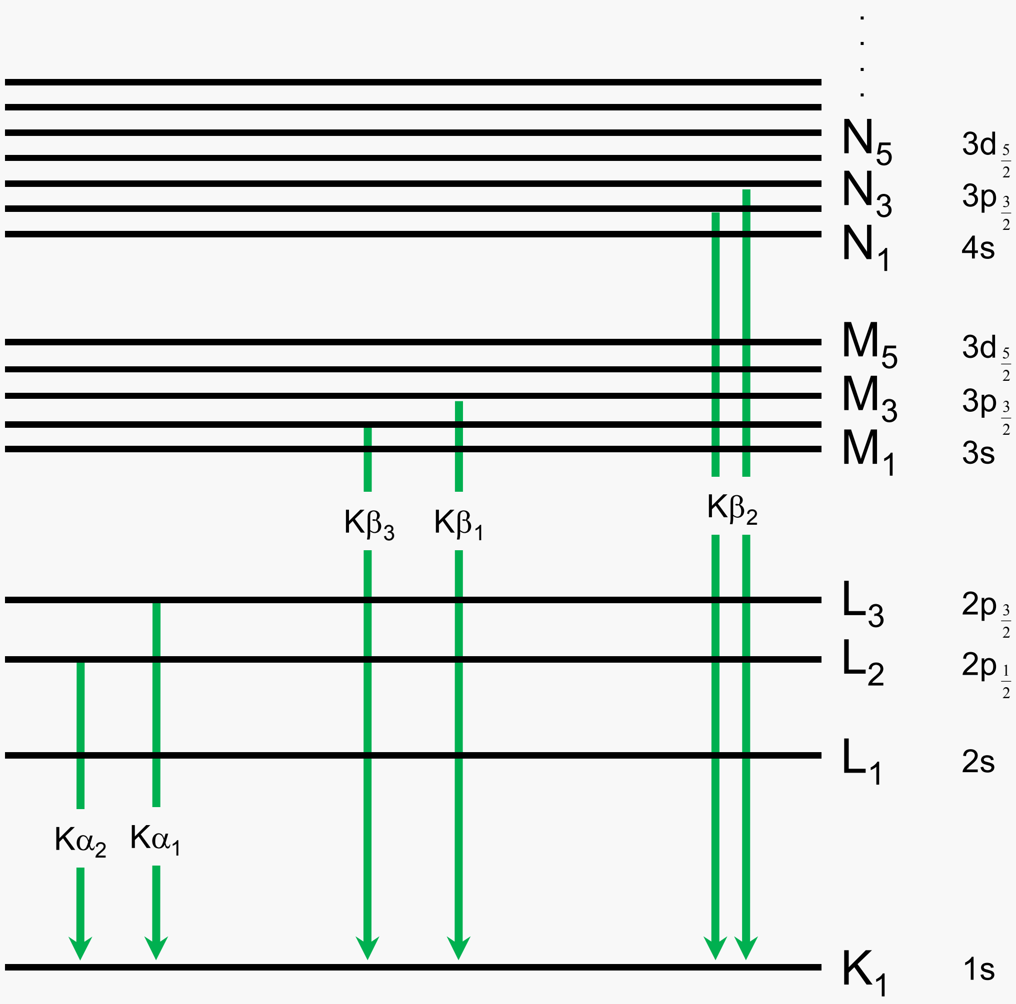
- Electrons are excited to a higher energy state

- Unstable at higher energies so electrons will decay to the lowest energy state

- Emission of light is the result

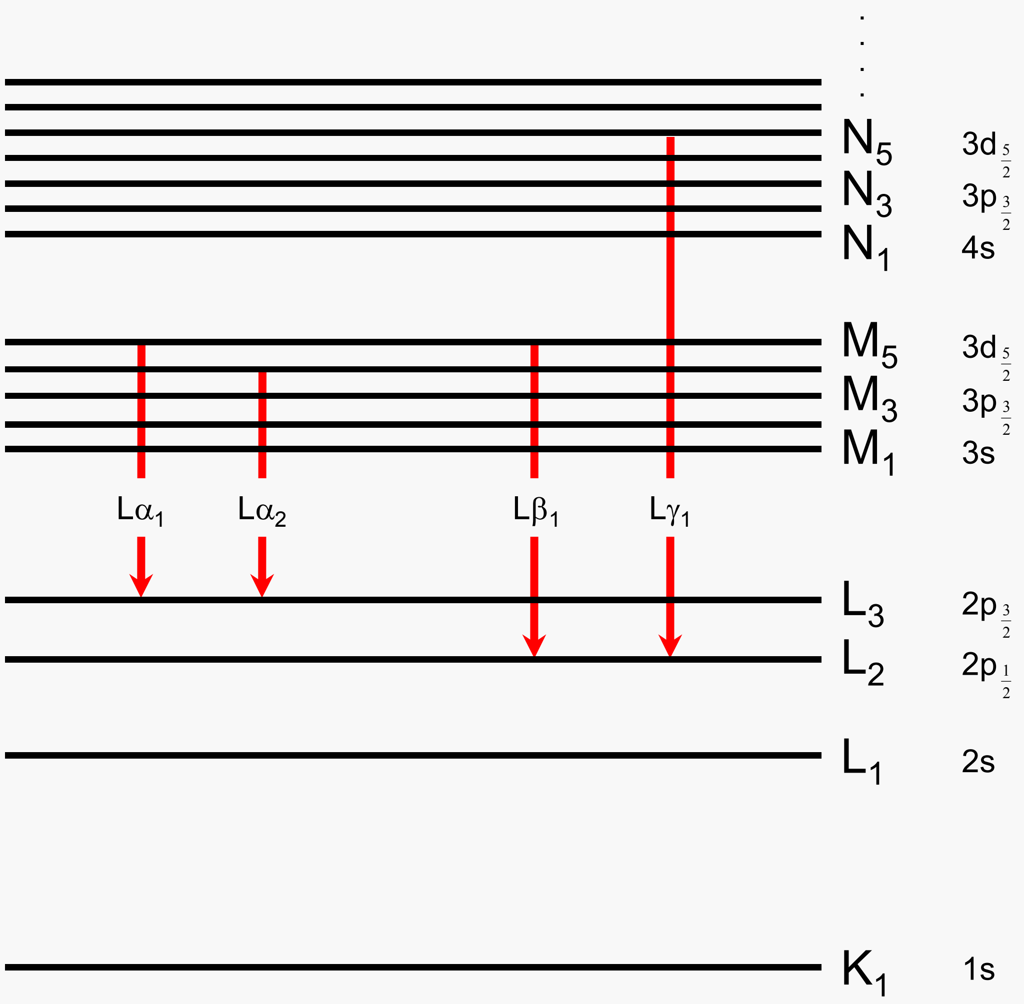
X-ray fluorescence

'K' Edges

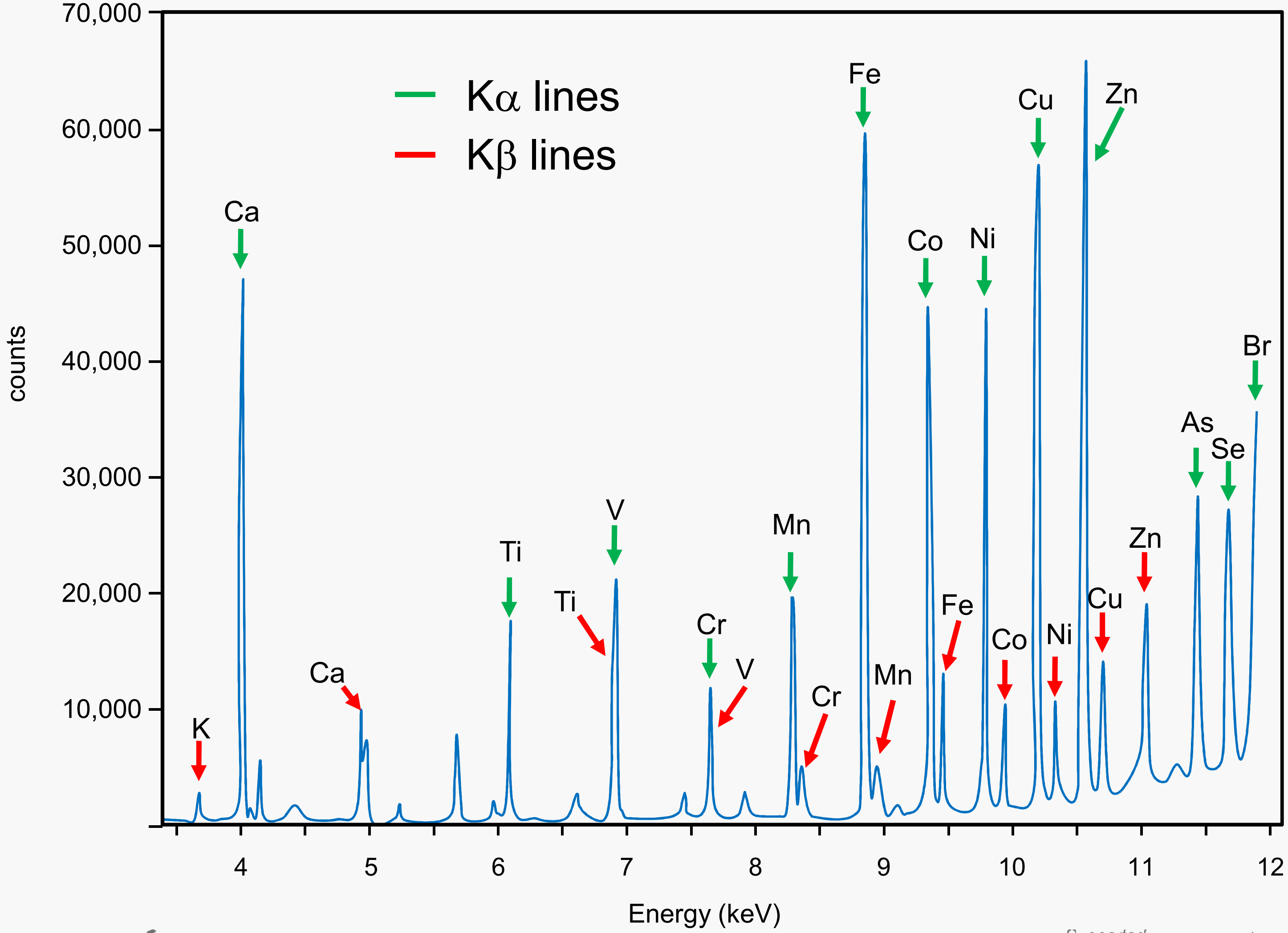


X-ray fluorescence

‘L’ Edges



X-ray fluorescence



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Principles of XRF analysis

Energy

- Qualitative
- Elemental determination
- Chemical information
- Spectroscopy

Intensity

- Counts or peak height
- Proportional to concentration
- Relative
- Quantitative
- Calibration is relatively straightforward

Detection of XRF, EDS and WDS

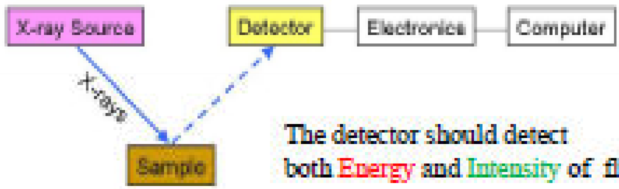
How to measure E and I.

Two methods of XRF analysis

(a) Energy dispersive spectroscopy

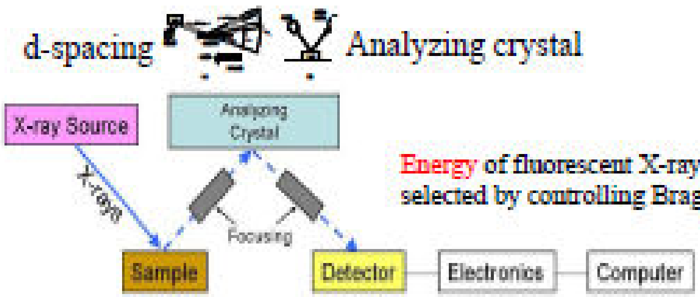
(b) Wavelength dispersive spectroscopy

EDS



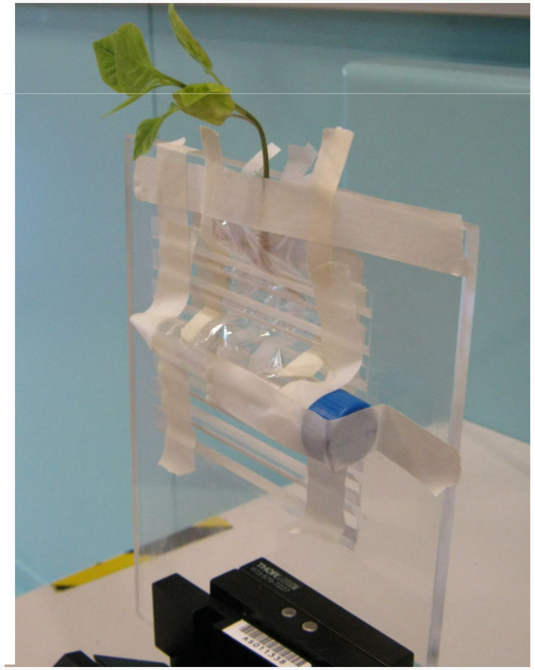
The detector should detect both Energy and Intensity of fluorescent X-ray

WDS

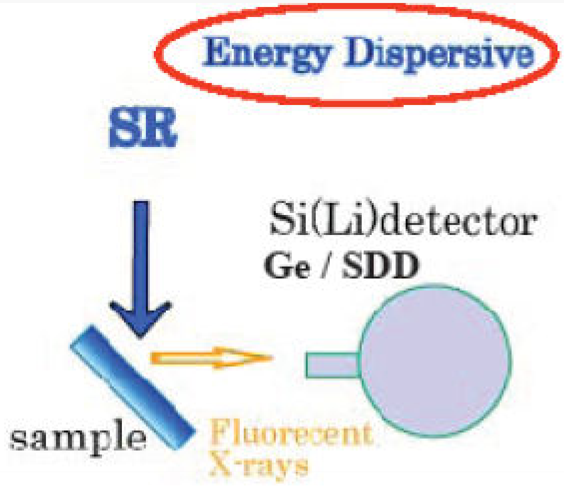


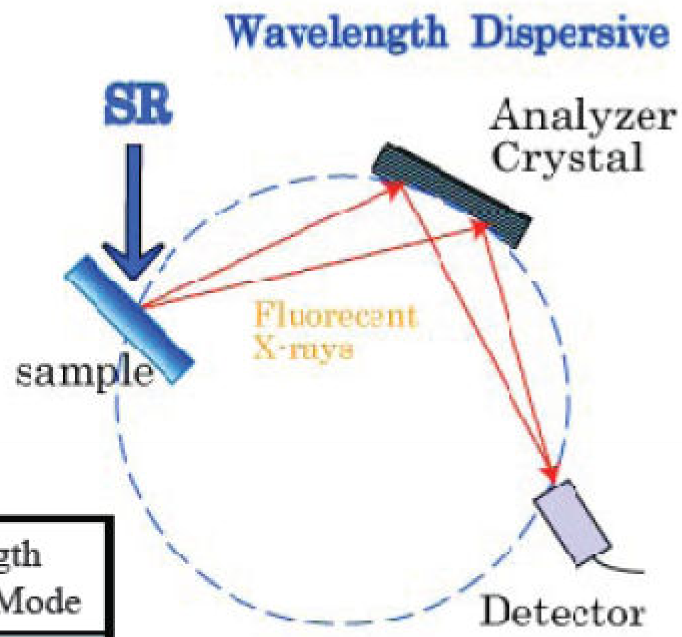
Energy of fluorescent X-ray can be selected by controlling Bragg angle.

©http://www.postech.ac.kr/dept/mse/axal/index.html



WDS and EDS





	Energy Dispersive Mode	Wavelength Dispersive Mode
Advantage	•High Efficiency •Multi-elemental detection	•High resolution •High S/B
Disadvantage	•Low resolution •Scattering background	•Low efficiency

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X-ray fluorescence microscopy (XFM) and 3D techniques	• Detector advances: Maia detector & event mode acquisition • Megapixel imaging • 3D techniques
Conclusions and future directions	• Summary: pros and cons of XRF • Future directions: e.g. 3D XANES imaging

X-ray focussing optics

- Introduction:
  - The promise of x-ray optics - diffraction limited focussing ~λ
- Diffractive optics:
  - Bragg diffraction
  - Diffraction gratings
    - Example: Fresnel zone plate
- Refractive
    - Example: compound refractive lens
- Reflective
    - Example: Kirk Patrick-Baez (KB) mirrors
- Combination optics
  - Multilayer coatings

Diffractive optics

•Bragg diffraction

$$m\lambda = 2d\sin(\theta_m)$$

•Grating diffraction

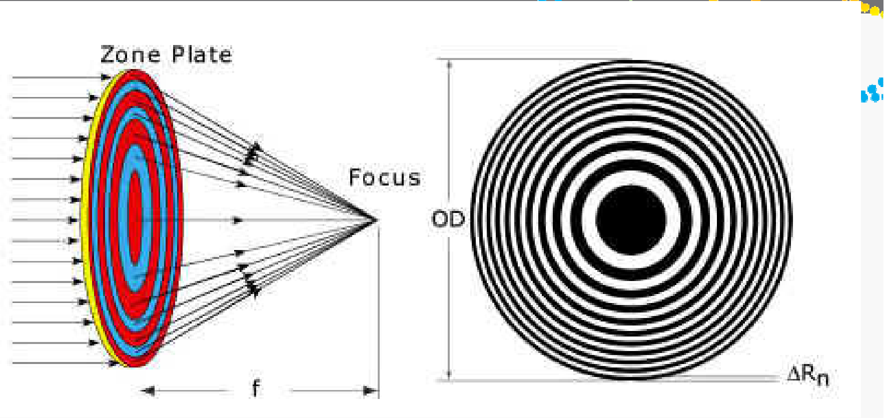
•Double crystal monochromator

•Exercise: how to achieve focussing using Bragg diffraction from a crystal

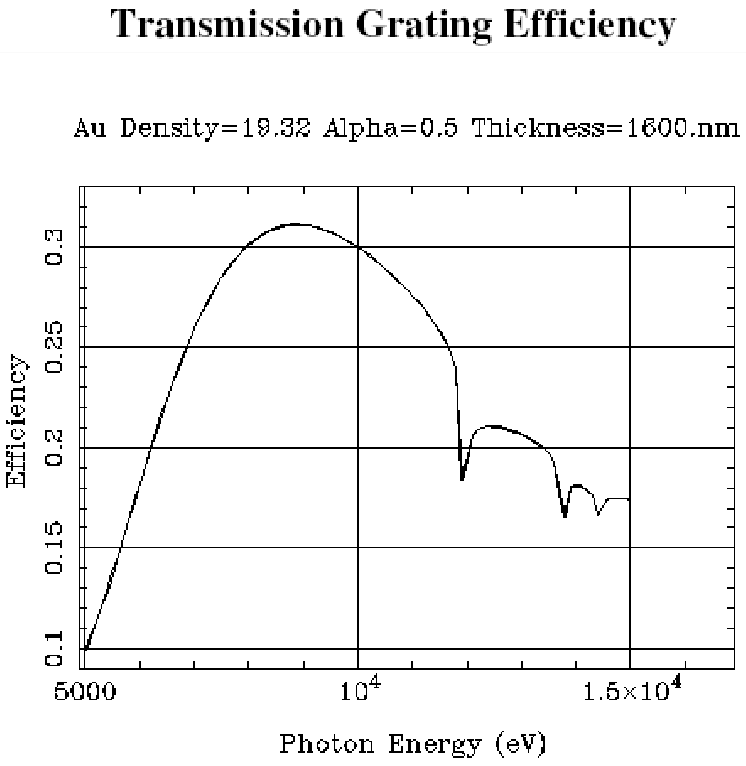
Grating diffraction

- Fresnel Zone plates:
- circular diffraction grating

$$Res = \frac{0.610\lambda}{NA} = 1.22\,\Delta r$$



- Efficiency of zone plate is determined by the transmission grating efficiency
- See:
- http://henke.lbl.gov/optical_constants/tgrat2.html



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Fresnel zone plates

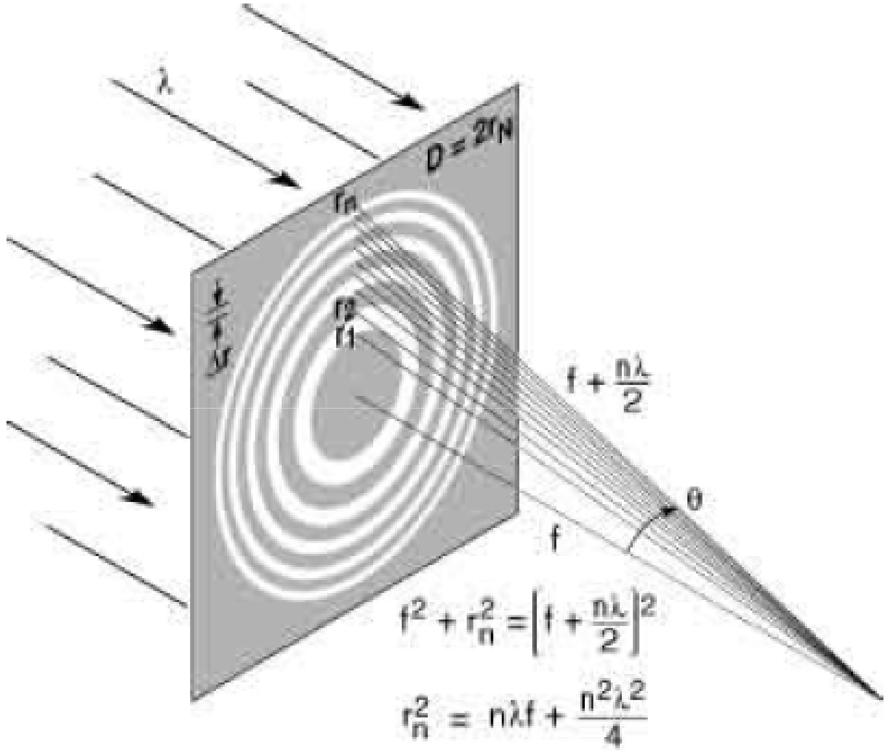
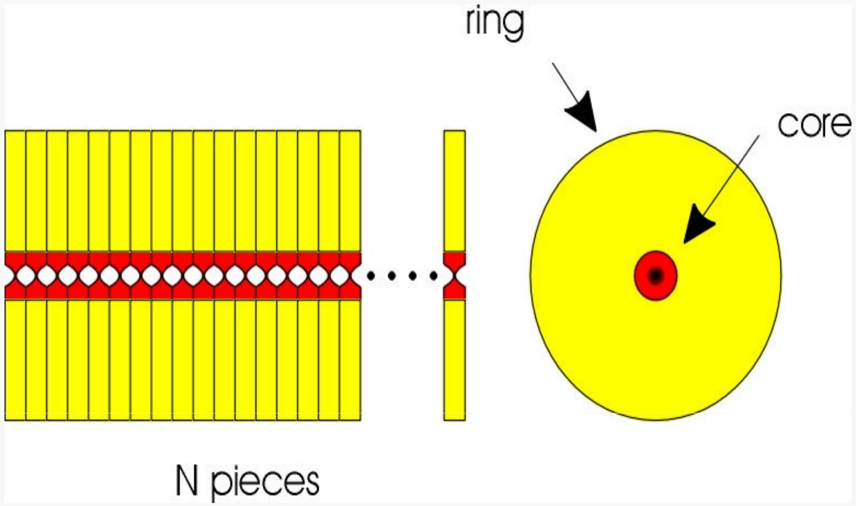
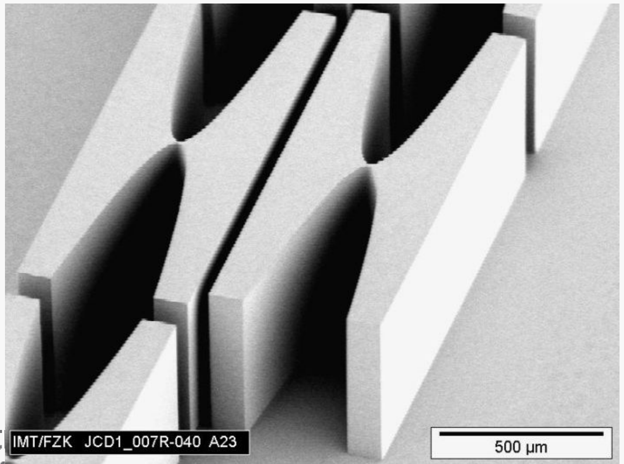
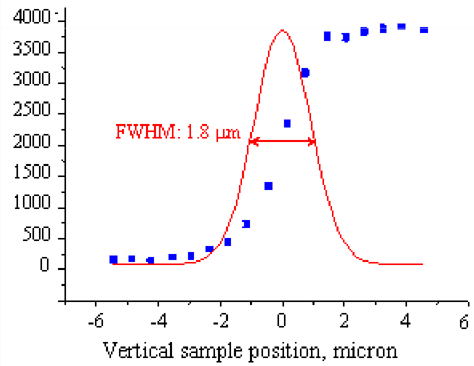


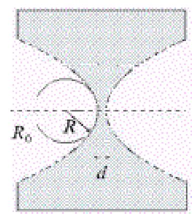
Fig. 4-8. *A Fresnel zone plate lens with plane wave illumination, showing only the convergent (+1st) order of diffraction. Sequential zones of radius r_n are specified such that the incremental path length to the focal point is nl/2. Alternate zones are opaque in the simple transmission zone plate. With a total number of zones, N, the zone plate lens is fully specified. Lens characteristics such as the focal length f, diameter D, and numerical aperture NA are described in terms of l, N, and Dr, the outer zone width. [Courtesy of Cambridge University Press, Ref. 3.]*

Compound refractive lens

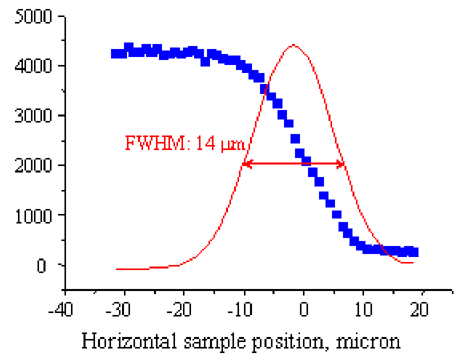




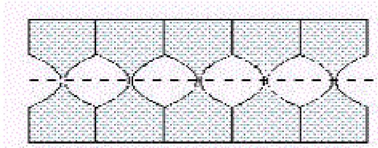




R: 0.2 mm
R_0: 0.45 mm
d: 0.01 mm
material: Al



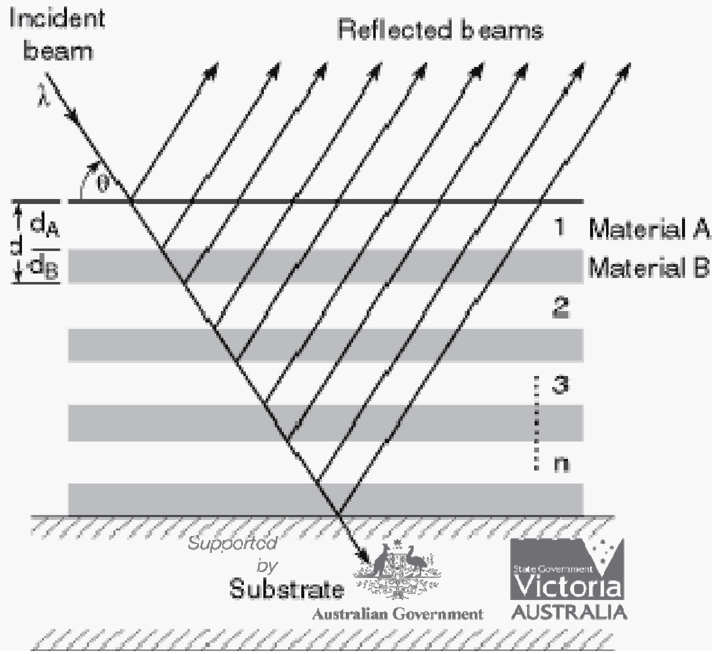
N lenses



Combination optics - multilayer coatings

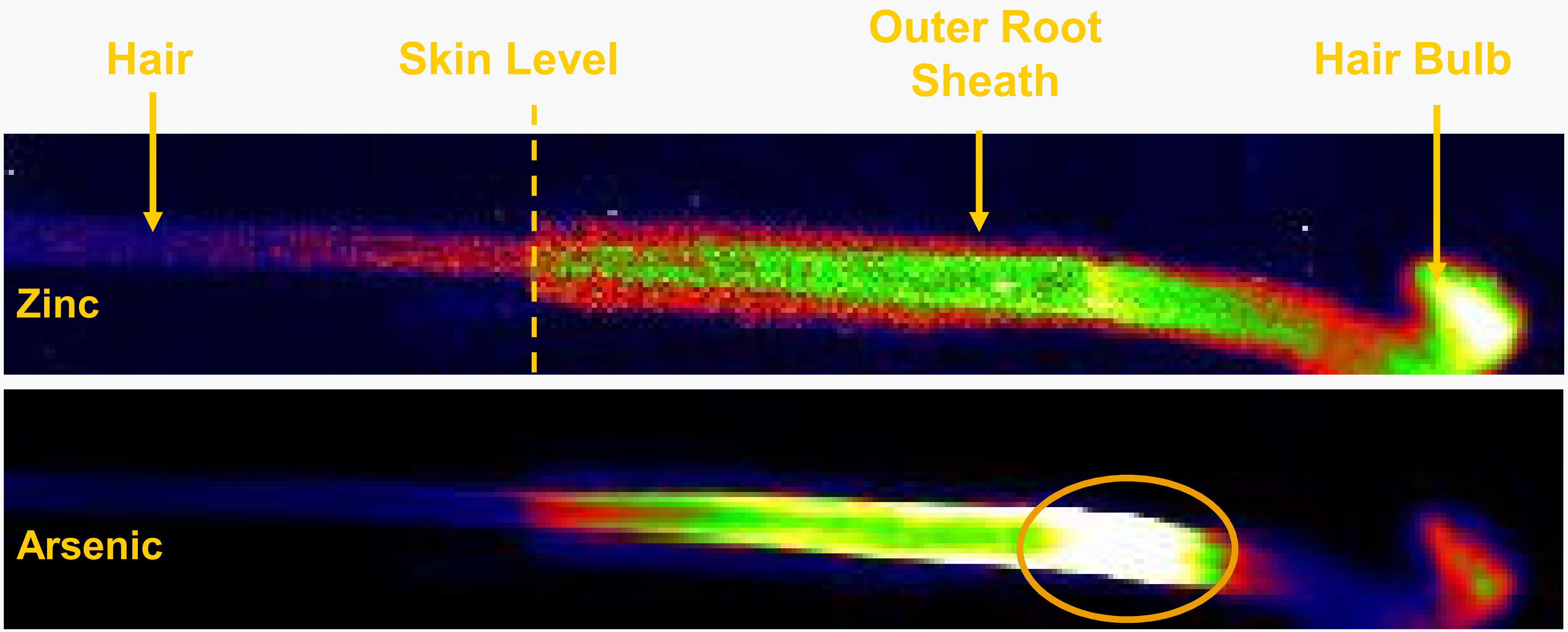
- Multilayers can be used as coatings for glancing incidence optics in the soft and hard x-ray region. Benefits are:
- larger angles of glancing incidence
  - improved collecting area over optics coated with a single metal layer
- energy selective effect
  - a reduction of the bandpass of the reflected radiation
- Multilayers are used to coat optical elements for instruments such as x-ray microprobes, spectrometers and monochromators at synchrotron beamlines.

- http://henke.lbl.gov/multilayer/mltutor.html



A legendary cold case

- Phar Lap's hair was analysed for heavy metals



High arsenic consistent with a large amount of arsenic ingested in the champion's last 30 hours of life

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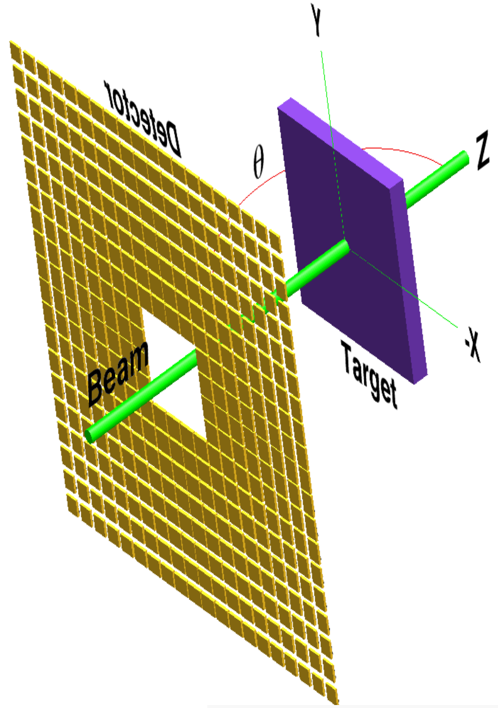
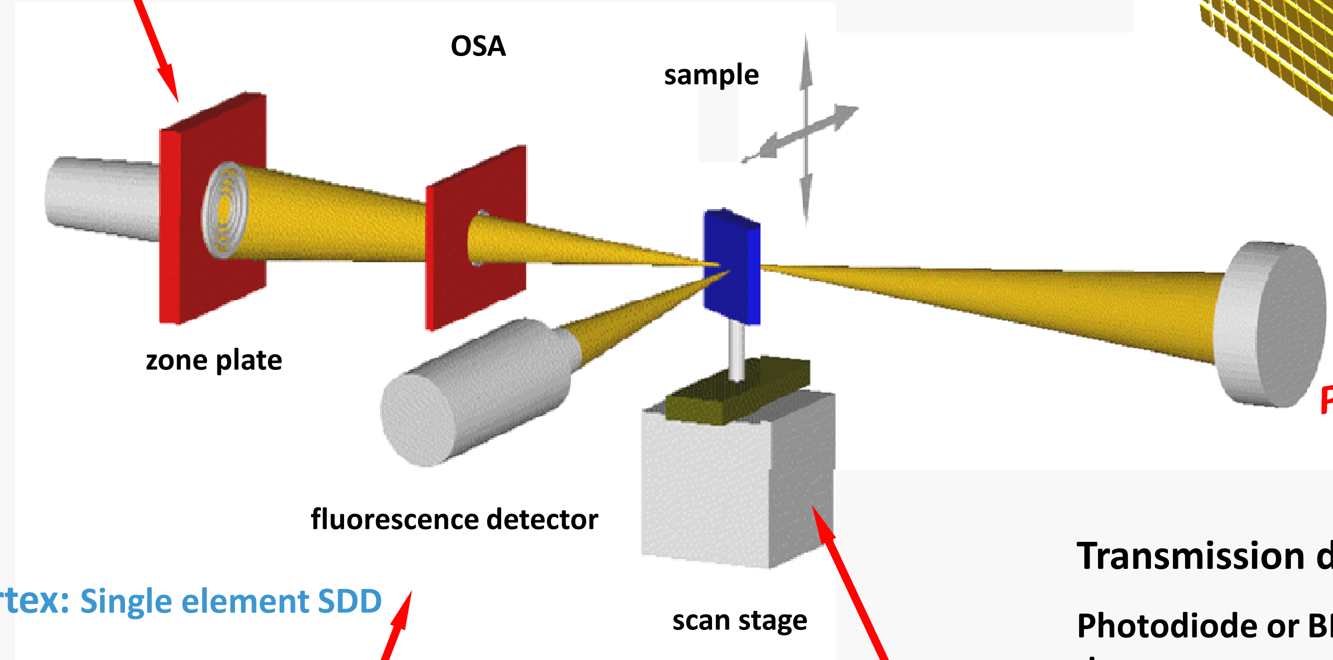
X-ray Fluorescence Microprobe



Fresnel zone plate (FZP) lenses:
~60-500 nm focus

Kirkpatrick-Baez (KB) mirrors: 1-10 μm focus (achromatic)

SXRF elemental imaging



X-ray beam
4-25 keV
undulator
monochromatic,
$\Delta E/E \sim 2\times10^{-4}$

Phase contrast imaging

Vortex: Single element SDD

Maia: planar silicon 384 detector array (CSIRO-BNL)

Stage: Precision XYZ

~10 nm resolution (FZP mode) with laser-interferometry encoders and feedback

Transmission detector:

Photodiode or BNL segmented detector

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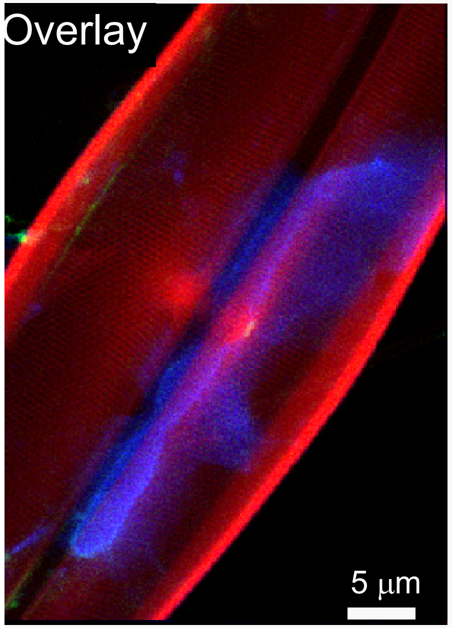
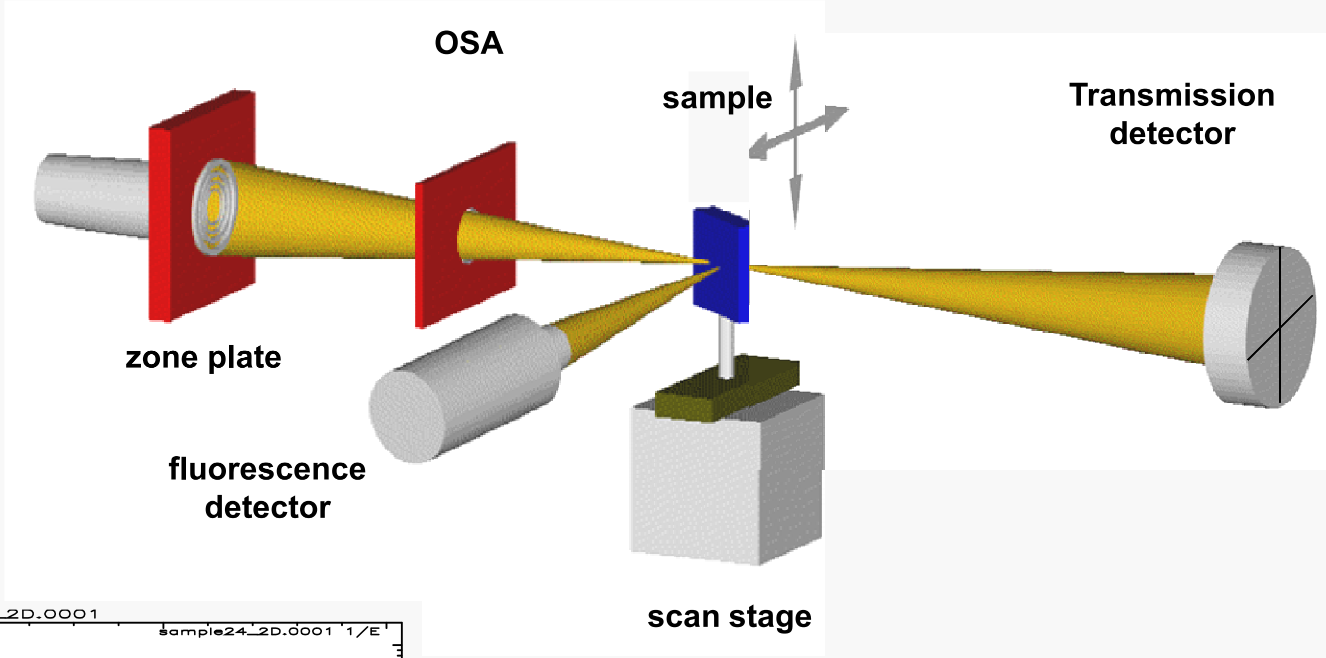
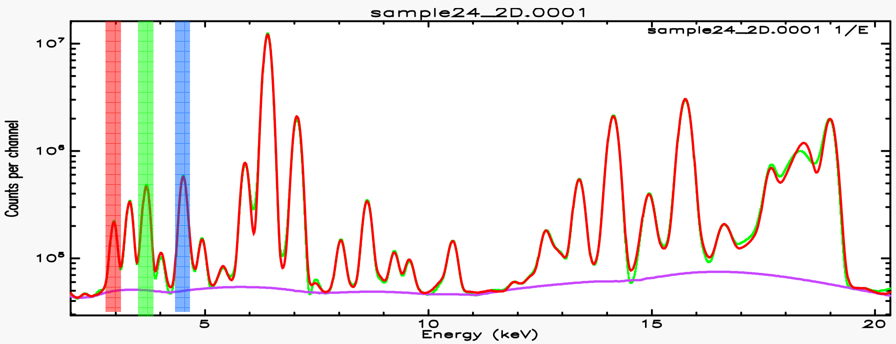
XFM – microprobe & nanoprobe

- - Spot on a specimen;   size: 60 – 500 nm,   DoF: ~150 µm
- - ‘Step and dwell’ or ‘on-the-fly’ scanning to build the image







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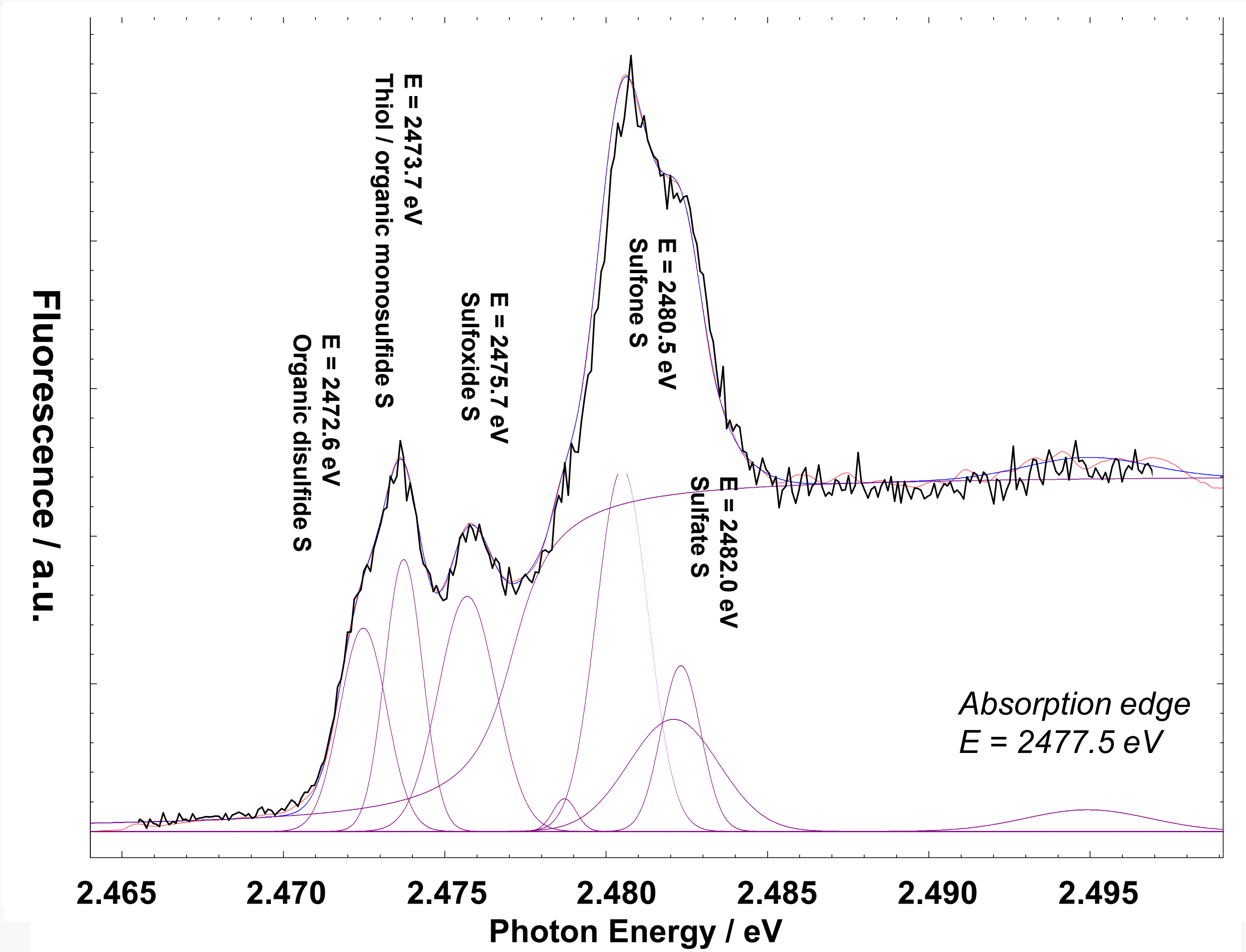
Spectroscopy example



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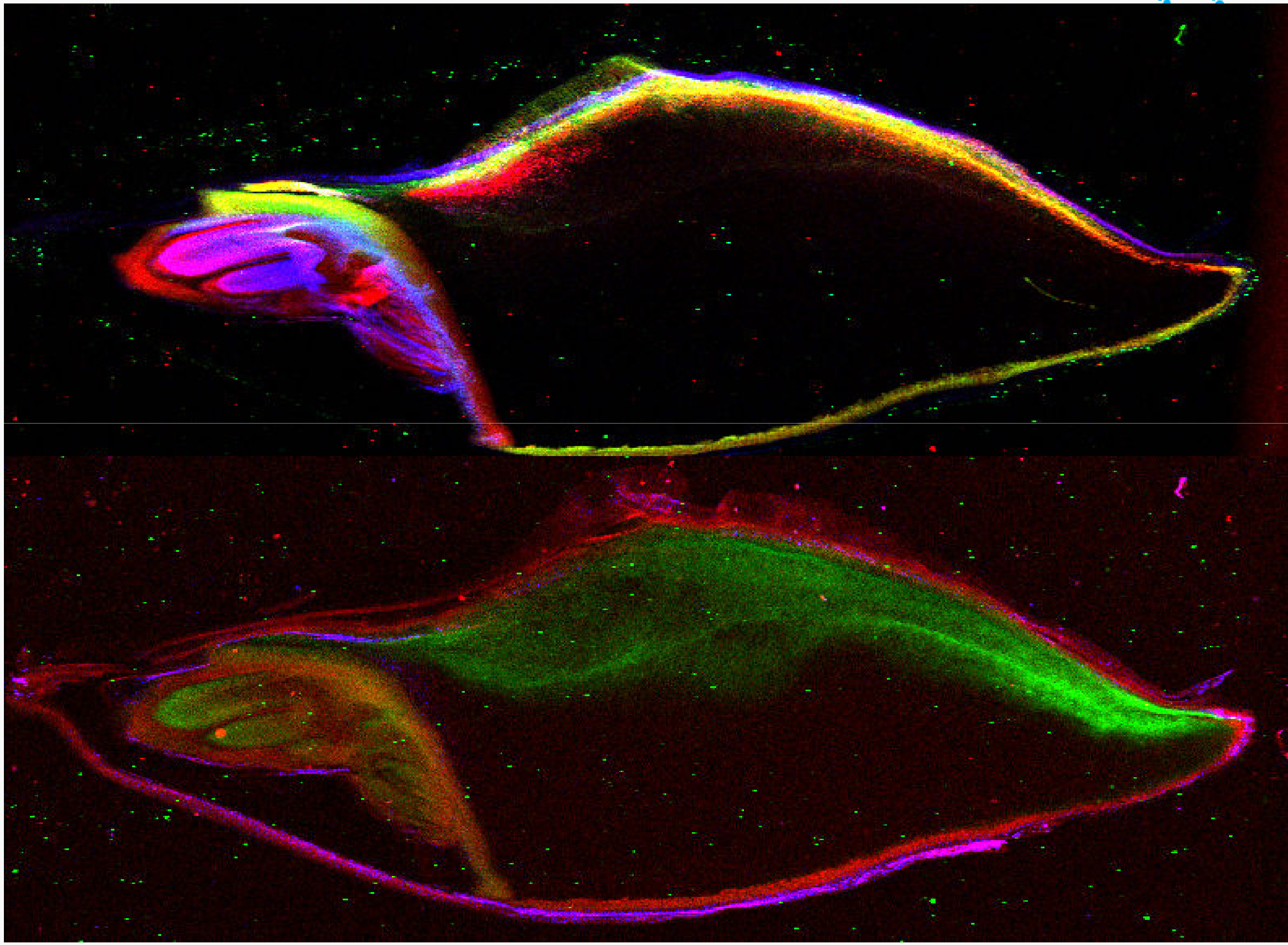
Environmental science – cereal grains

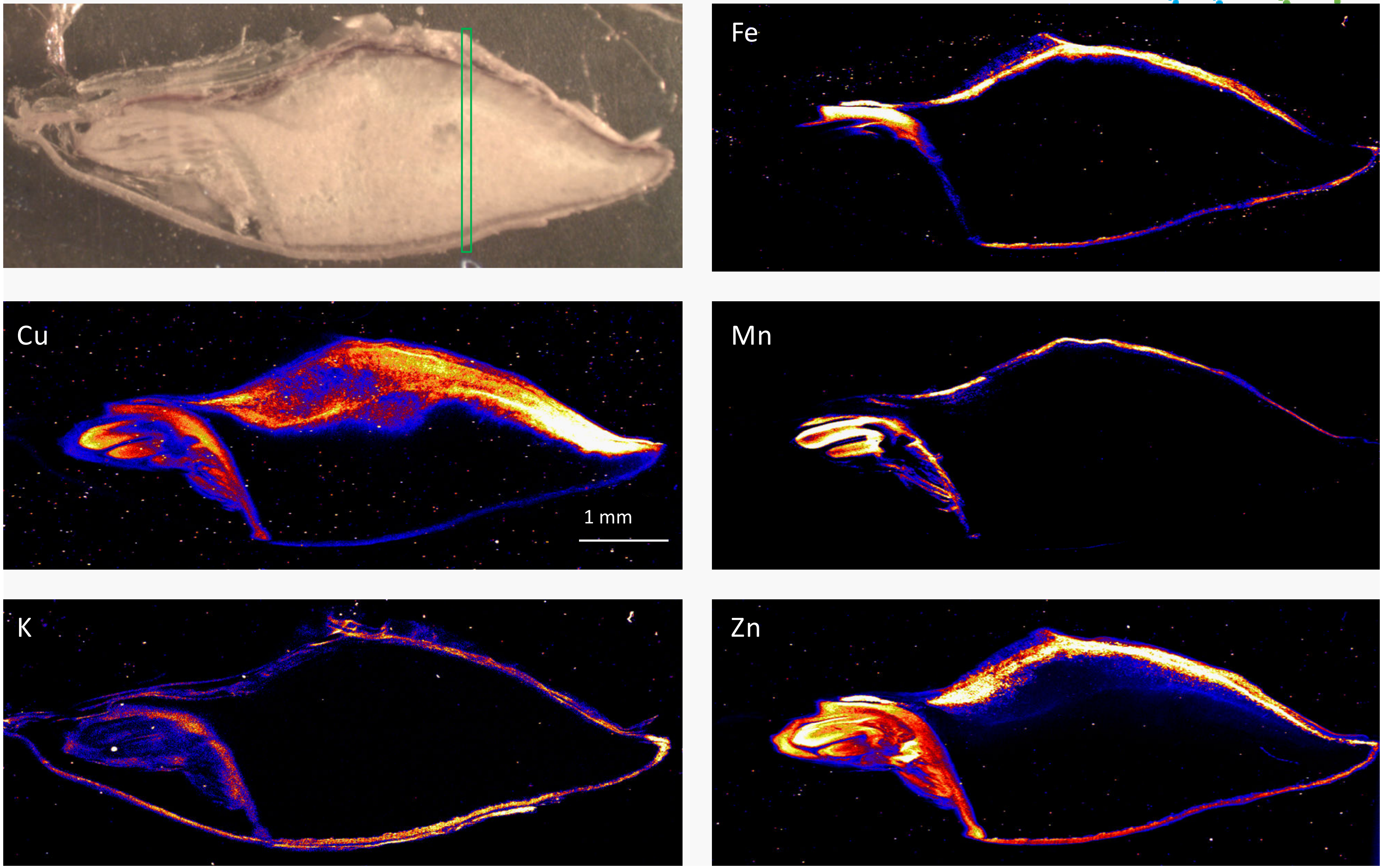
Potassium
Copper
Calcium



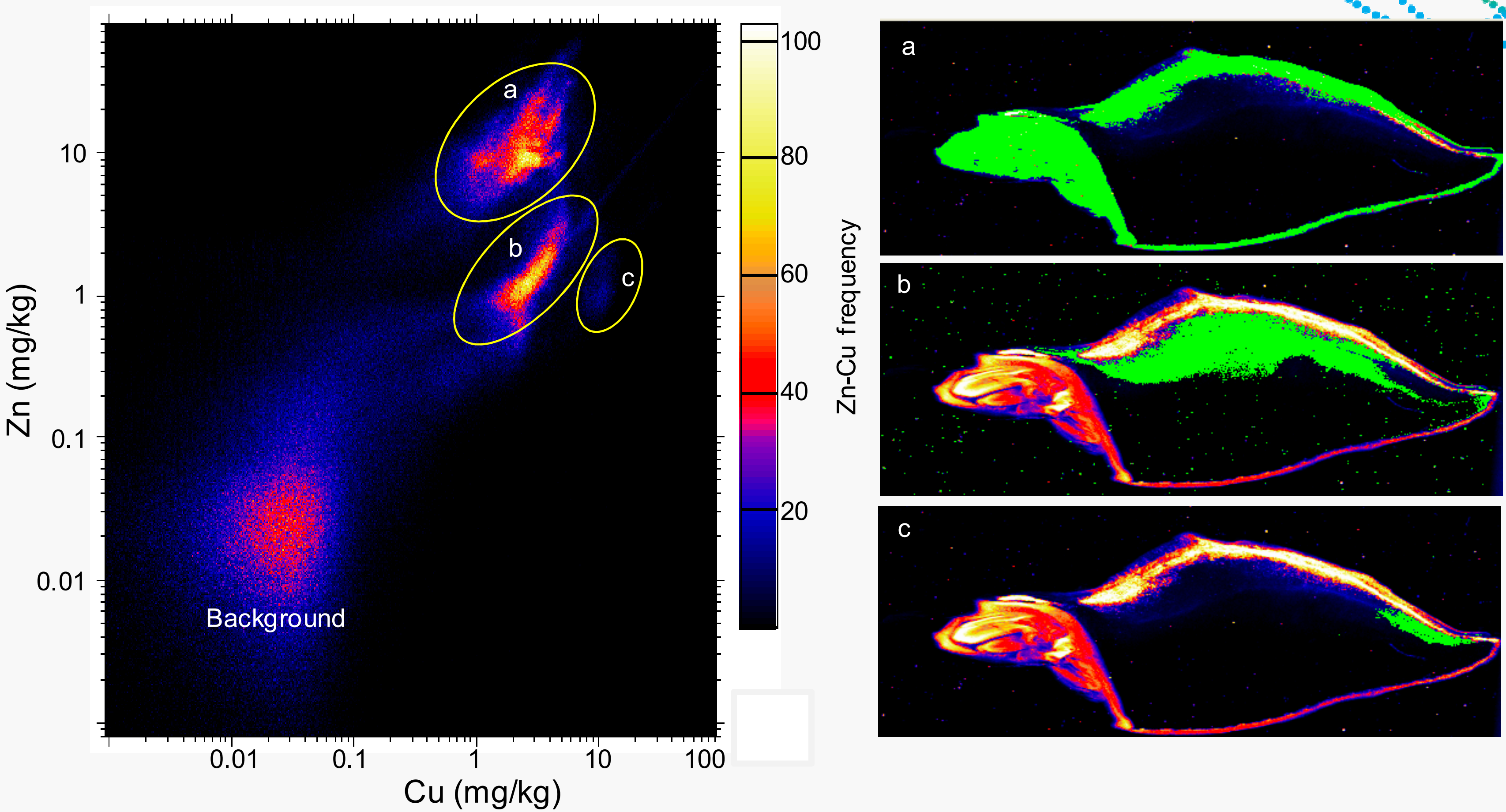
Zinc
Iron
Manganese

Enzo Lombi et al.
Uni South Australia

Micronutrient distribution in barley grain



High definition detailed analysis of elemental correlations



Enzo Lombi, *et al*. Journal of Experimental Botany. **62**, 273–282 (2011)
“Megapixel imaging of (micro)nutrients in mature barley grains.”

Iron work to boost rice diets

Challenge: Despite being a major food source for billions of people in developing countries, polished or white rice does not have enough iron, zinc or pro-vitamin A to meet daily nutritional requirements.

Approach: Iron-enriched rice is very difficult to develop with conventional breeding methods, so Australian researchers used gene technology to increase the amount of iron in the endosperm, the white part of the rice grain. The new rice variety has up to four times the iron and twice the zinc content of ordinary rice. The Australian Synchrotron showed where the iron and zinc were stored in the rice endosperm, down to sub-micron levels.

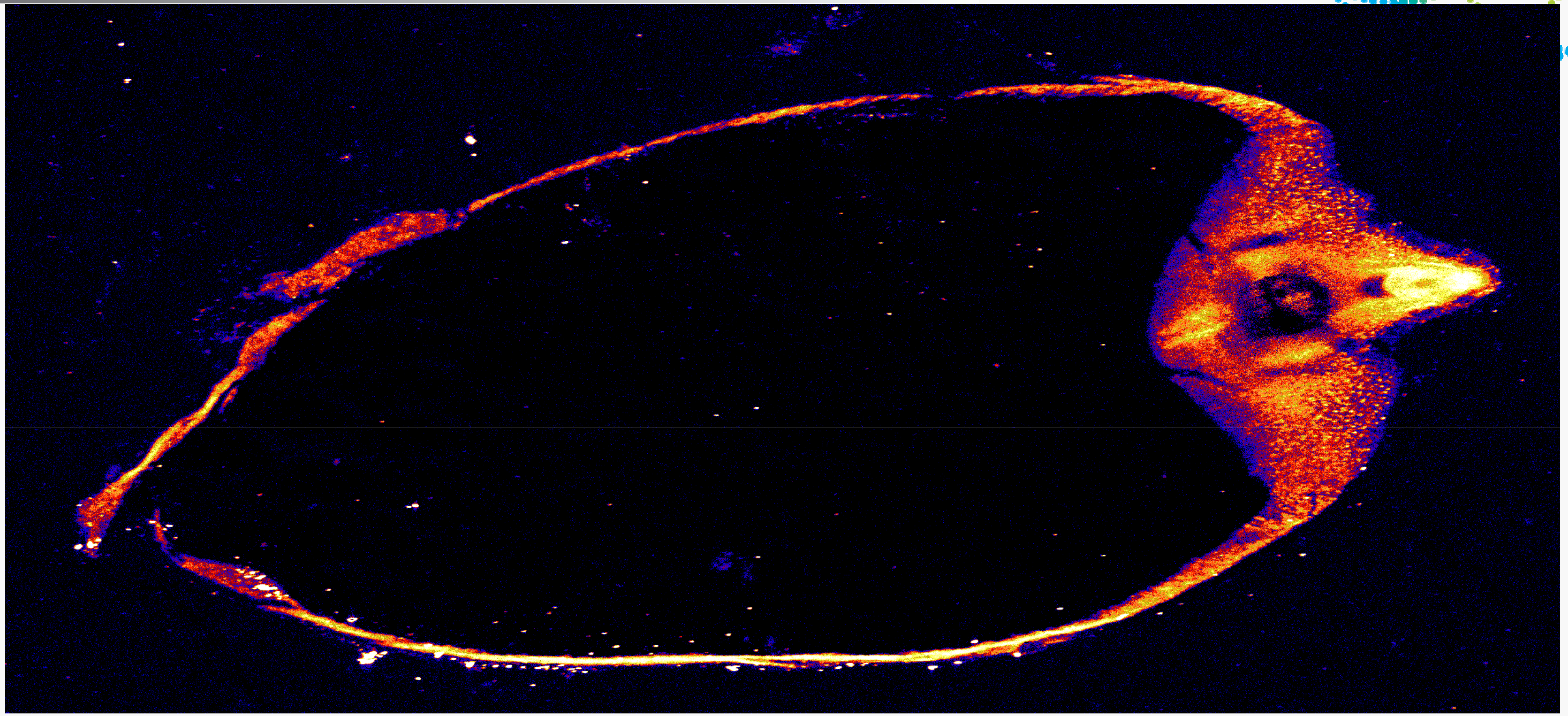
Benefit: The rice will now undergo field trials to ensure that the enriched levels of iron and zinc in the endosperm can be maintained in a field environment.

Collaborators:
Australian Centre for Functional Plant Genomics
Universities of Melbourne, Adelaide and South Australia
Australian Synchrotron

National Research Priorities: promoting and maintaining good health.

Top image: Alex Johnson (University of Melbourne and Enzo Lombi (University of South Australia)

Iron uptake to endosperm of rice grains



• **Iron deficiency** Most common nutritional deficiency disorder in the world.

• Over **2 billion people** (**30%** world's population) suffer

Alex Johnson, *et al*. PloS ONE. **6**, e24476 (2011) "Constitutive Overexpression of the OsNAS Gene Family Reveals Single-Gene Strategies for Effective Iron- and Zinc-Biofortification of Rice Endosperm."

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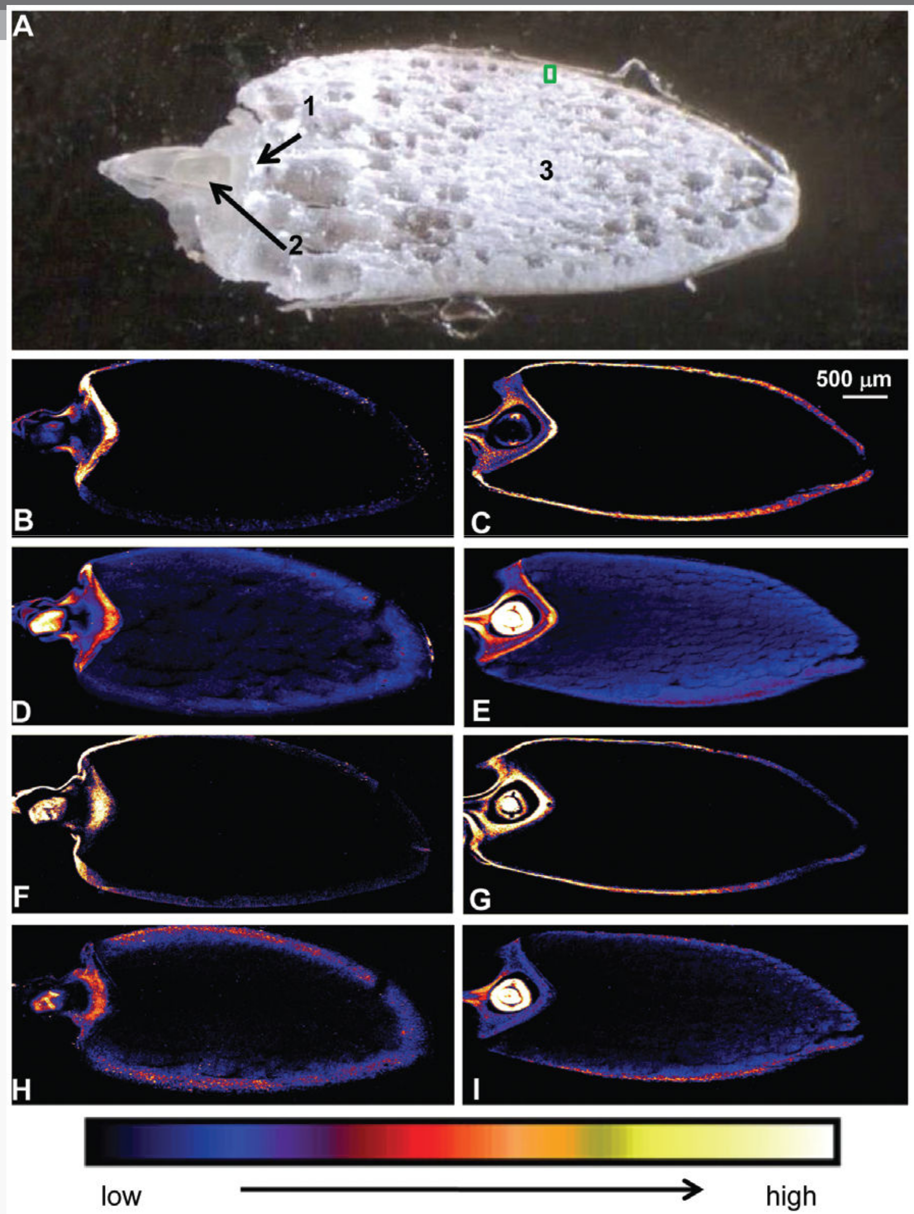
Iron and zinc uptake to rice endosperm

location of
1 scutellum
2 embryo
3 endosperm

WildType

OE-OsNAS2A



Fe

Zn

Mn

Cu

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Maia detector array and imaging system

XFM beamline, Australian Synchrotron

- **Capture spatial detail in complex natural samples** from **~2 µm to >50 mm scales**

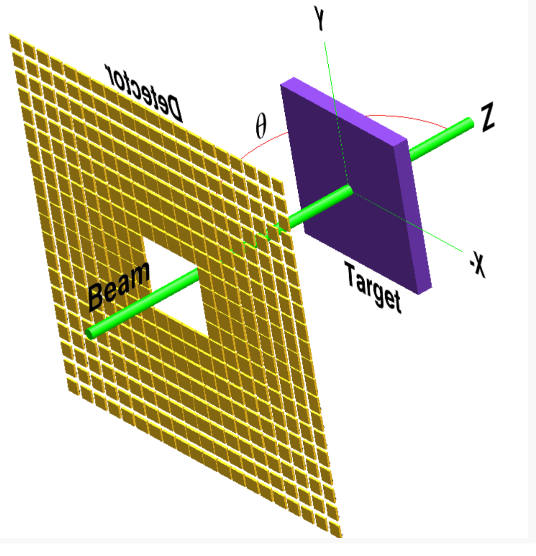
  → images **~100 M pixels** or more

- **Pixel transit times down to 50 µs**

  → count rates to **10 M/s** typical (40 M/s peak)

- **Real-time spectral deconvolution**

  → real-time display of element images



Maia detector

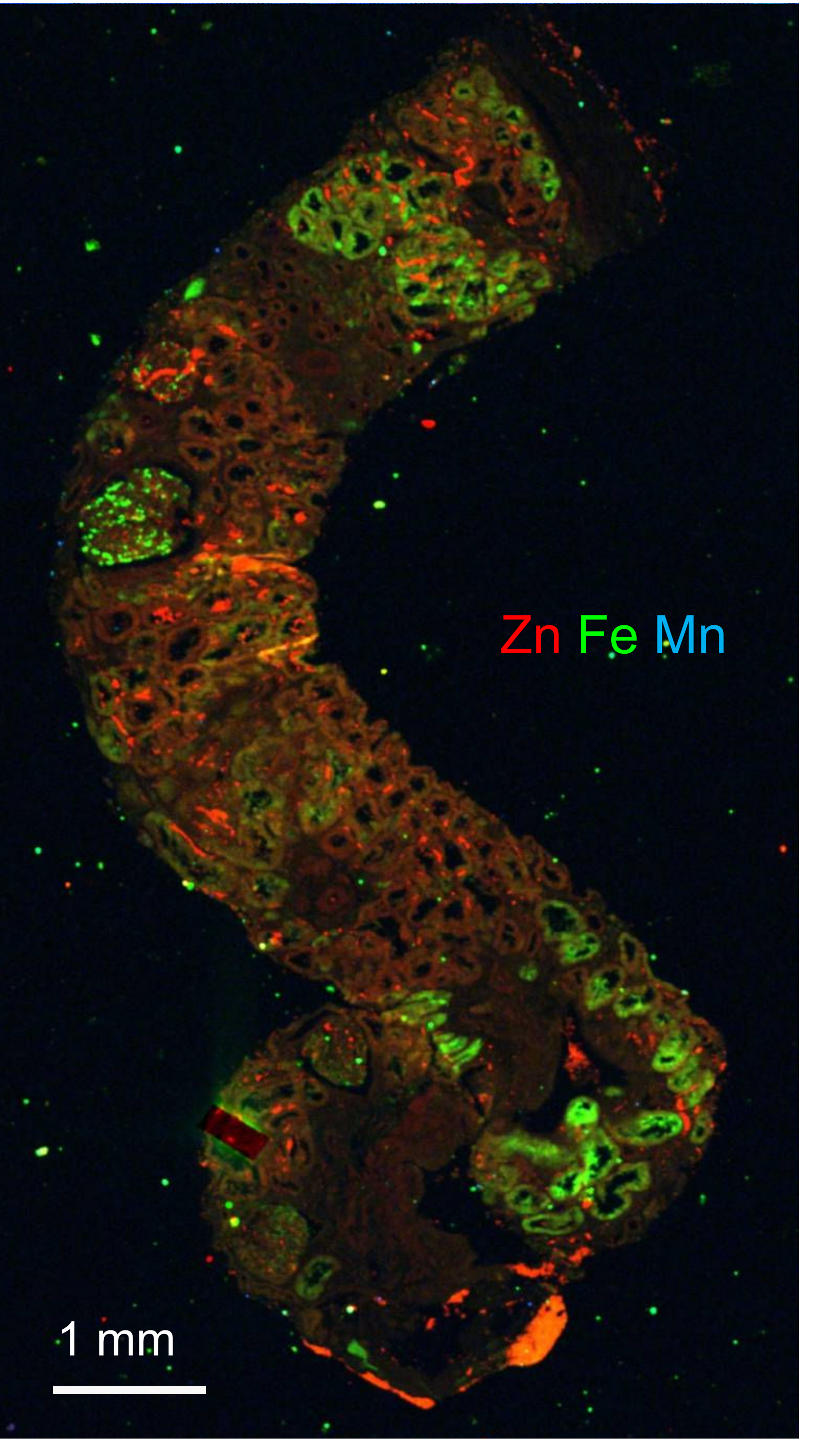
✓ 384 detector array

✓ annular backscatter

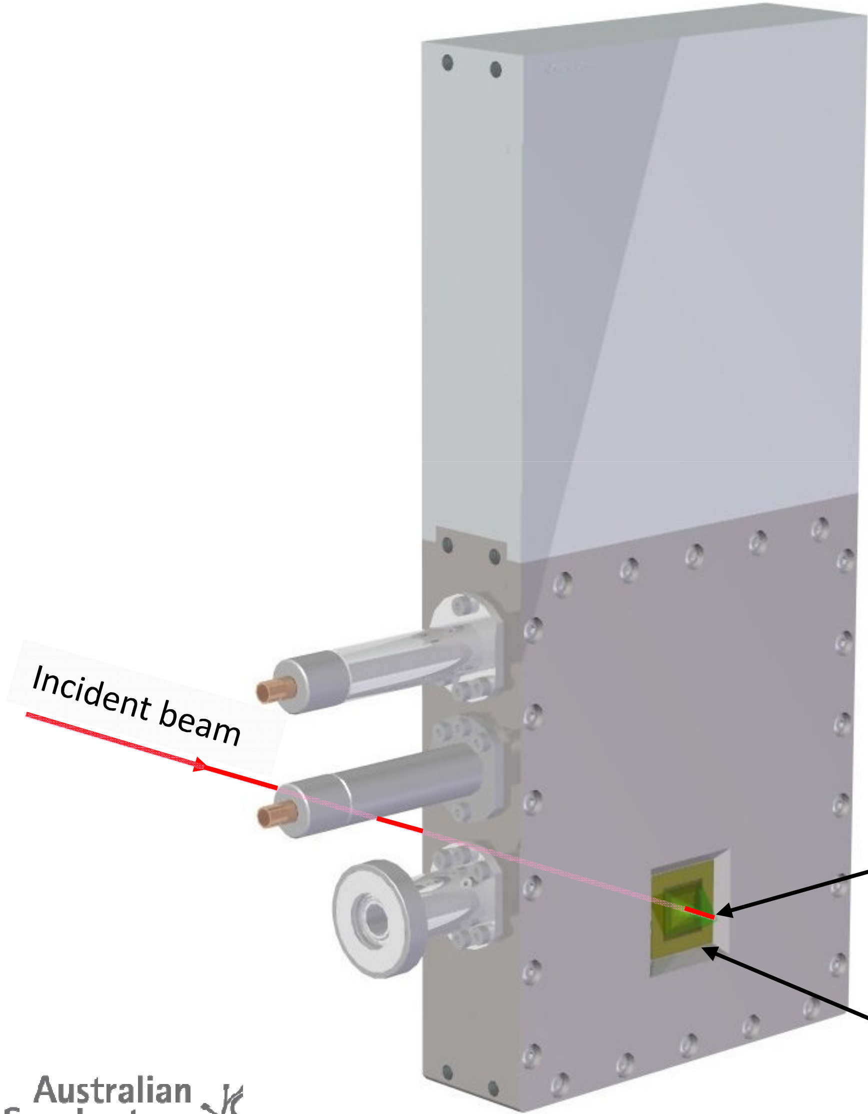
✓ 1.2 sr solid-angle

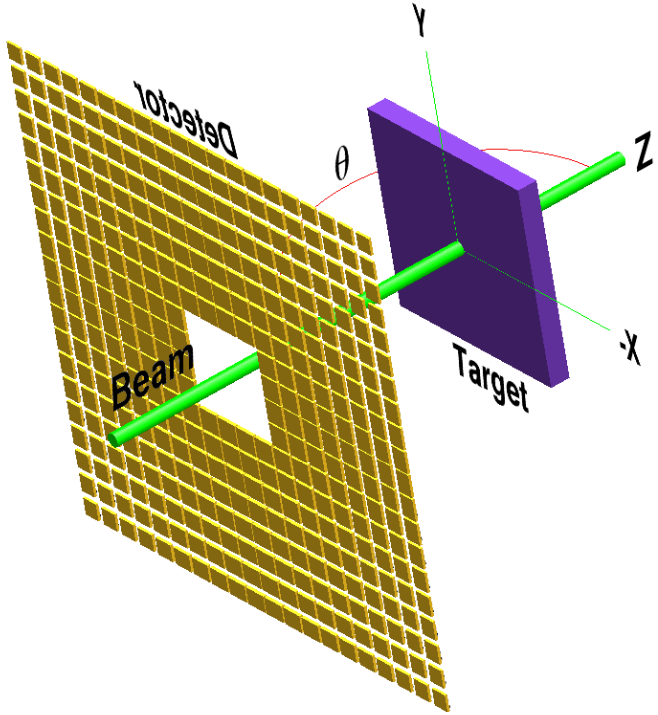
✓ Event mode

✓ Real-time processing



Maia detector: external view



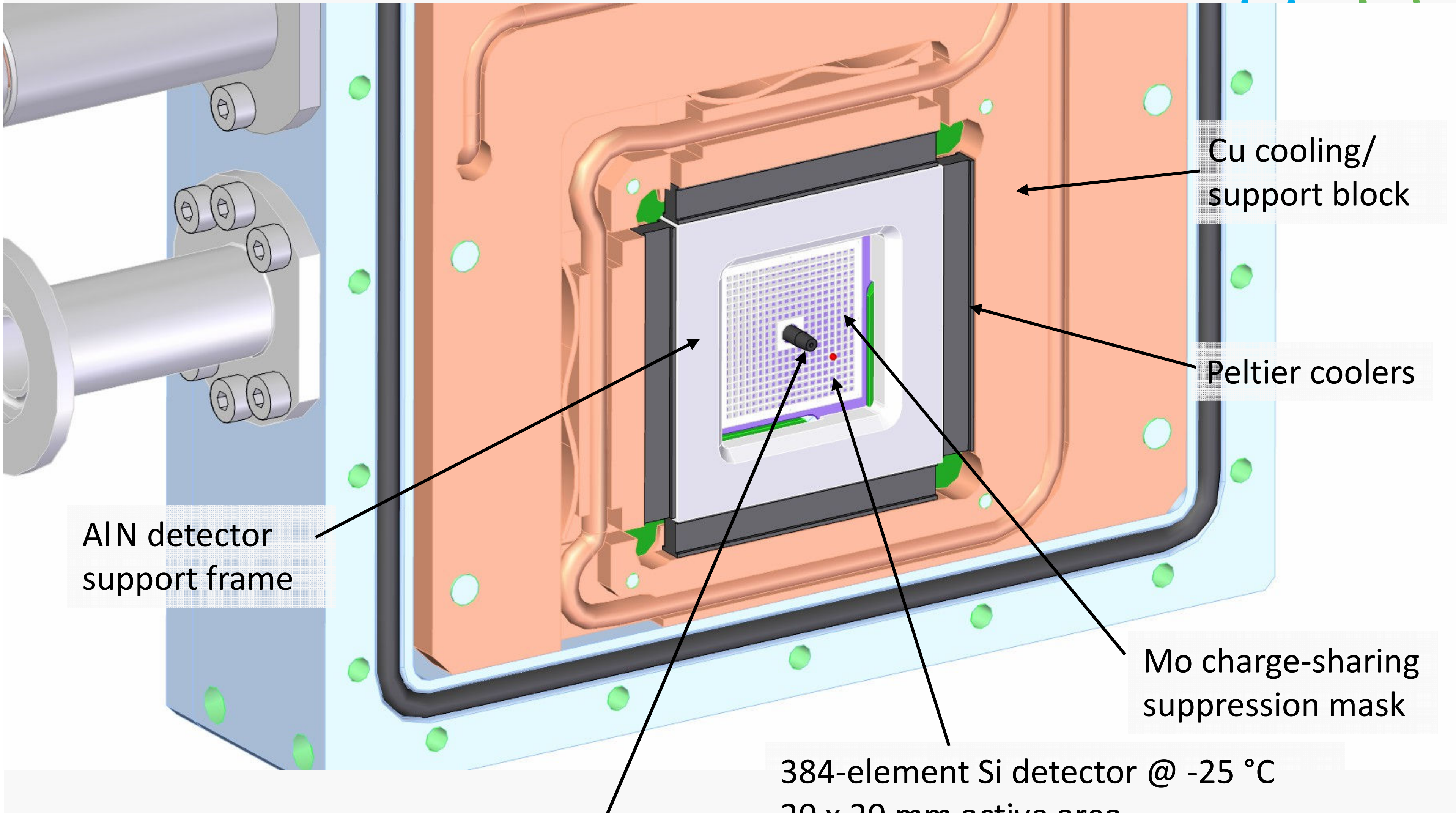


Optimum sample position
- ~1.5 mm from front face
- 10 mm from detector wafer

Beryllium window

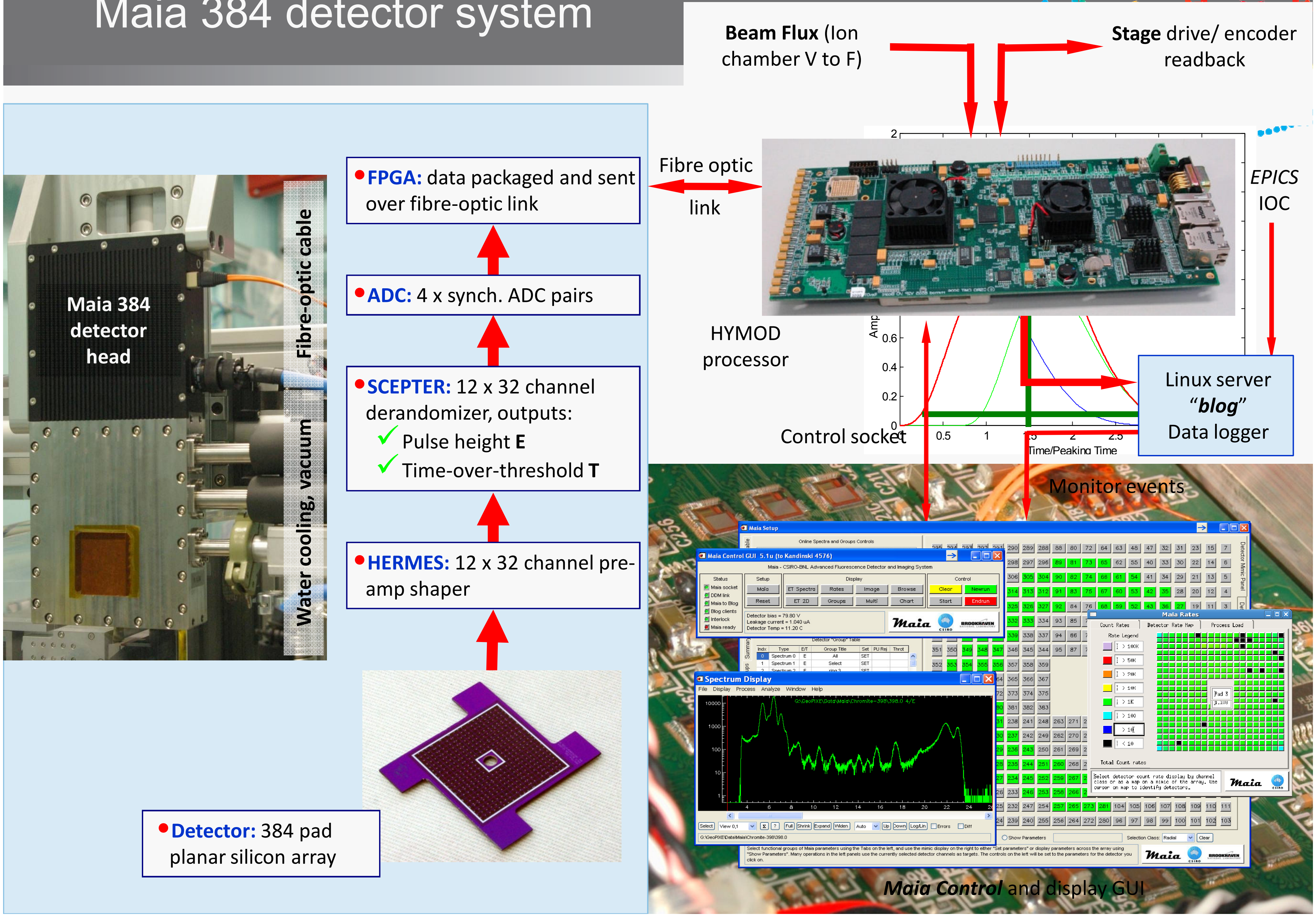
Kirkham *et al.*, AIP Conf. Series 1234 (2010) 240.

Maia detector:detector wafer, sample side

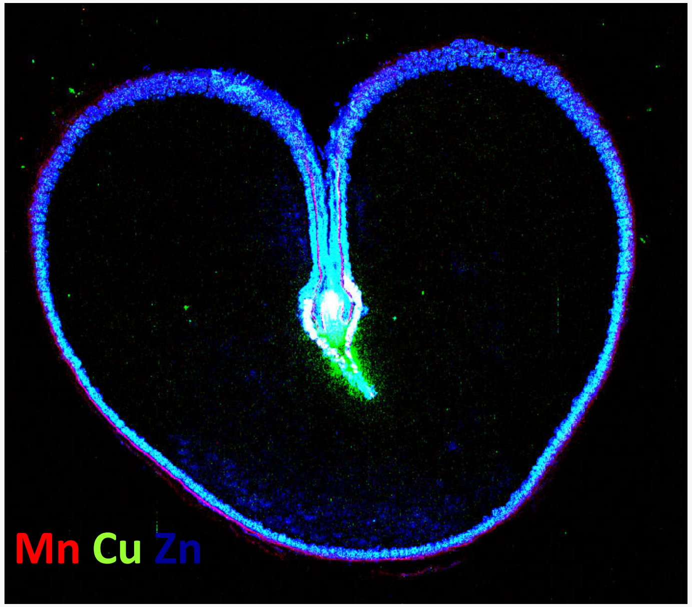


Kirkham *et al.*, AIP Conf. Series 1234 (2010) 240.

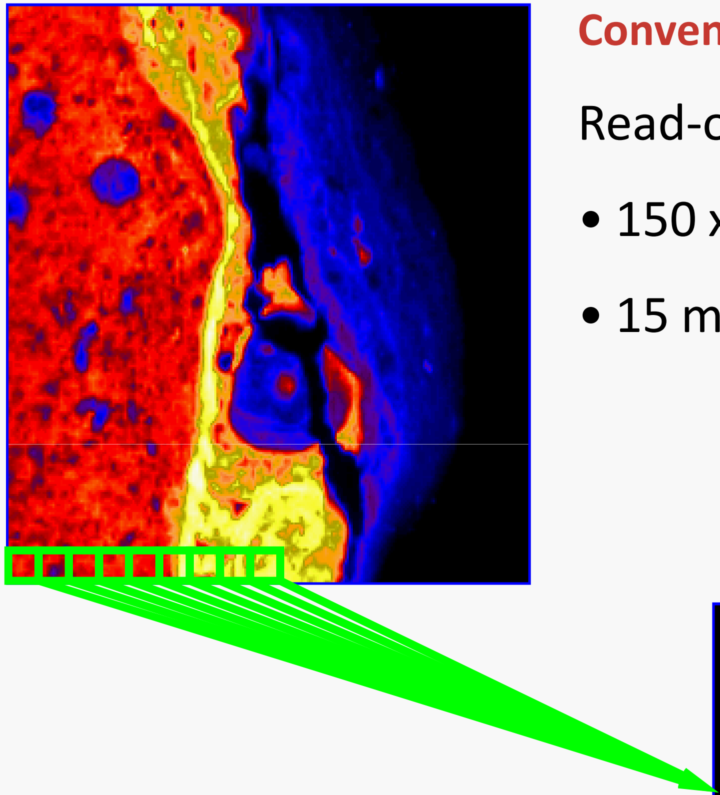
Maia 384 detector system



Maia384 at XFM



Full Spectral Data Collection: Raster sample through beam

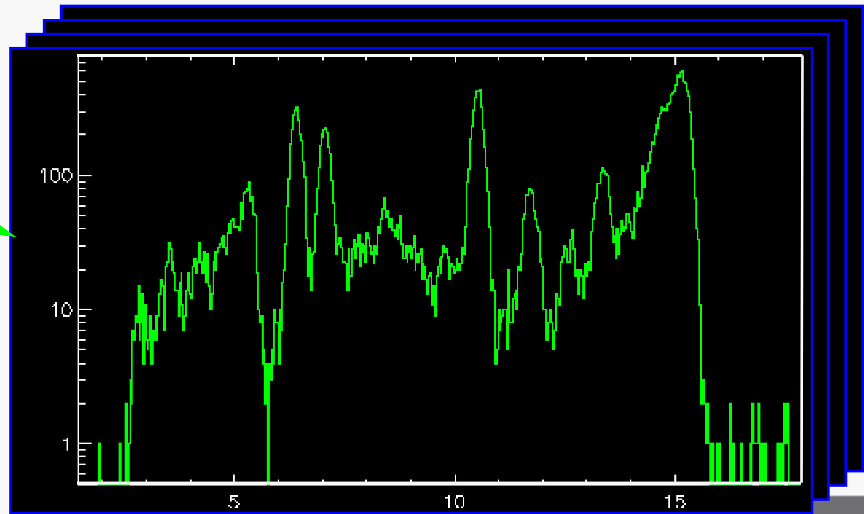


Conventional synchrotron approach:

Read-out ***N*** full spectra at each pixel (~1 sec)

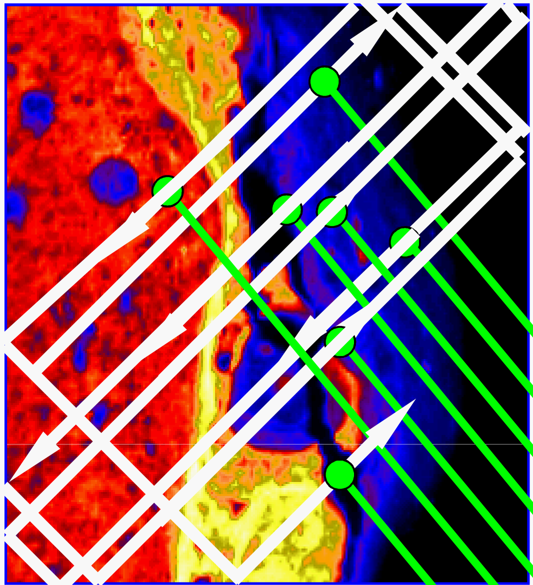
- 150 x 150 pixels → ~6-7 hours
- 15 minutes → ~30 x 30 pixels

Detector array: ***N*** detectors



Raster sample in X,Y through microbeam

Full Spectral Data Collection: Event-by-event processing



Nuclear Physics Approach:

Sample *X,Y* for each detected X-ray event

- Freedom to use high scan rates
- Real-time processing of event stream

List-mode data stream:

X_1, Y_1, E_1, n_1
X_2, Y_2, E_2, n_2
X_3, Y_3, E_3, n_3
X_4, Y_4, E_4, n_4
X_5, Y_5, E_5, n_5
X_6, Y_6, E_6, n_6
X_7, Y_7, E_7, n_7

X_i	X coordinate
Y_i	Y coordinate
E_i	Energy
n_i	Detector #

Used for Nuclear Microprobe and now SXRF at Australian Synchrotron XFM

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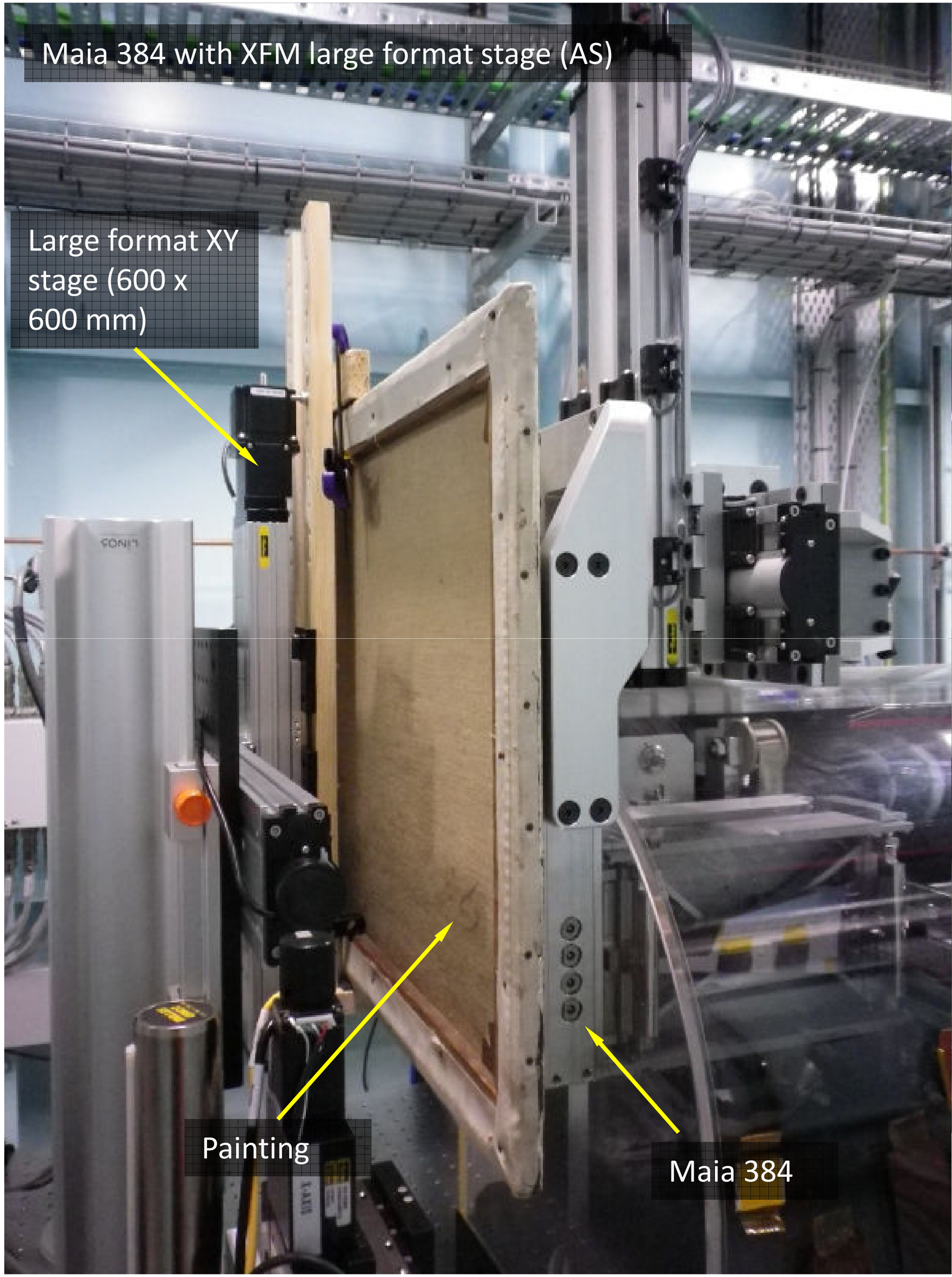
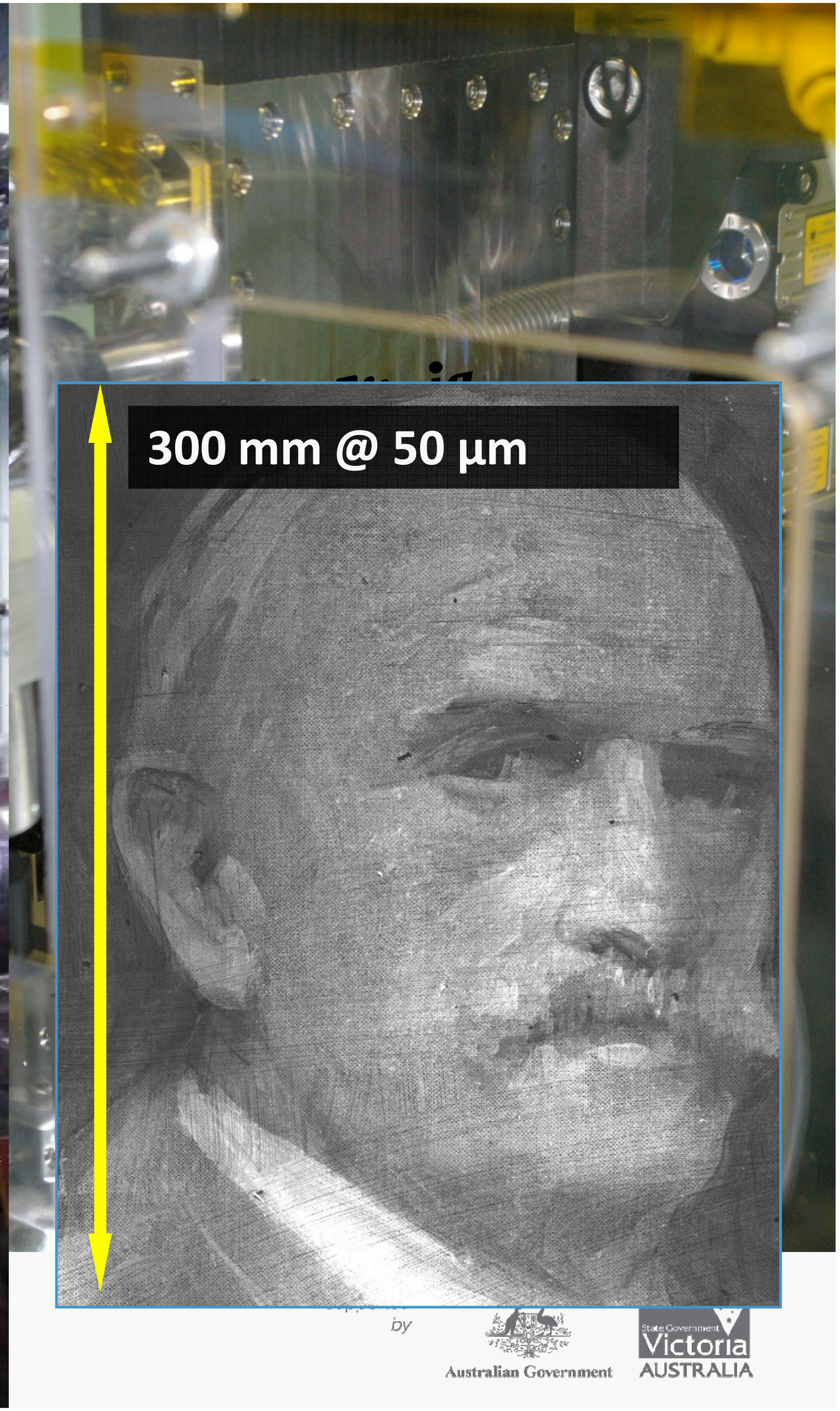
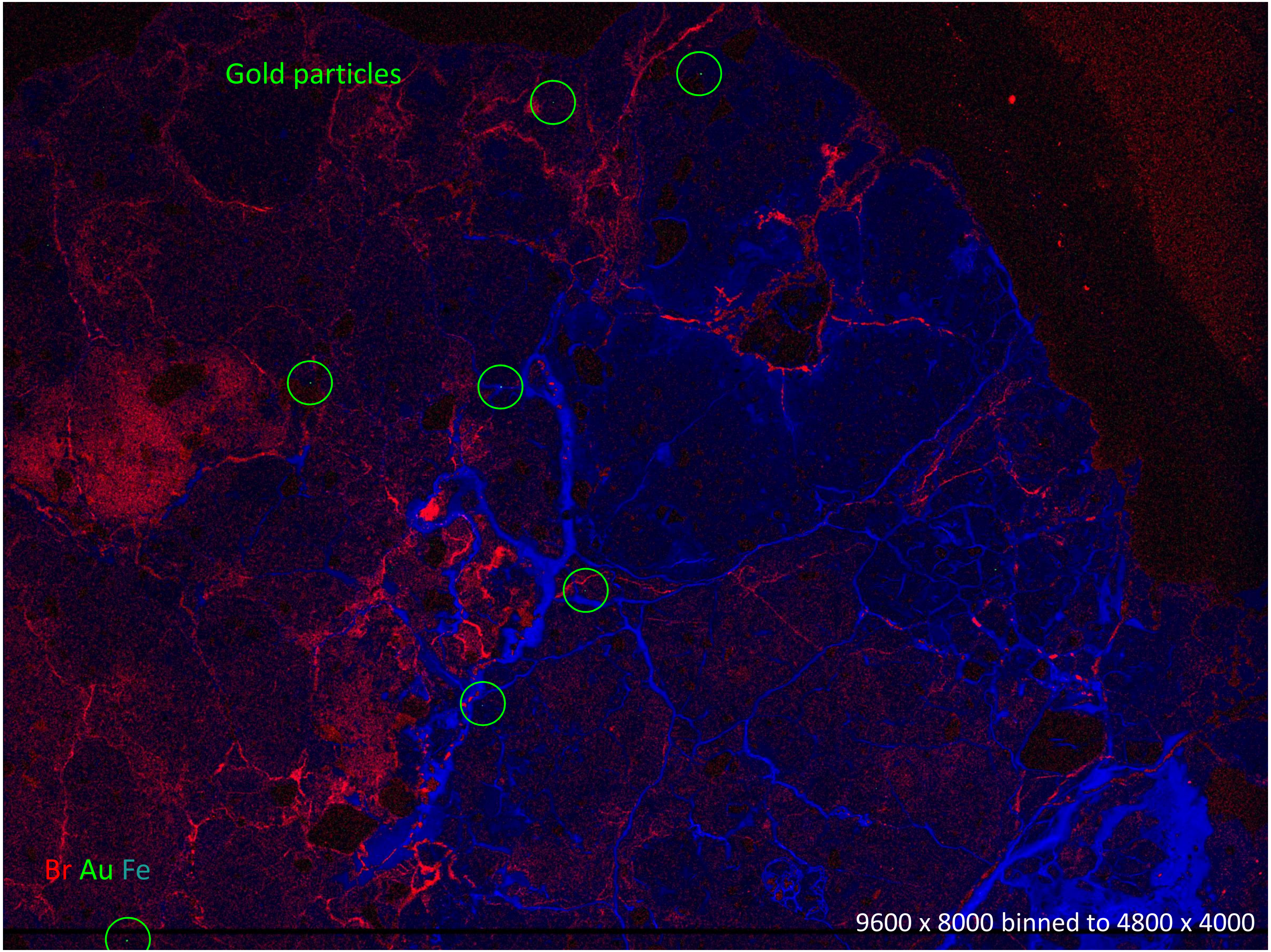

Maia 384 with XFM large format stage (AS)
Large format XY stage (600 x 600 mm)
Painting
Maia 384


300 mm @ 50 µm
by
Australian Government
Victoria
AUSTRALIA

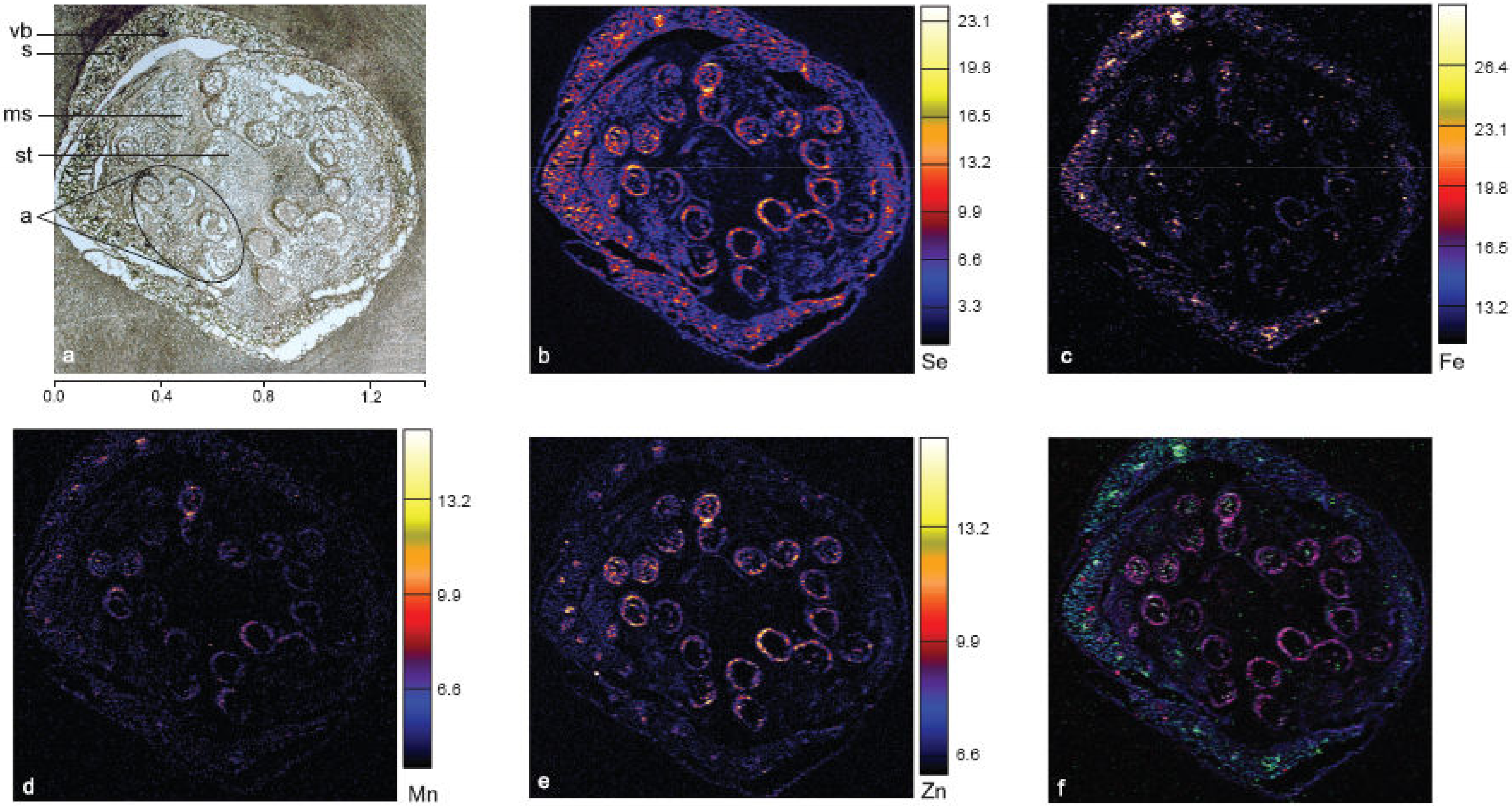
Outline of Lecture

Introduction to X-ray fluorescence (XRF)	• Interaction of X-rays with matter • Principle of X-ray fluorescence analysis • Applications and examples
Synchrotron radiation and XRF analysis	• Highly Brilliant X-ray Source: high sensitivity • Parallel beam with small divergence: microprobe • Energy tunability: elemental selectivity and XAS and spectroscopy
X-ray fluorescence microscopy (XFM) and 3D techniques	• Detector advances: Maia detector & event mode acquisition • **Megapixel imaging** • 3D techniques
Conclusions and future directions	• Summary • Pros and cons of XRF • Future directions: 3D XANES imaging


Gold particles
Br Au Fe
9600 x 8000 binned to 4800 x 4000

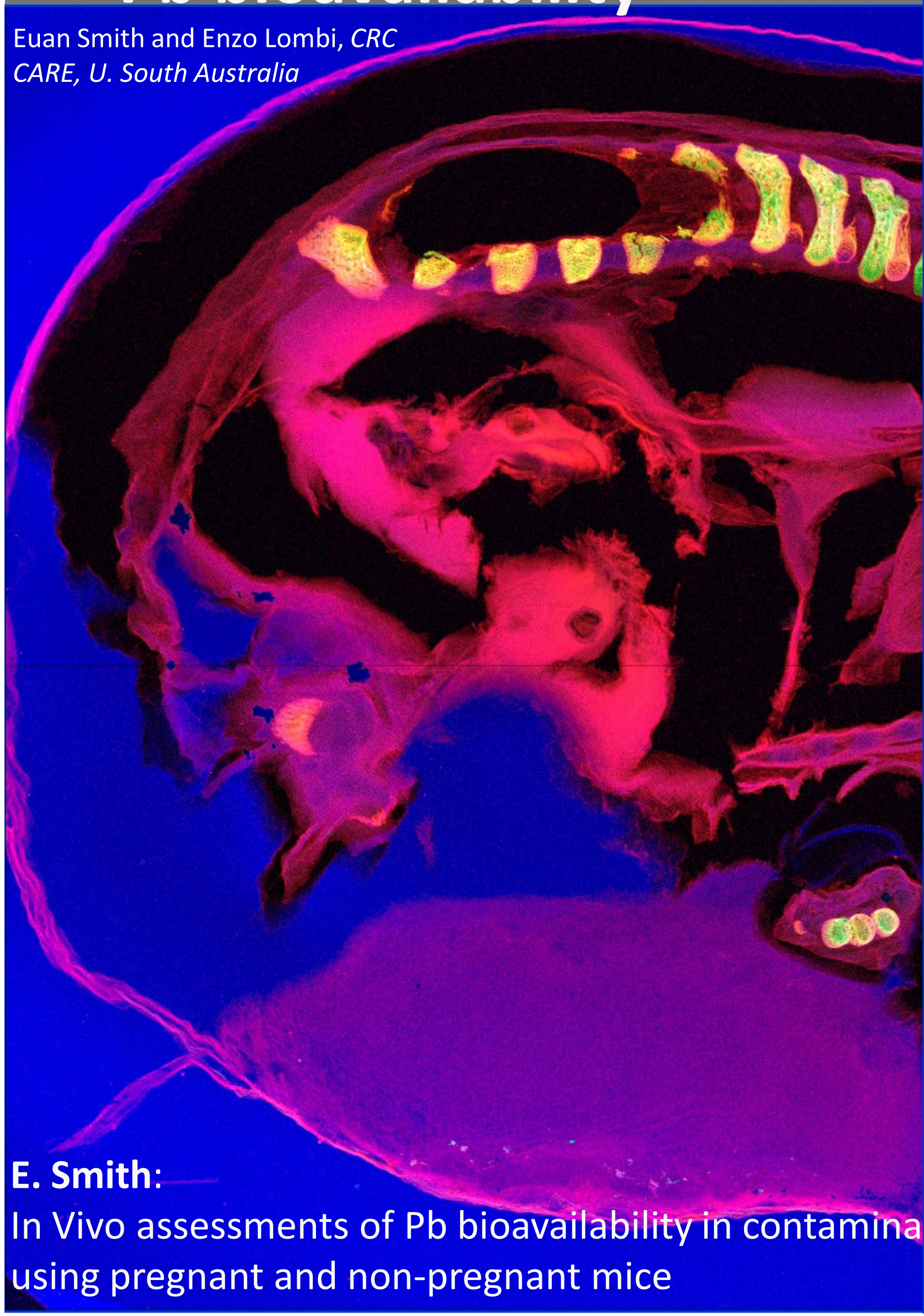
Se bio-fortification in broccoli

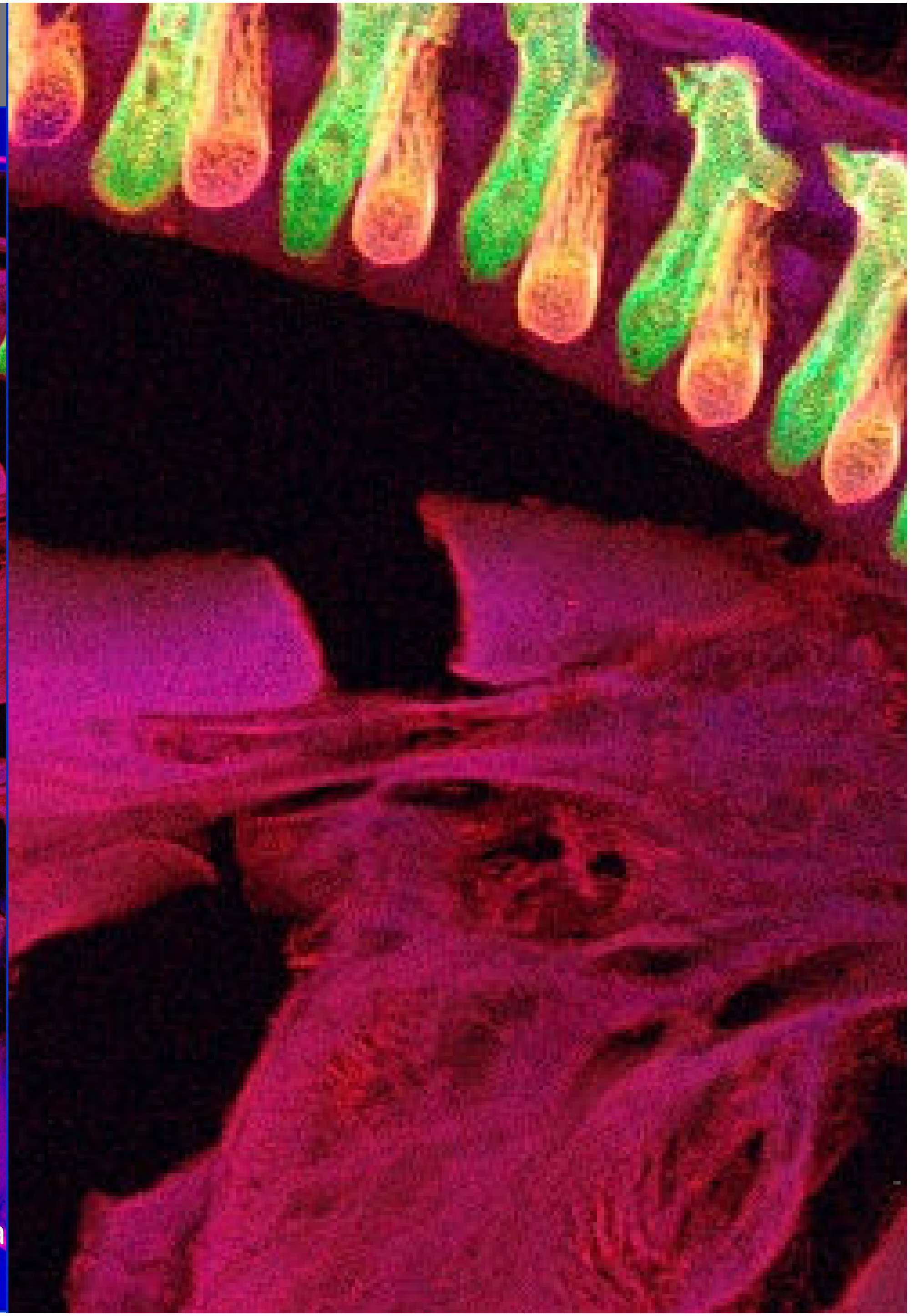
- Marian McKenzie NZ Institute for plant and food, Plant, Cell & Environment



Pb bioavailability

Euan Smith and Enzo Lombi, *CRC CARE, U. South Australia*



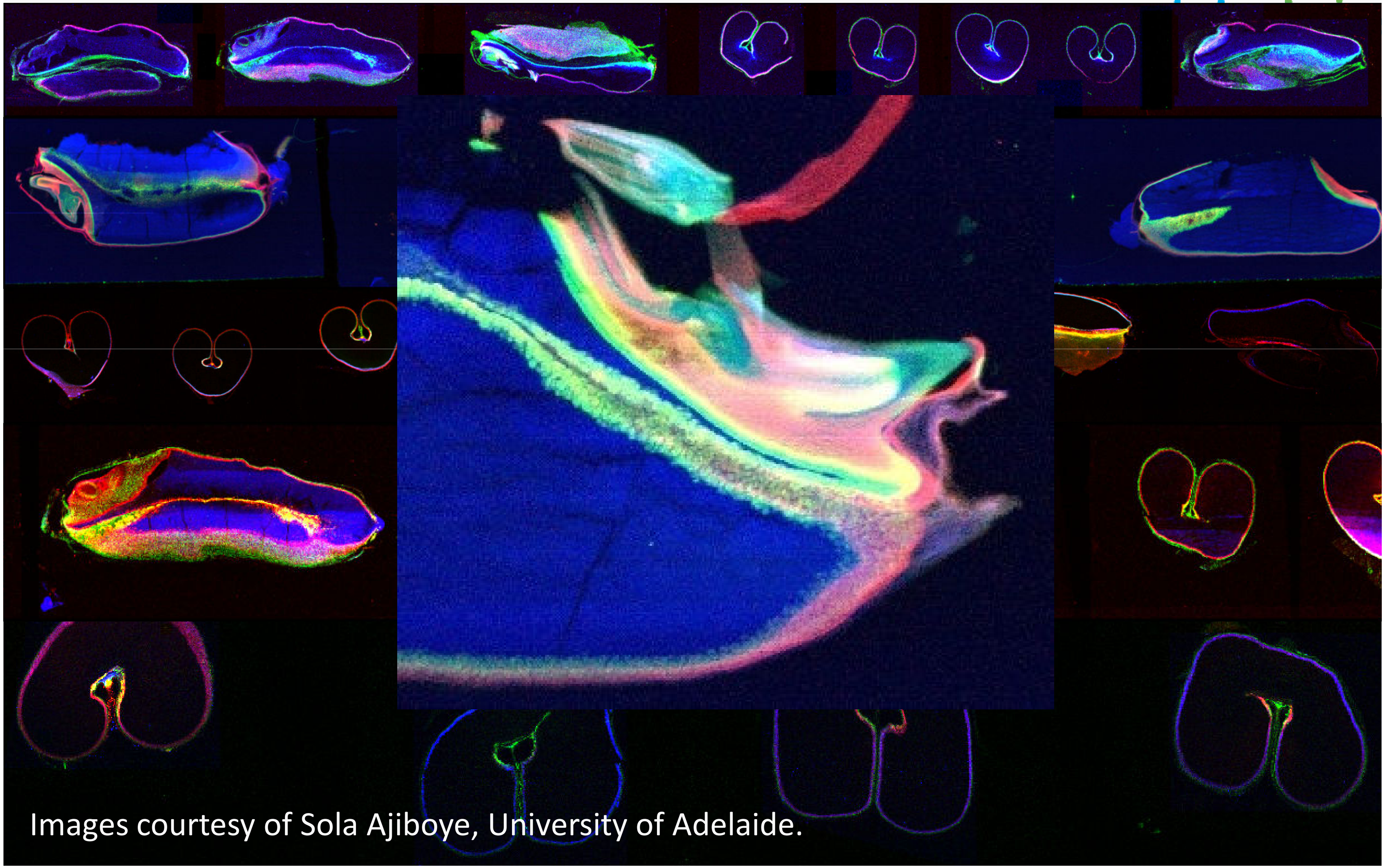


E. Smith:

In Vivo assessments of Pb bioavailability in contamina

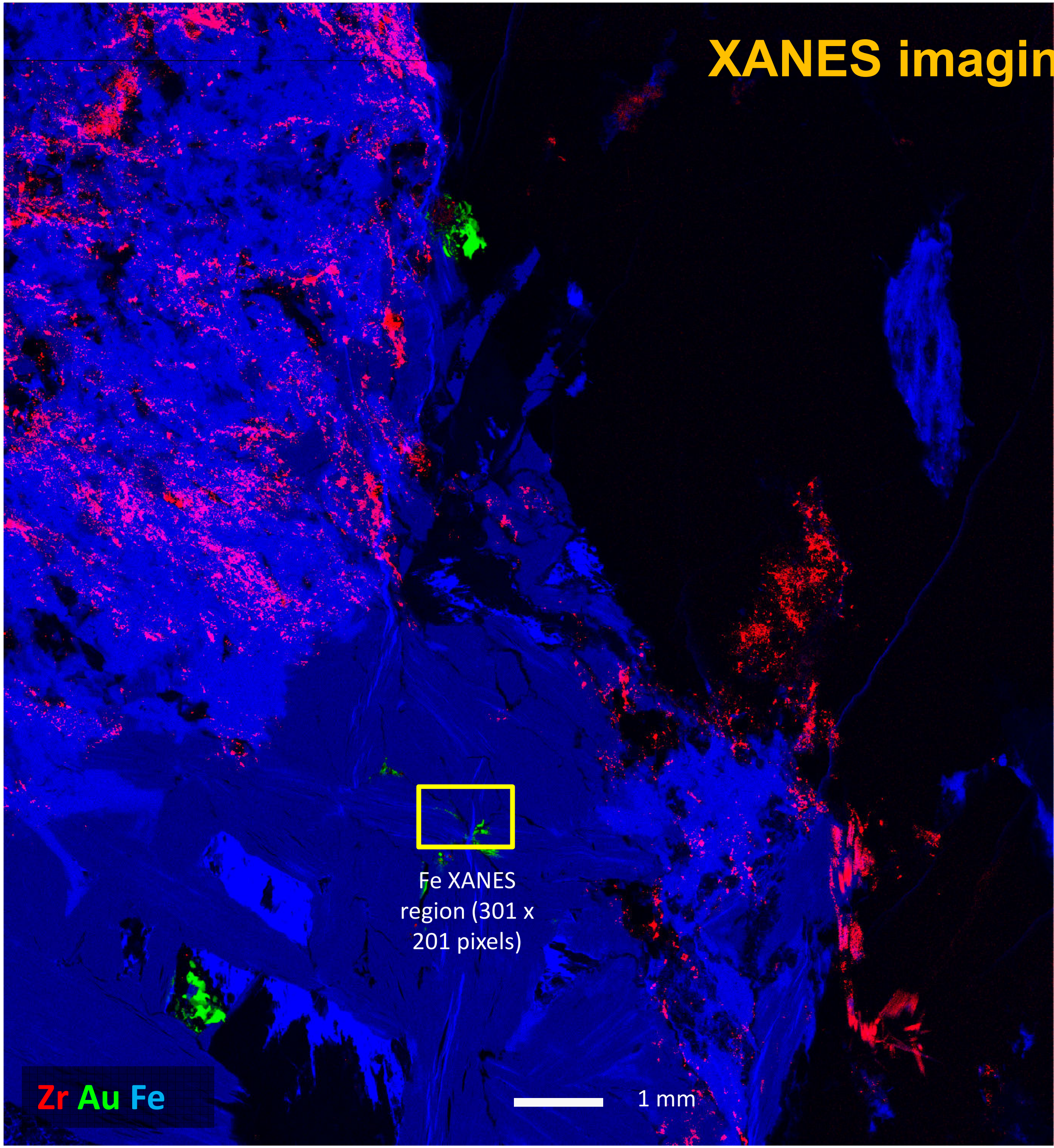
using pregnant and non-pregnant mice

Sampling studies: wheat grain sections



Images courtesy of Sola Ajiboye, University of Adelaide.

XANES imaging with Maia

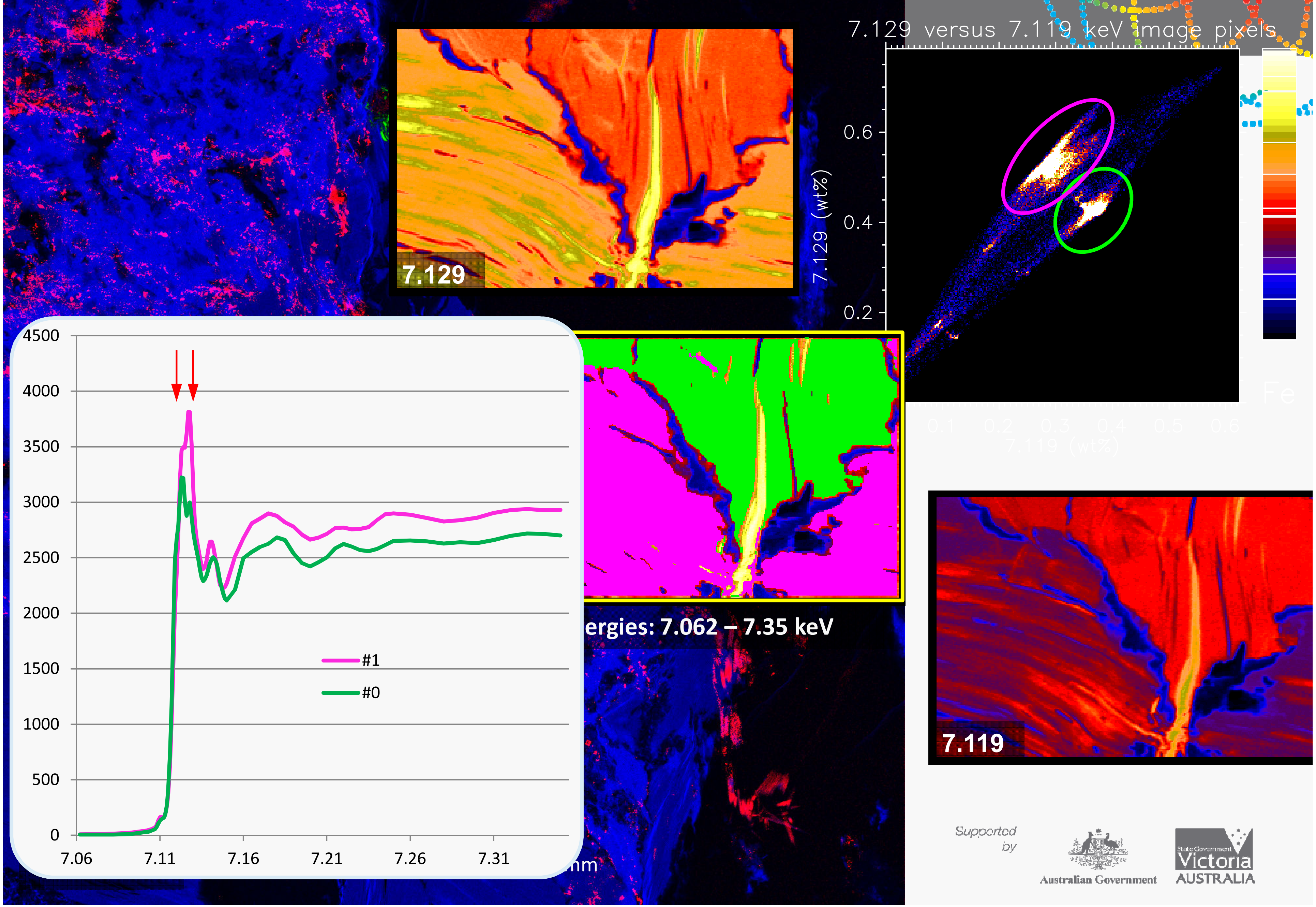


- Gold ore forming environment
  - ✓ Clues to nature of gold bearing fluid

12 x 13 mm, 4001 x 4334 pixels

Supported by Australian Government State Government Victoria AUSTRALIA

XANES imaging with Maia



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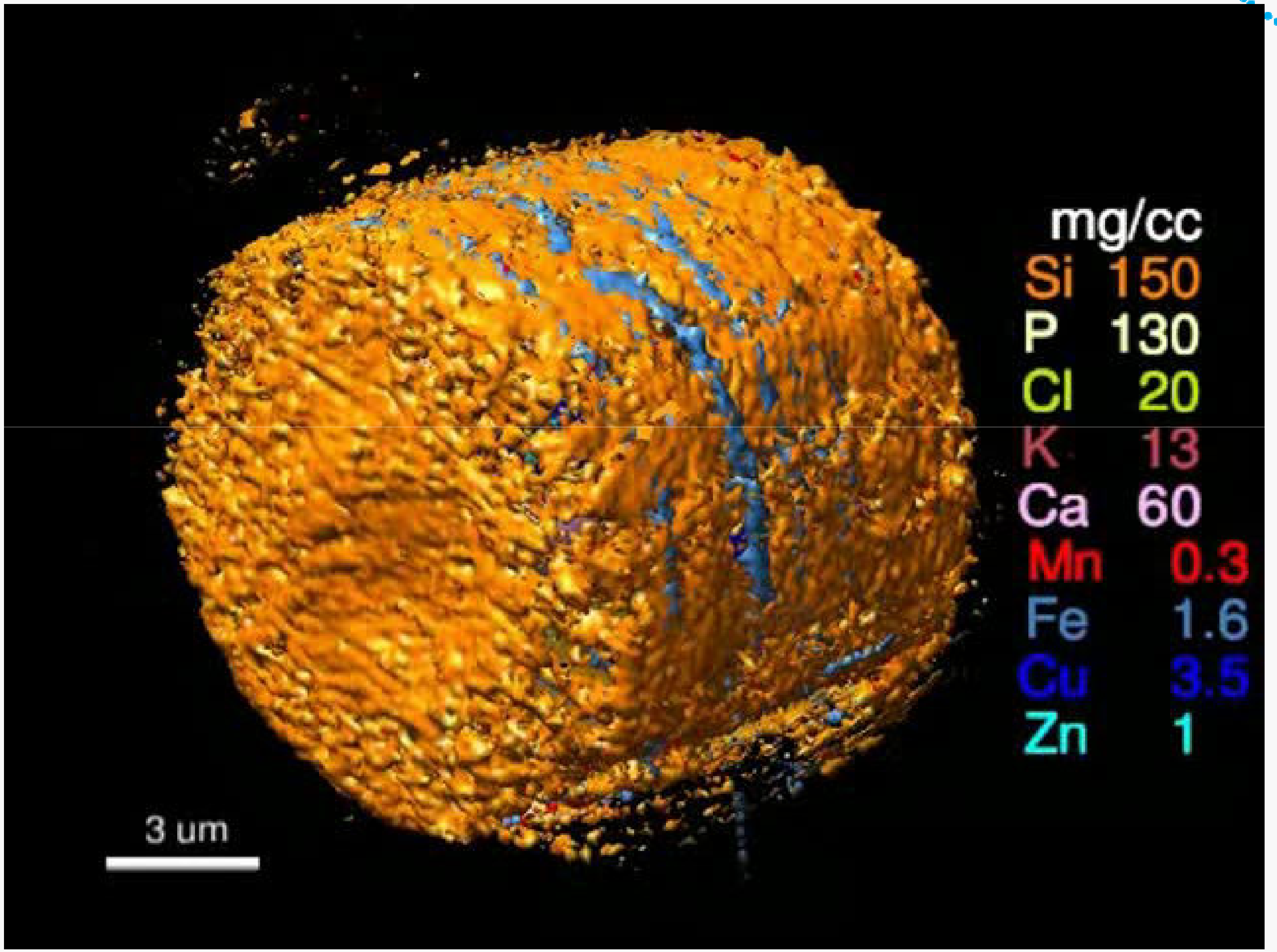
Fluorescence tomography



Martin de Jonge, *et al*., **PNAS 107**, 15676 (2010).

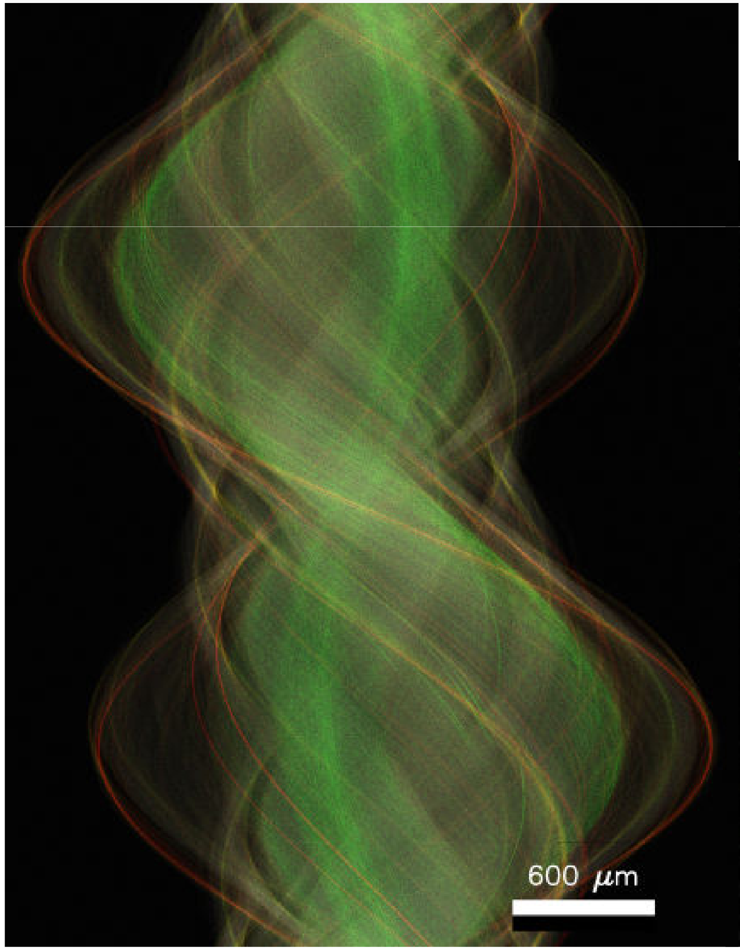
3D example: Arsenic, germanium and selenium speciation and localization in rice grain

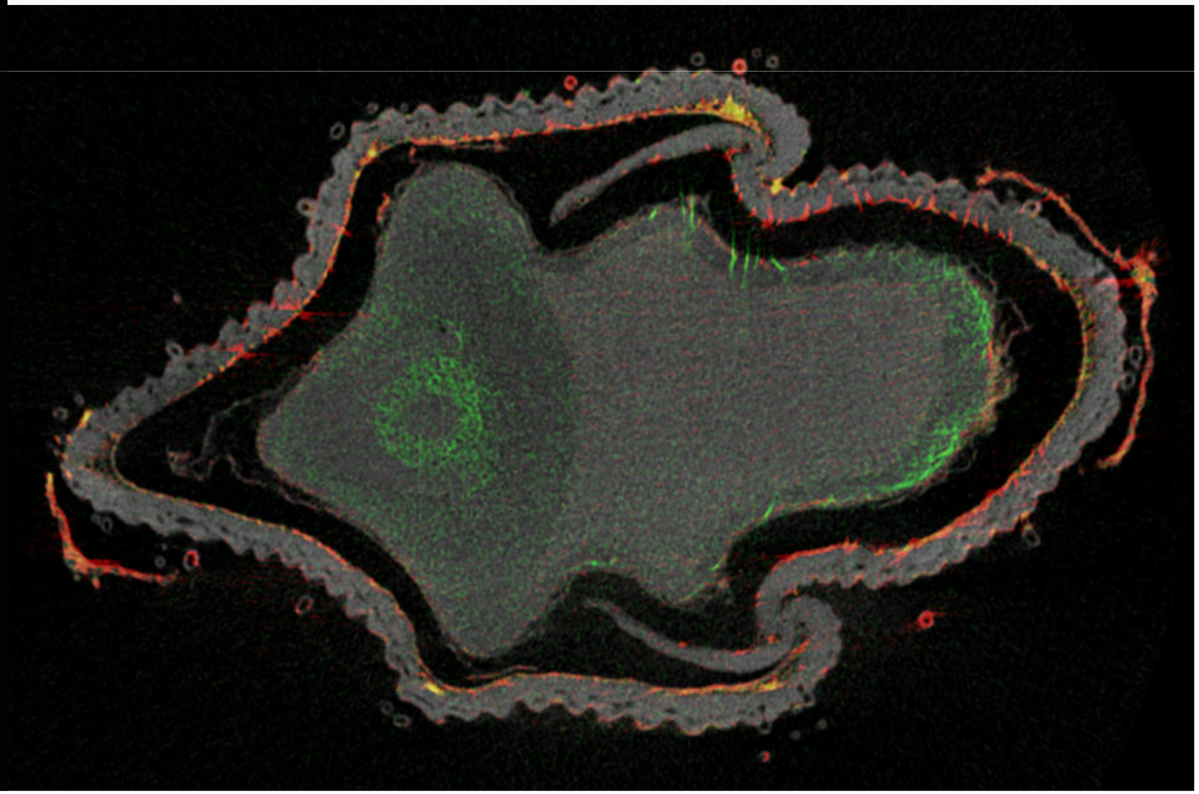
Meharg, de Jonge, et al, Analytical and Bioanalytical Chemistry

2000 projections, 2 micron pixel, recon. resolution = 5 microns.

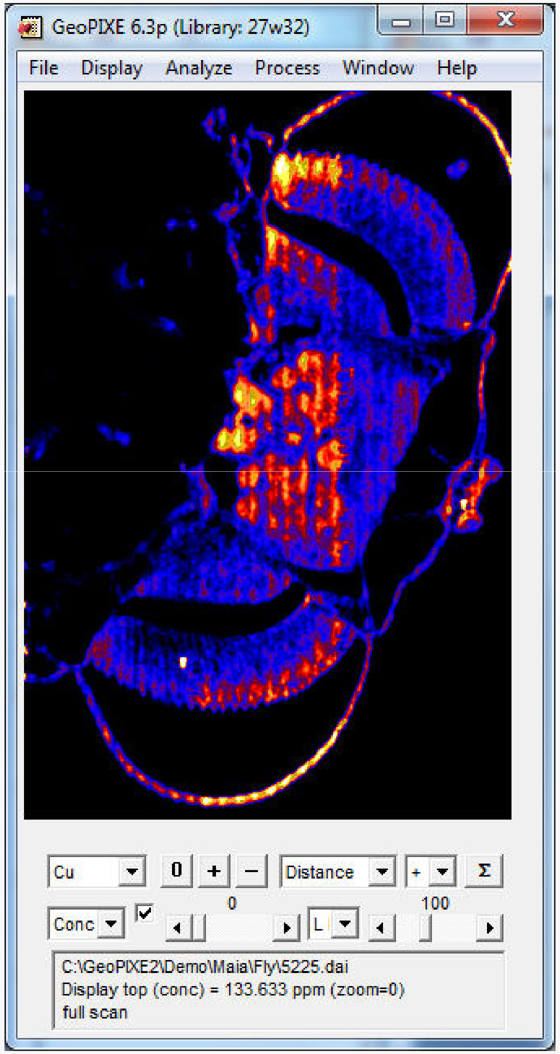
Red = Germanium, Green = Zinc, White = Compton scatter

Investigating silicic acid pathways for arsentie





Data processing: PyMca, Maps, **GeoPIXE**, ...



PyMca

- http://pymca.sourceforge.net/

MAPS

- http://stefan.vogt.net/downloads.html/

GeoPIXE

- http://www.nmp.csiro.au/GeoPIXE.html

- Full spectrum fitting at each pixel, data point

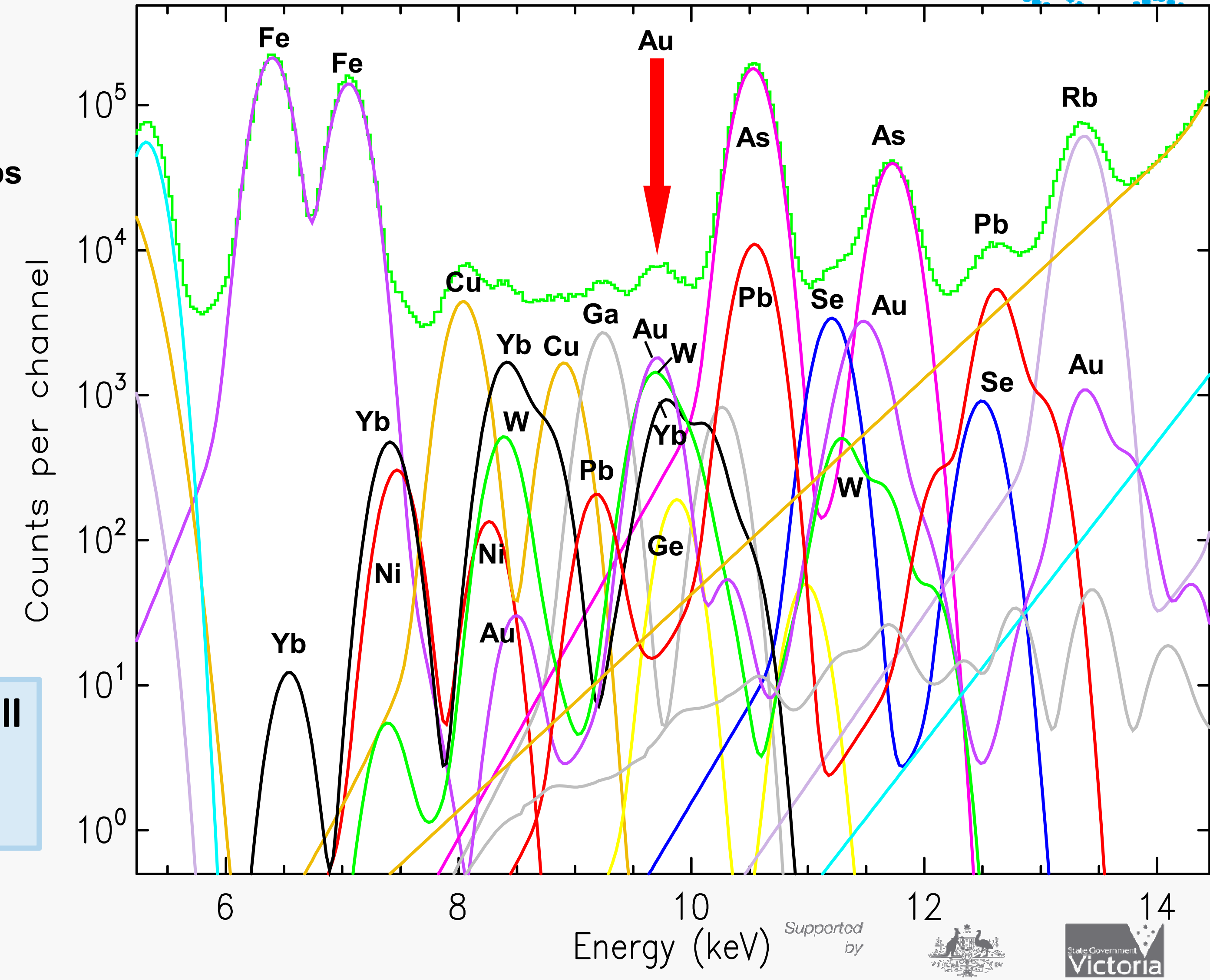
Geological and environmental samples: Need to unfold complex overlaps …

e.g. **Au L_α overlaps**

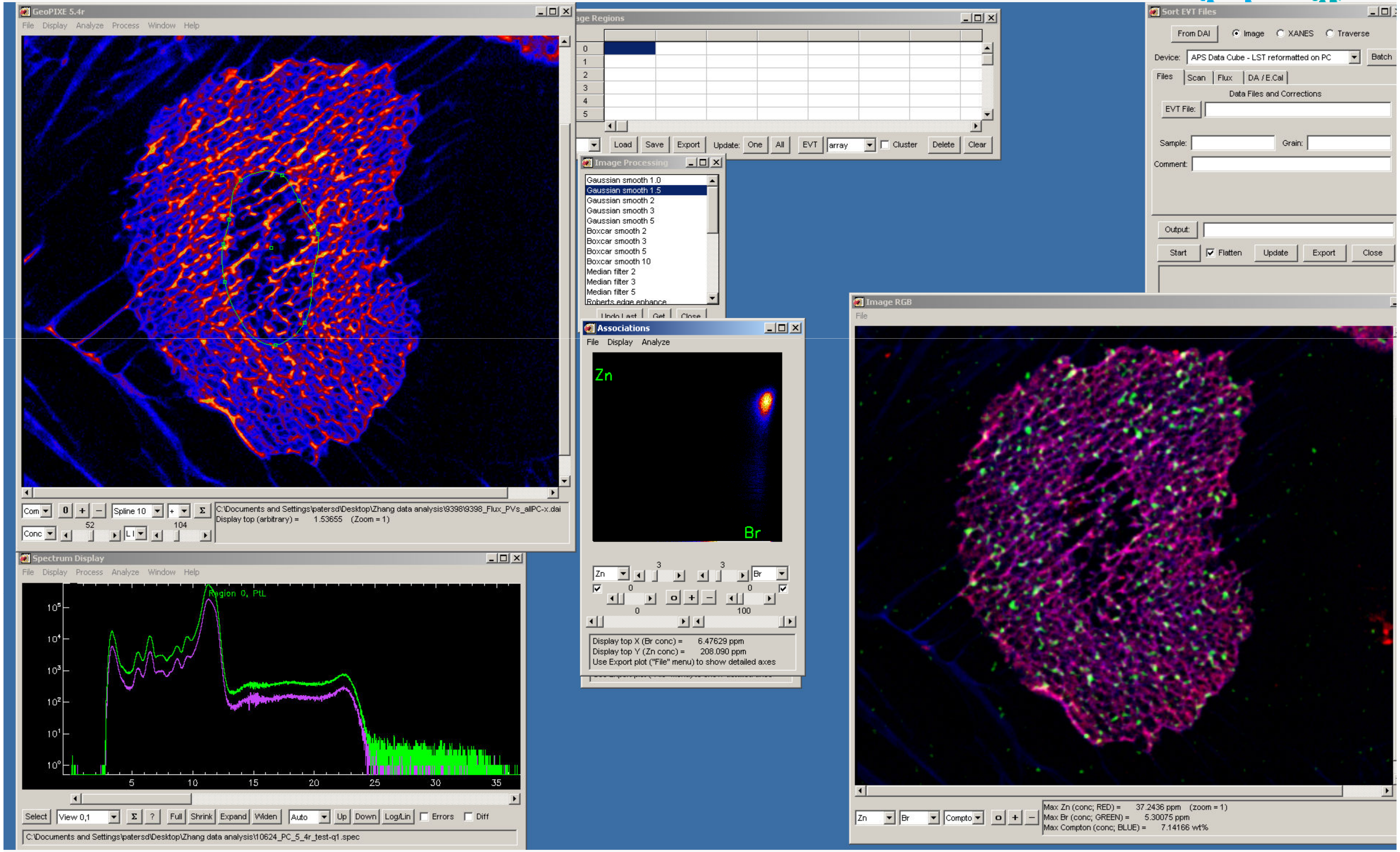
1. W $L_{\beta 1,2}$
2. Yb $L_{\gamma 1}$
3. Zn K_β
4. Ge K_α
5. As tails

…

Need full "fit" to all spectral components

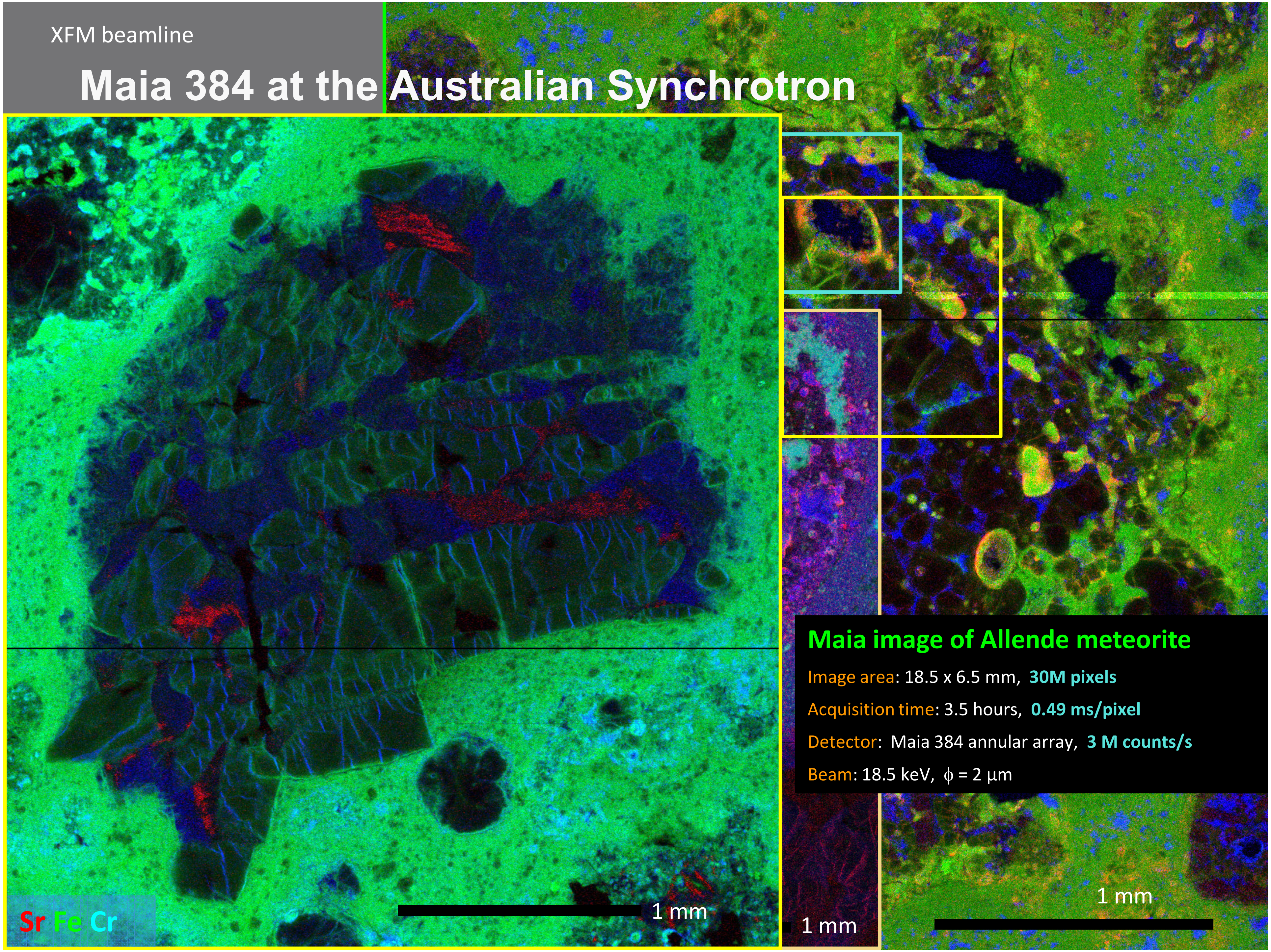


GeoPIXE for quantitative verifiable analysis



XFM beamline

Maia 384 at the Australian Synchrotron



Maia image of Allende meteorite

Image area: 18.5 x 6.5 mm, **30M pixels**

Acquisition time: 3.5 hours, **0.49 ms/pixel**

Detector: Maia 384 annular array, **3 M counts/s**

Beam: 18.5 keV, ϕ = 2 µm

Spectromicroscopy

Claire Weekley *et al.*

Metabolism of selenite in human lung cancer cells: X-ray absorption and fluorescence studies, Journal of American Chemical Society, **133**, 18272-18279 (2011).

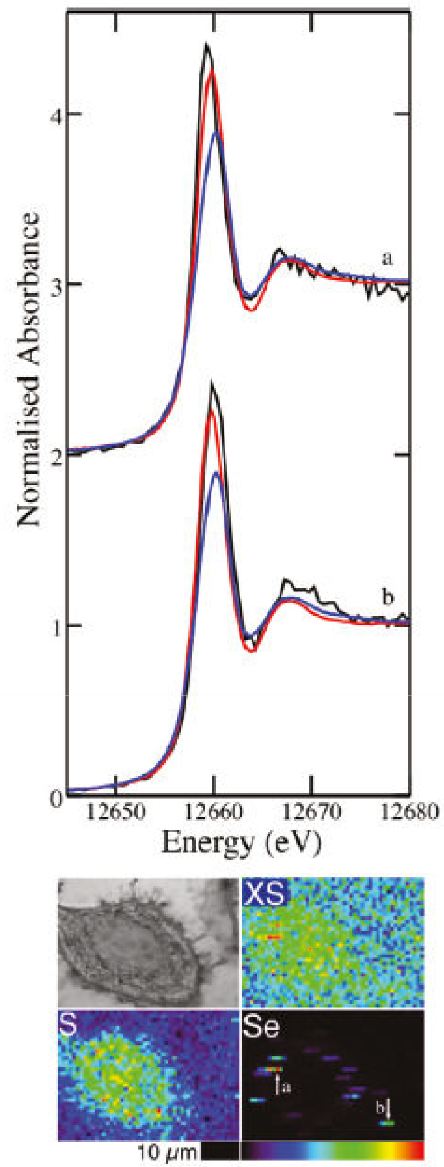


Figure 7. Se K-edge μ-XANES spectra of Se hotspots in an A549 cell treated with 5 μm selenite. The experimental spectra (a and b, black) are overlaid with the spectra of elemental Se (red) and GSSeSG (blue). The optical micrograph (top left) and scattered X-ray (XS) and elemental distribution maps of S and Se of the cell are shown with arrows indicating the locations from which spectra (a) and (b) were collected.

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Conclusions and future directions	• **Summary: pros and cons of XRF** • Future directions: e.g. 3D XANES imaging

Summary: pros and cons of XRF

Pros and advantages

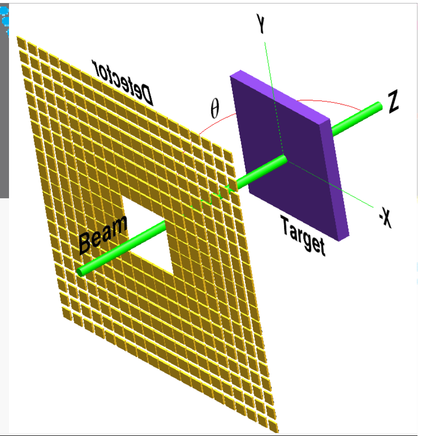
- Non-destructive multi-elemental analysis in parallel (EDS)
- Two dimensional mapping and 3D
- Easy to carry out the analysis and interpret the results
- Optical system for EDS analysis is straightforward
- Infinite field of view, any sample size, from sub-cellular to paintings.
- *in situ, in vivo*, in air, specialized sample environments: temperature, pressure, ...
- Concentration major (%), minor, and trace (ppm) many elements in complex matrix
- Combine with other techniques for more power. E.g. X-ray diffraction and XAFS

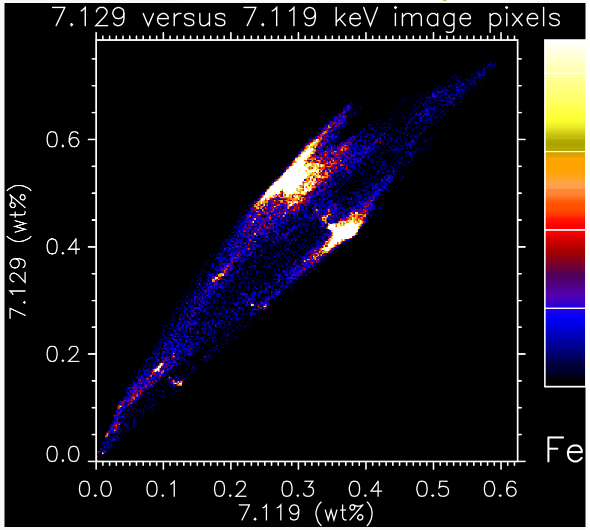
Cons and limitations

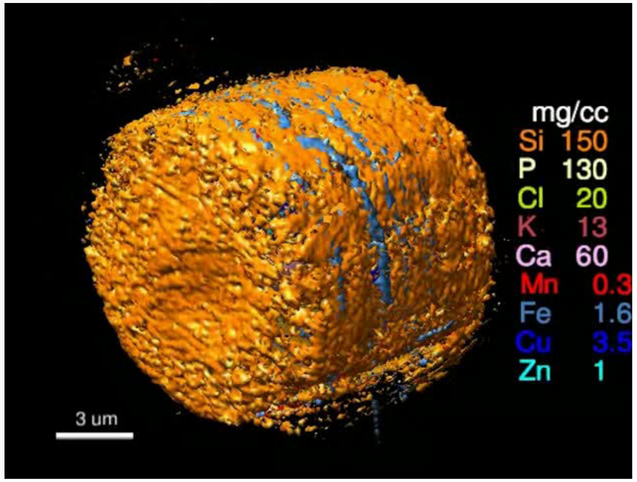
- Microprobe analysis: sample thickness ~ beam size, prep of thin sections can be difficult
- Relatively slow and time consuming: proportional to number of pixels
- Low excitation efficiency for light elements
- Detailed calibration is required to high precision quantitative analysis
- Sample damage, radiation damage can be an issue & should be considered
- Photo-reduction/oxidation of the component elements.
- Lines can overlap difficult to deconvolute

Future directions

- Detector advances continue
- Event mode data acquisition becomes routine
- Full spectrum measured at a pixel
- 3D techniques
  - Tomography
  - XANES imaging (chemical state imaging)
- 4D techniques
  - 3D chemical state imaging, XANES tomography
  - Time based 3D studies







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Acknowledgements XFM

- Martin de Jonge, Daryl Howard, Simon James, Kathryn Spiers
- XFM
- Jonathan McKinlay, Wayne Lewis, Andy Starritt, Mark Bennett, Mick Kusel, Emmanuel Vettoor, … AS

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- Chris Ryan, Robin Kirkham, Gareth Moorhead, Murray Jensen,
- CSIRO
- Pete Siddons NSLS

Maia detector team

NSLS/BNL

- Pete Siddons
- Tony Kuczewski
- Arthur Zhi Yong Li
- Gianluigi De Geronimo
- Don Pinelli
- Angelo Dragone
- Paul O'Connor

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- Martin de Jonge
- Daryl Howard
- Simon James
- Kathryn Spiers

CSIRO MSE

- Robin Kirkham
- Paul Dunn
- Gareth Moorhead
- Murray Jensen
- Peter Davey
- Roshan Dodanwela

CSIRO ESRE

- Chris Ryan
- Stacey Borg
- Rob Hough
- James Cleverley
- Jamie Laird

Users (example data)

- Barbara Etschmann
- Jöel Brugger
- Enzo Lombi
- Erica Donner
- Peter Kopittke
- Euan Smith
- Babasola Ajiboye
- Mike McLaughlin
- Hugh Harris
- Mel Lintern
- Steve Barnes
- Belinda Godel
- Aaron Stewart
- Richard Banati
- Andy Tomkins
- Damian Myers

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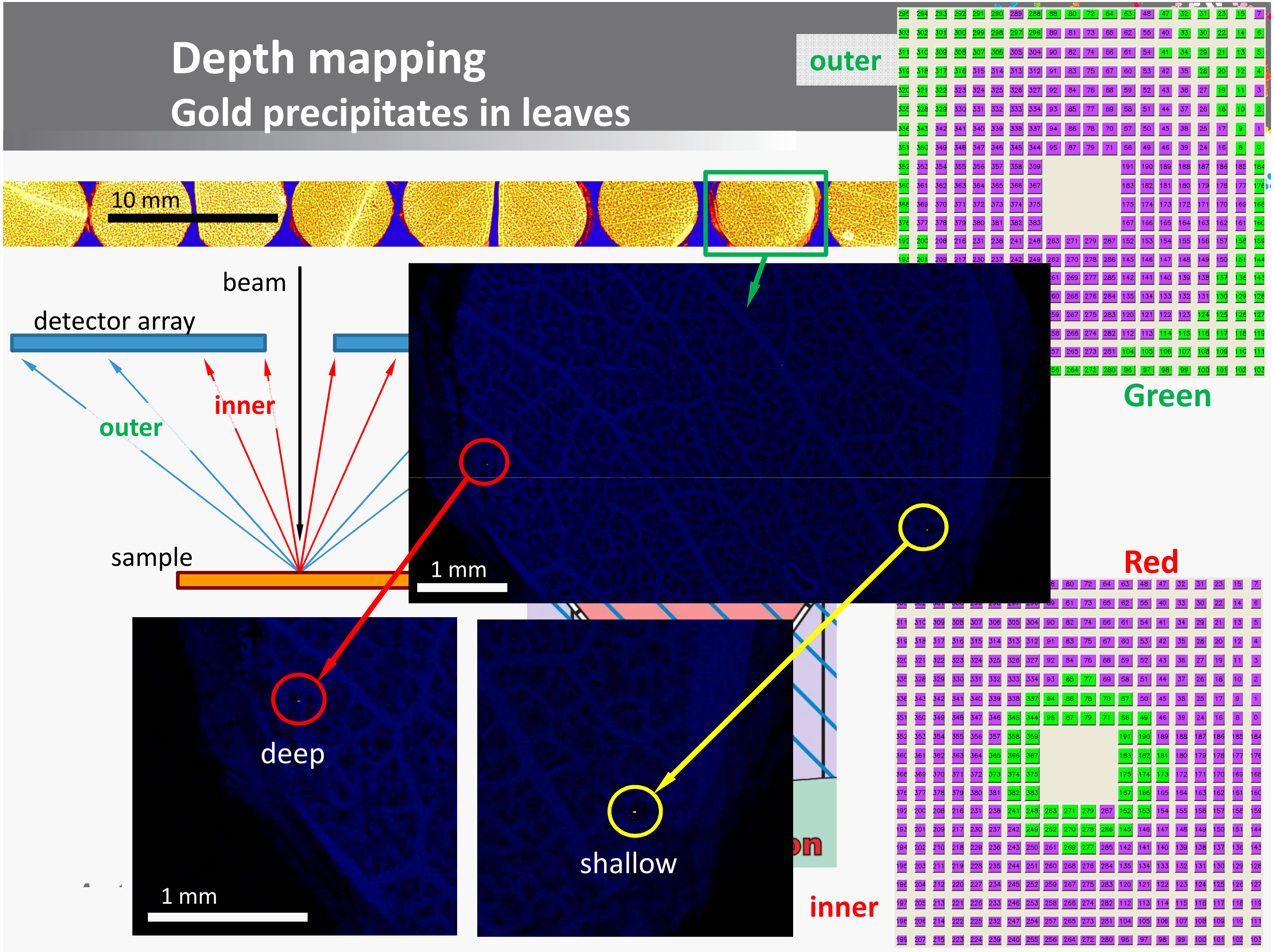
Depth mapping
Gold precipitates in leaves



Conceptual design

D. Paterson, *et al.*, AIP Conf. Proc. **879**, 864 (2007).
B. Lai, *et al.*, AIP Conf. Proc. **879**, 1313 (2007).
I. McNulty, *et al.*, Rev. Sci. Instrum. **67**, 9 CD-ROM (1996).