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X-ray fluorescence microscopy

AOFSRR School

13 August 2024

David Paterson, Daryl Howard , Andrew Langendam,
Keith Bambery,...

Science. Ingenuity. Sustainability.

Outline

X-ray Fluorescence Microscopy

- Context with other microscopies
- XFM beamline capabilities
- High definition ⇔ high resolution

XFM How does it work?

- Microprobe
- Scanning microscopy
- X-ray fluorescence => element determination

Beyond 2D

- XANES Imaging => Chemical speciation
- Real time imaging, e.g. plant physiology
- Tomography

Ptychography Research examples

- Coherent diffraction imaging
- Micro-diffraction
- Research examples

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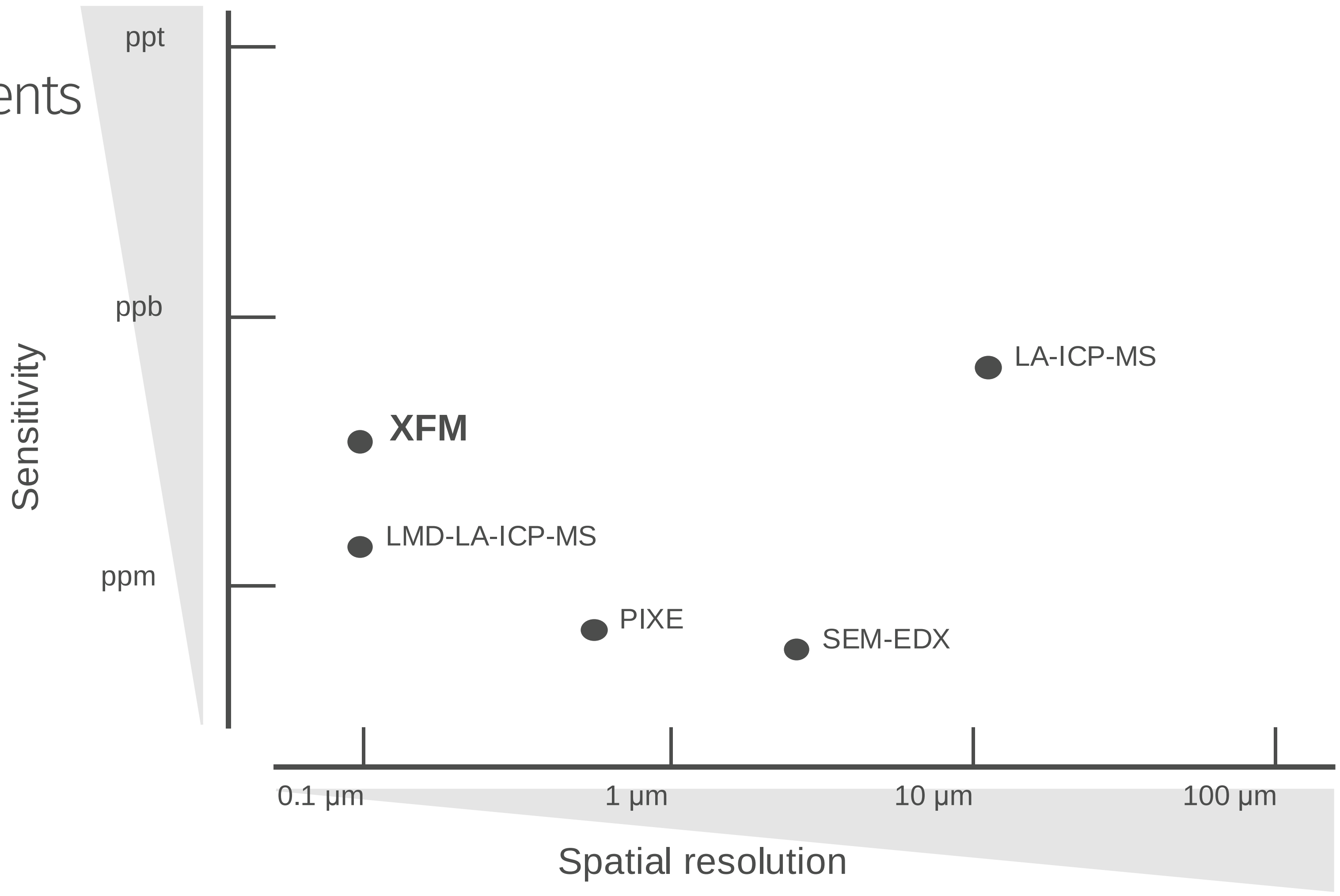
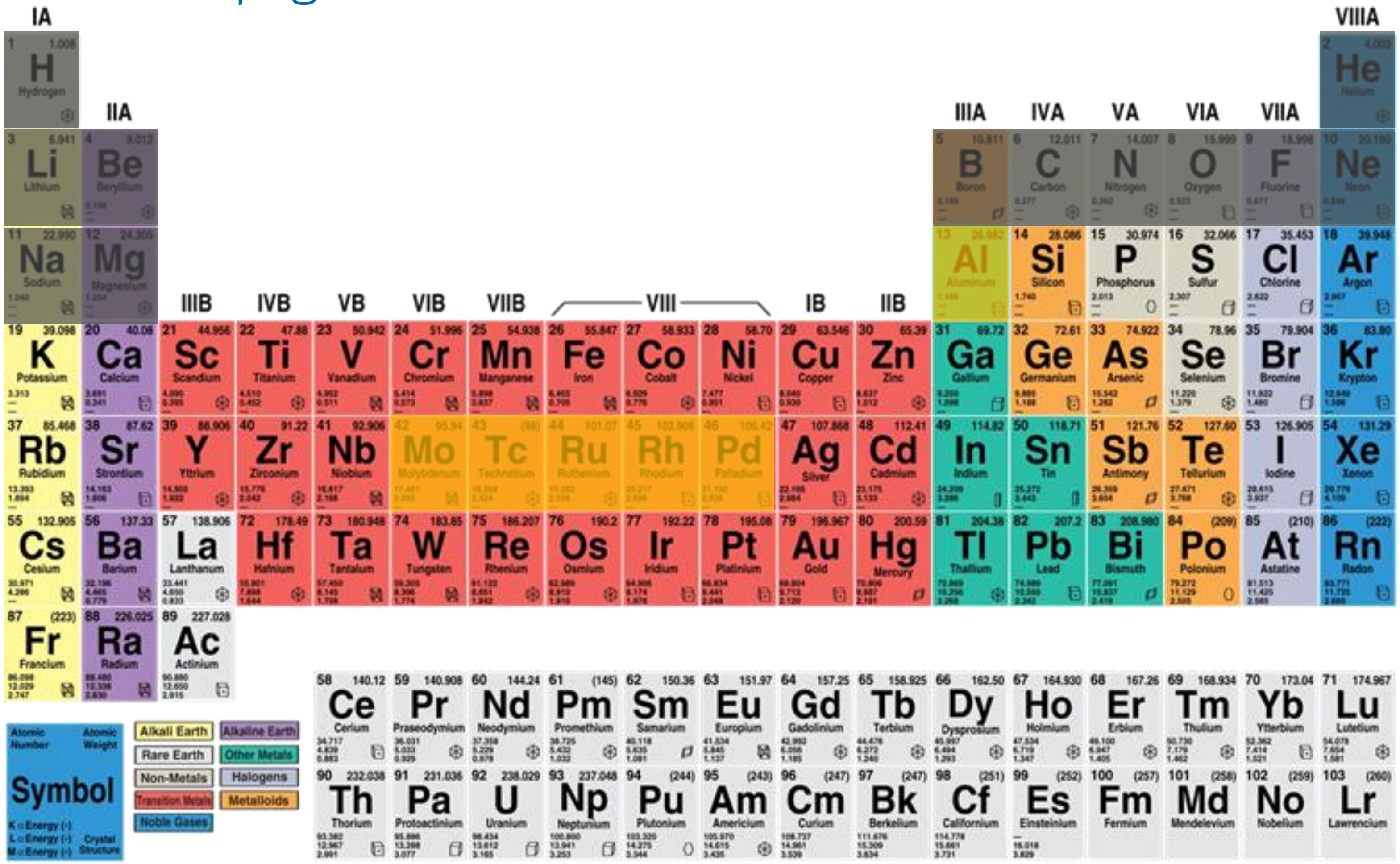
X-ray Fluorescence Microscopy (XFM)

- Simultaneous access to 10+ elements
- No contrast agents required
- Quantitative
- High signal-to-noise ratio
  - ppb sensitivity, improving with Z
- Little sample damage
- Extended penetration depth
  - Study “intact” specimens
- Sensitive to chemical bonding
  - XANES mapping



X-ray Fluorescence Microscopy Beamline information

- www.ansto.gov.au/user-access/instruments/australian-synchrotron-beamlines/x-ray-fluorescence-microscopy
- asuserwiki.atlassian.net/wiki/spaces/UO/pages/22609927/XFM+Beamline
- Email: as-xfm@ansto.gov.au

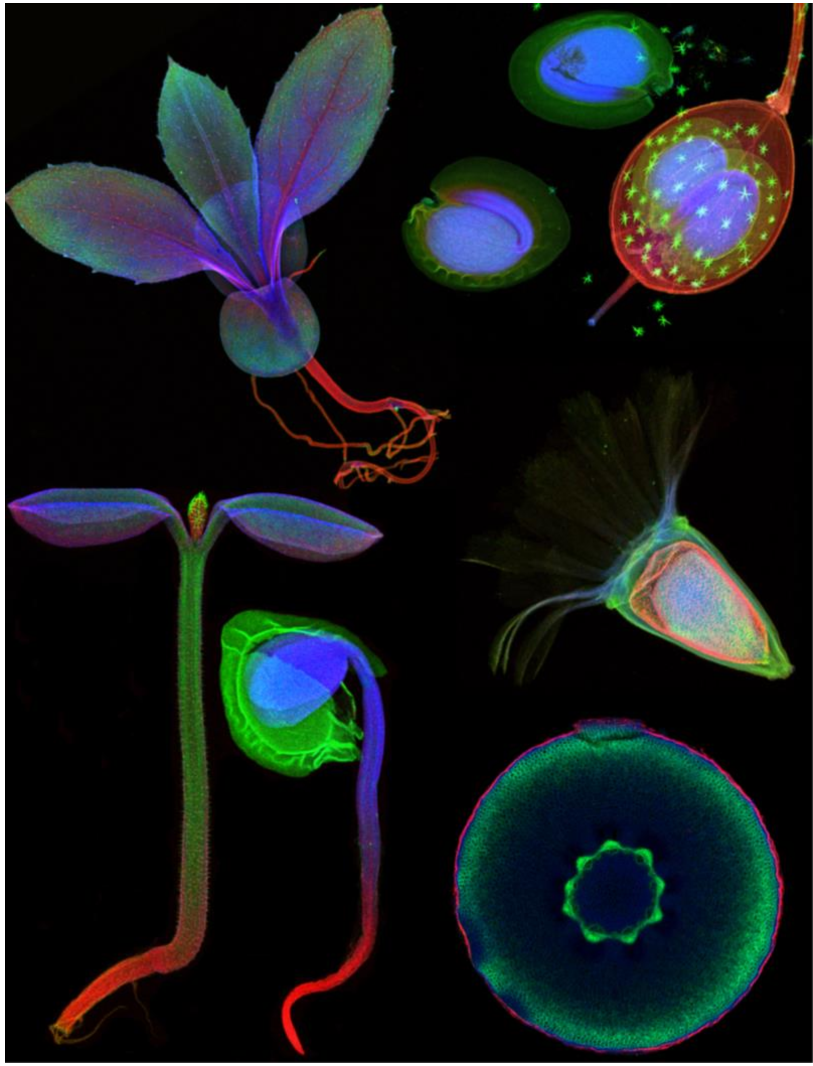


X-ray Fluorescence Microscopy

Energy range: 4 to 25+ keV

- Hard X-ray microprobe ΔE/E ~10-4
- 2 µm focal spot = resolution
- X-ray fluorescence mapping (µ-XRF)
- X-ray fluorescence µ-XANES => XANES imaging
- X-ray fluorescence tomography
- Scanning X-ray Diffraction Microscopy, Ptychography

Nanoprobe 60–300 nm resolution Soon!



Probe	Resolution	Field of View H X V
KB Microprobe	**2 µm**	**150 X 100 mm**
Milliprobe	50 µm	600 X 1200 mm

XFM staff

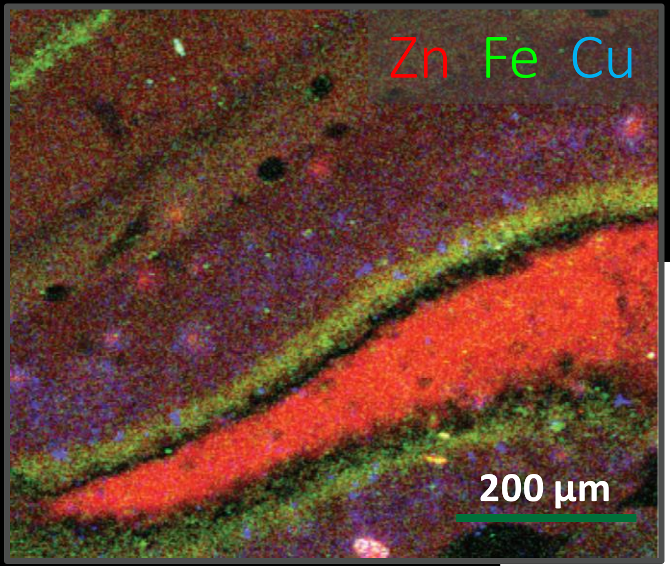
Daryl Howard
Expertise
Chemistry, XRF data analysis, micro-XANES imaging milliprobe and cultural heritage studies

Andrew Langendam
AKA The meteorite hunter
Expertise
Geo-chemistry, geology, planetary science, XRF data analysis

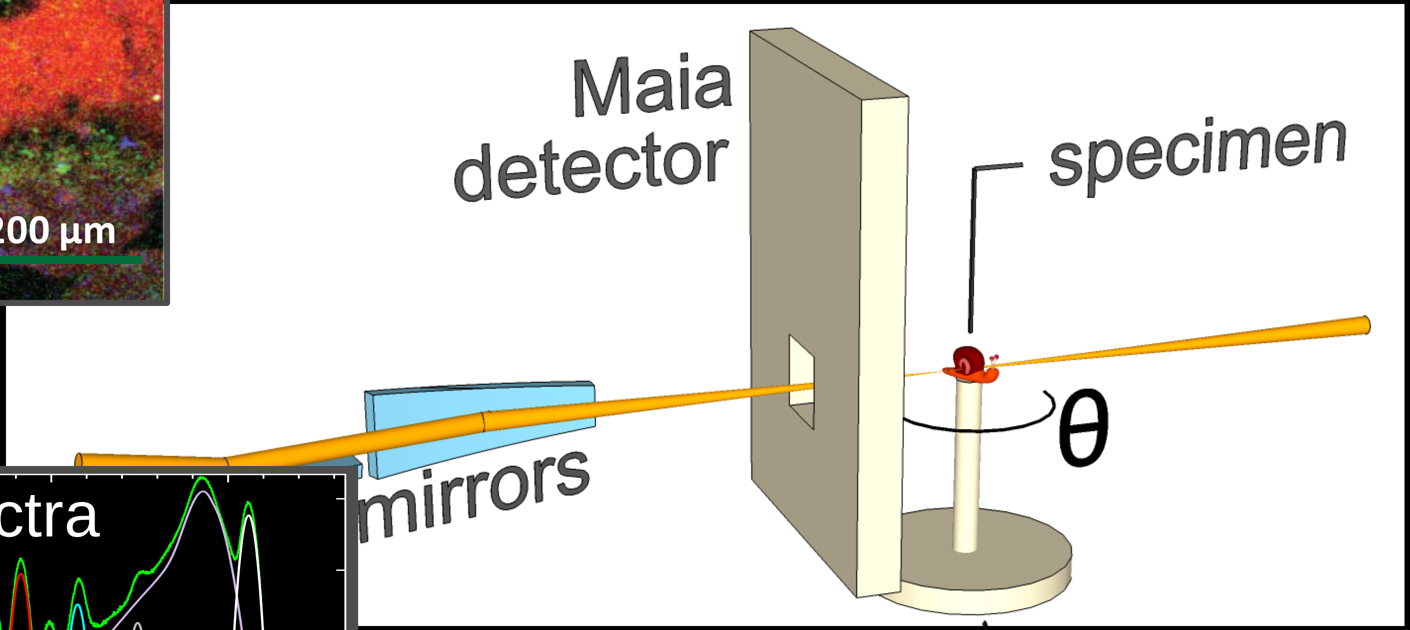
David Paterson
Expertise
Physics, XRF data analysis, X-ray microscopy, XFM applications in environmental science

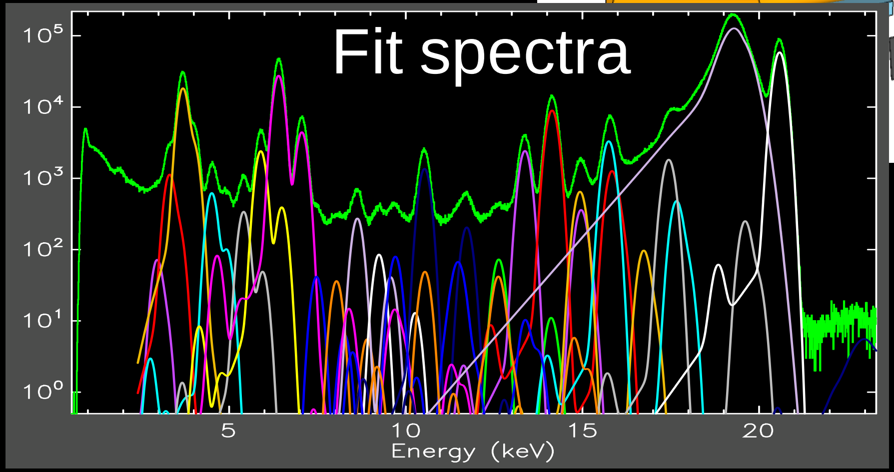
Martin de Jonge
Cameron Kewish
Michael James
Gary Ruben
Simon James
Carl Yang
…

X-ray Fluorescence Microscopy

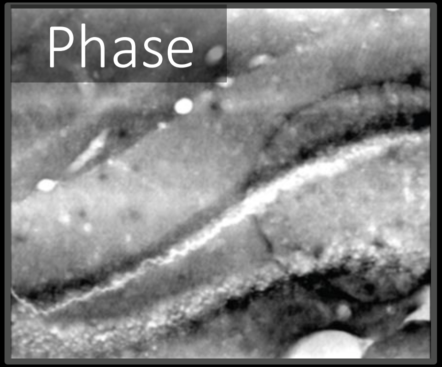


1. Form a spot on a specimen
2. Collect (fluorescence + scatter) *and* stage position signals *while* scanning



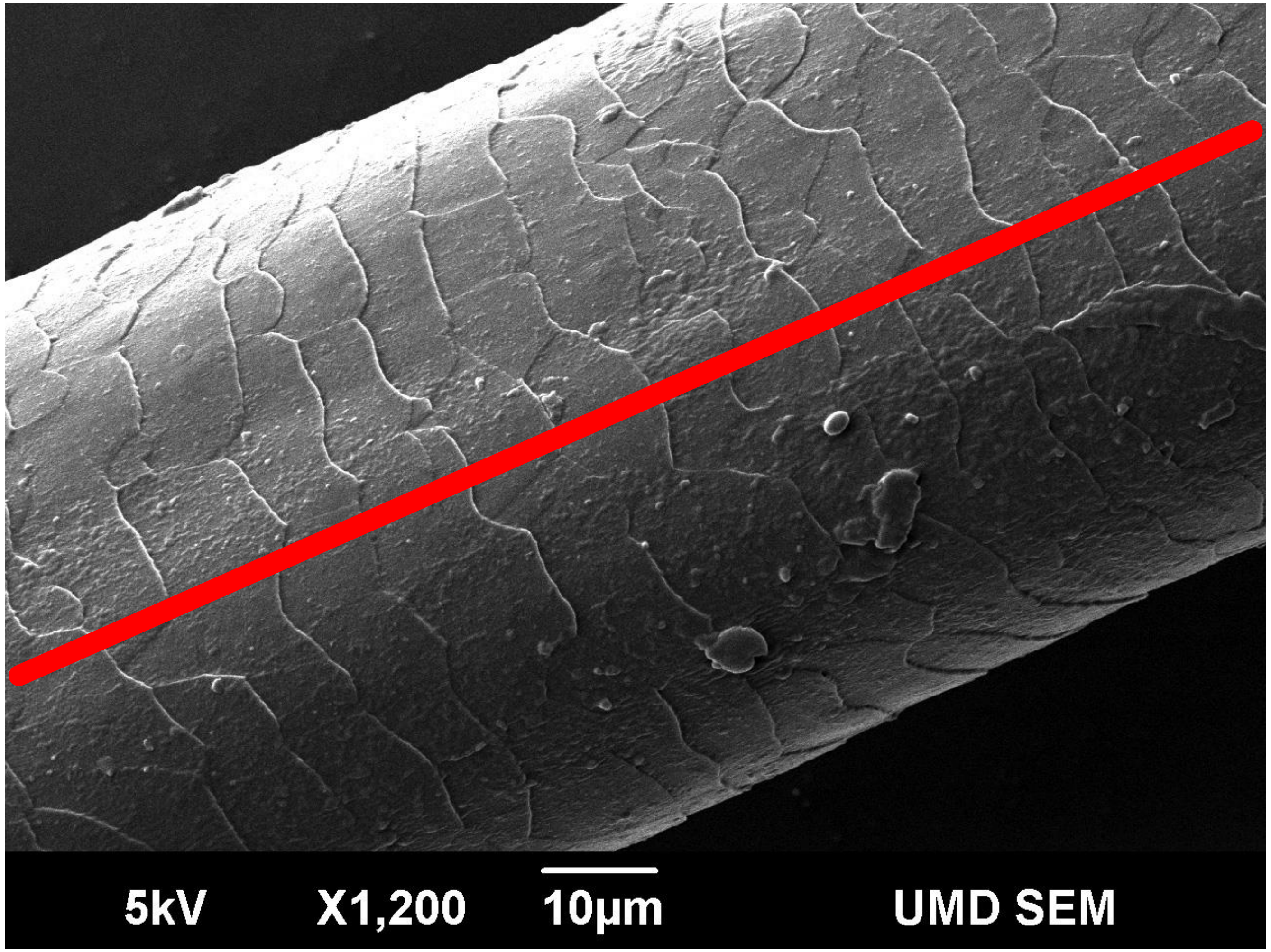


XFM @ AS:
~2 µm FWHM
~1e10 ph / s



How big is the focused X-ray beam?

Human Hair

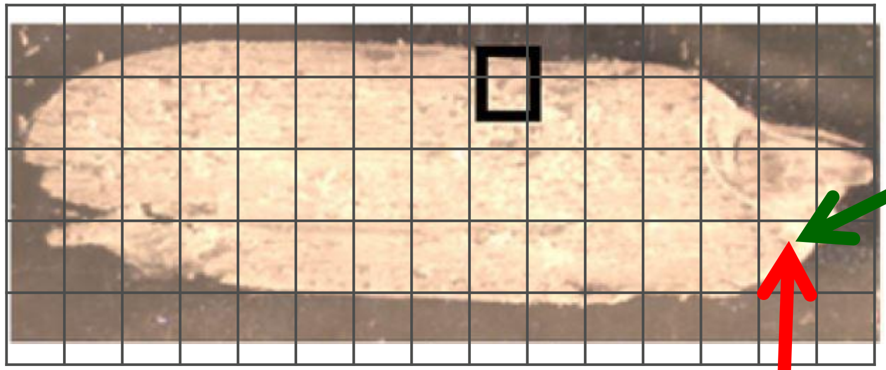


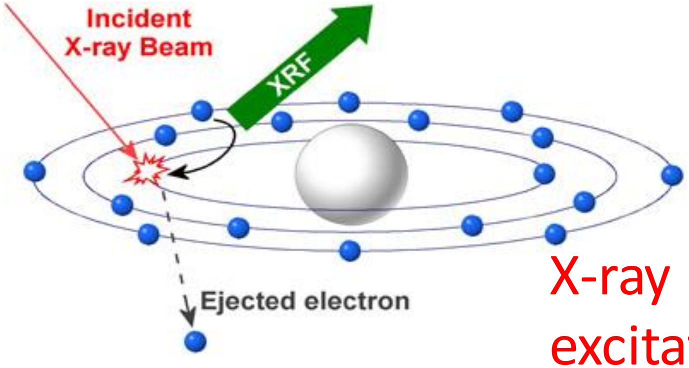
nisenet.org

Size of beam = **2 µm**
relative to width of hair

X-ray Fluorescence Microscopy

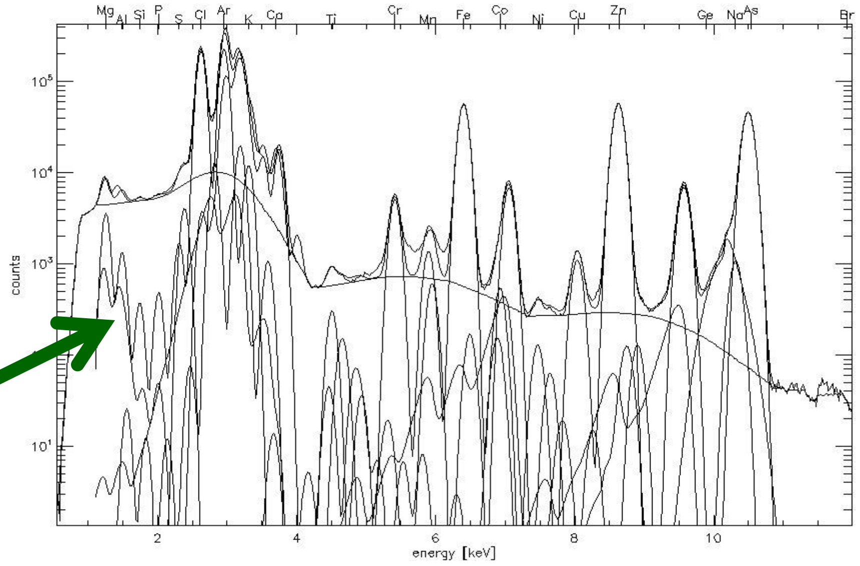
rice grain section

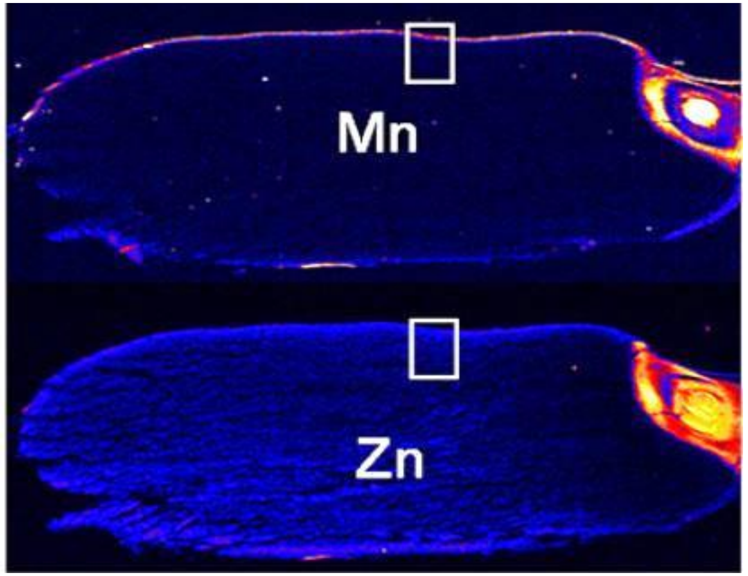




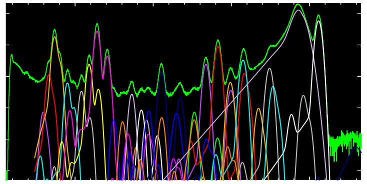
Hansen et al. J. Cer. Sci. 56 (2012) 307

X-ray
excitation beam
(monochromatic)



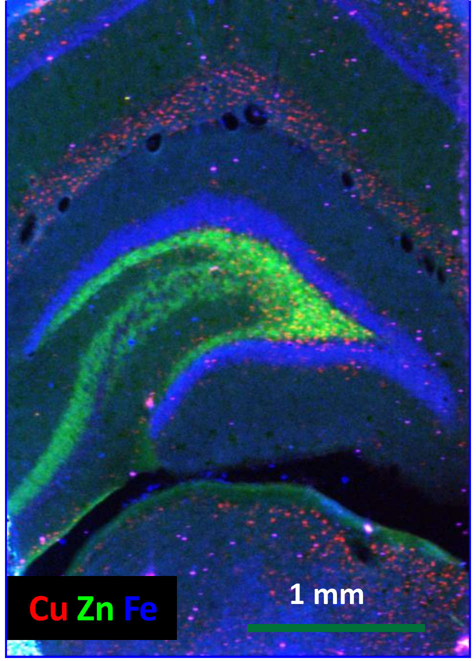


XFM – ideal for bio-metals



Simultaneous access to **10^{+} elements**
Z > 14 ~ Si

High sensitivity - sub-ppm; sub-mM; 1e-12g / s



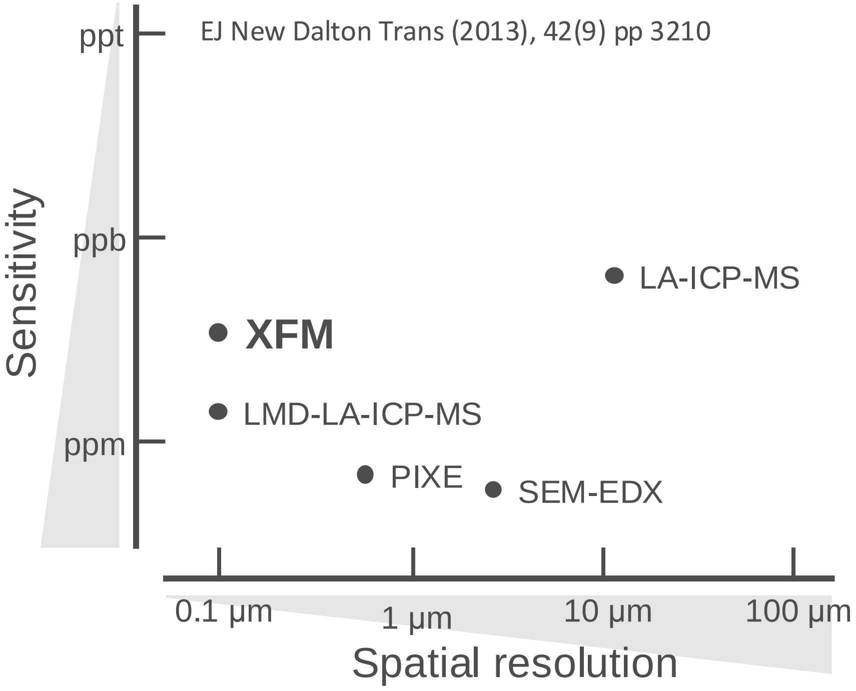
Native contrast - no dyes or contrast agents necessary - but possible!

Quantitative

Non-destructive / minor damage

Extended penetration & DoF
- study intact cells & sections

Sensitive to **chemical speciation** via XANES spectroscopy



concept with thanks - & apologies - to S Vogt, APS.

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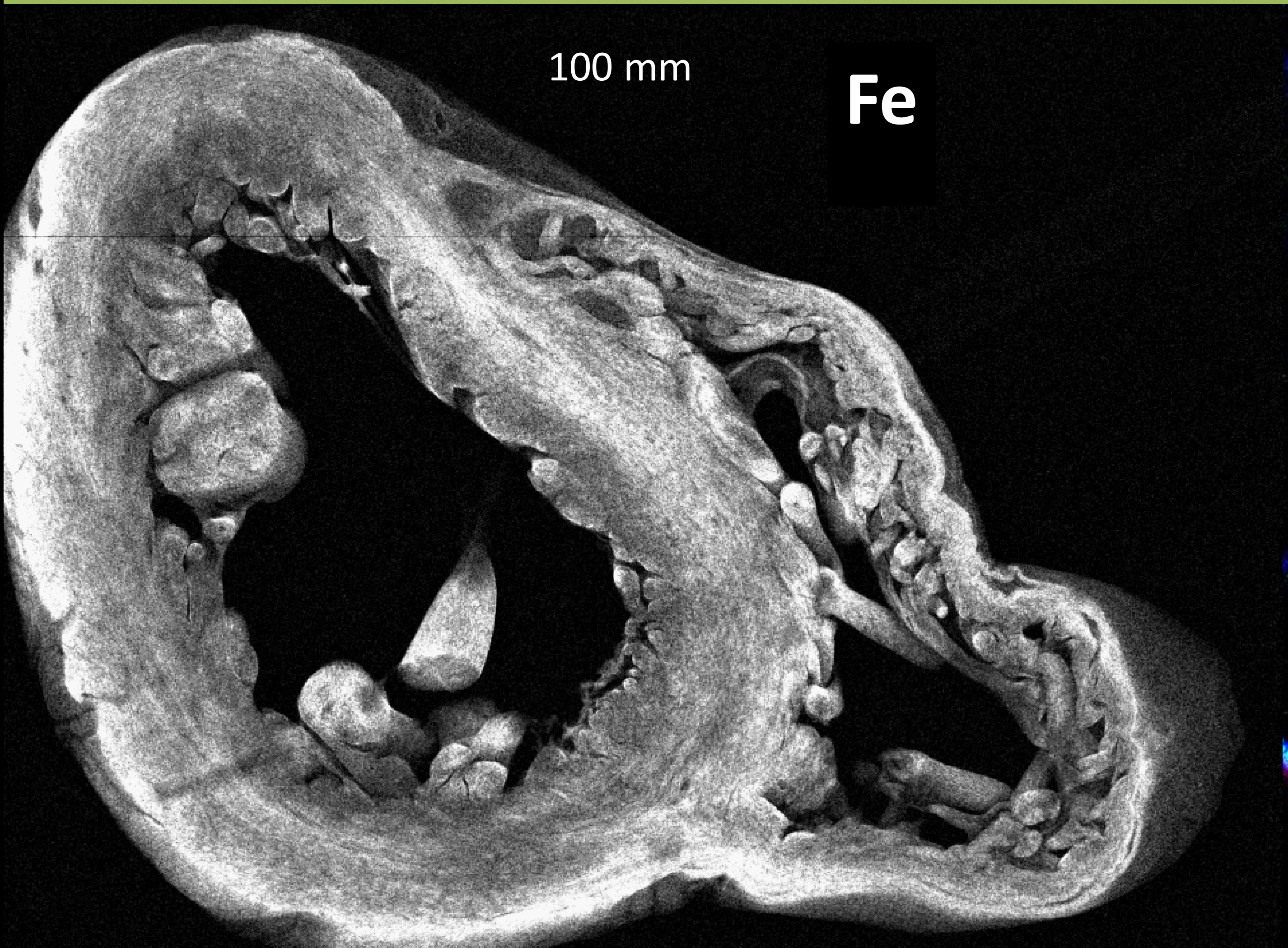
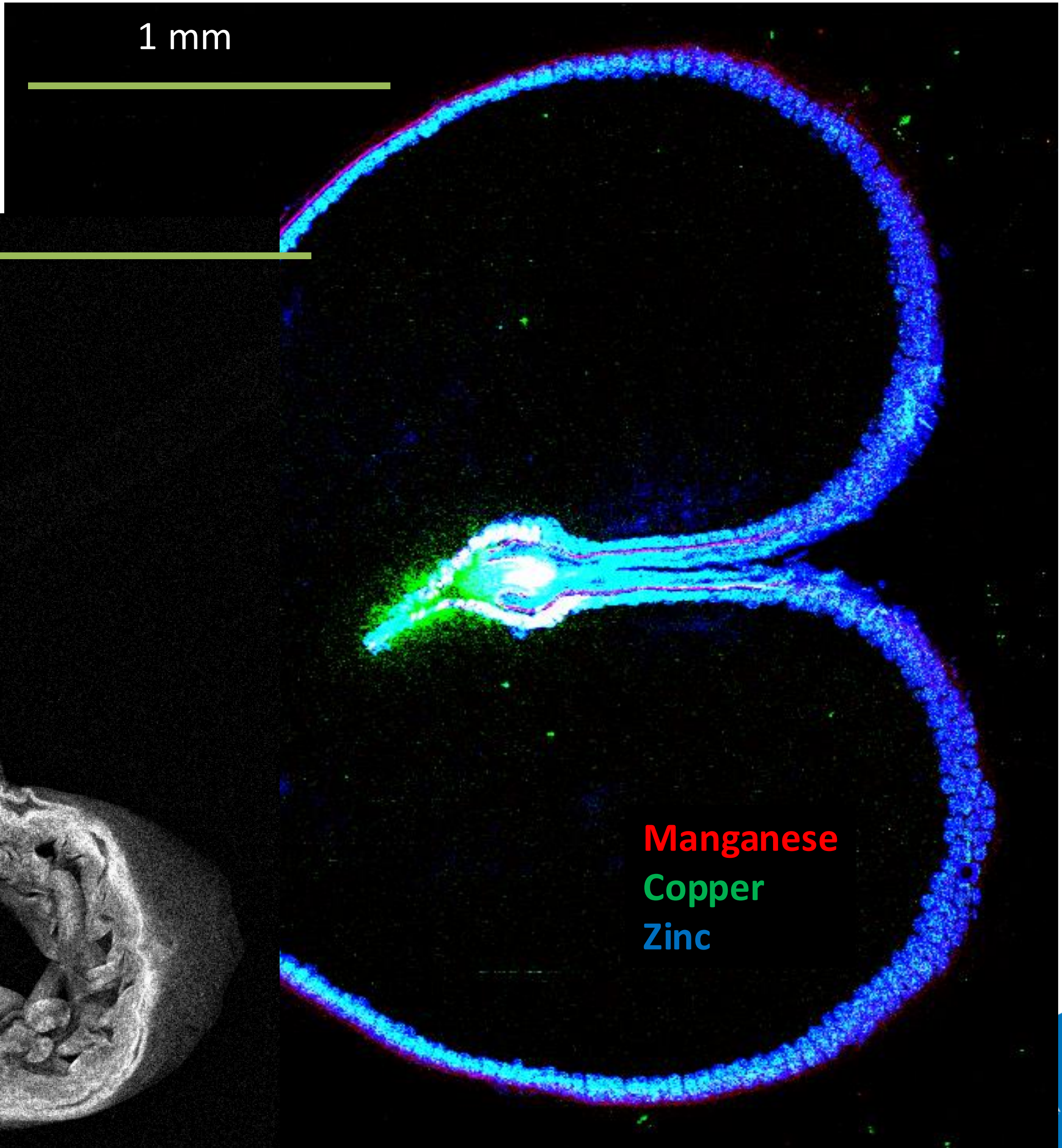
Imaging across multiple length scales





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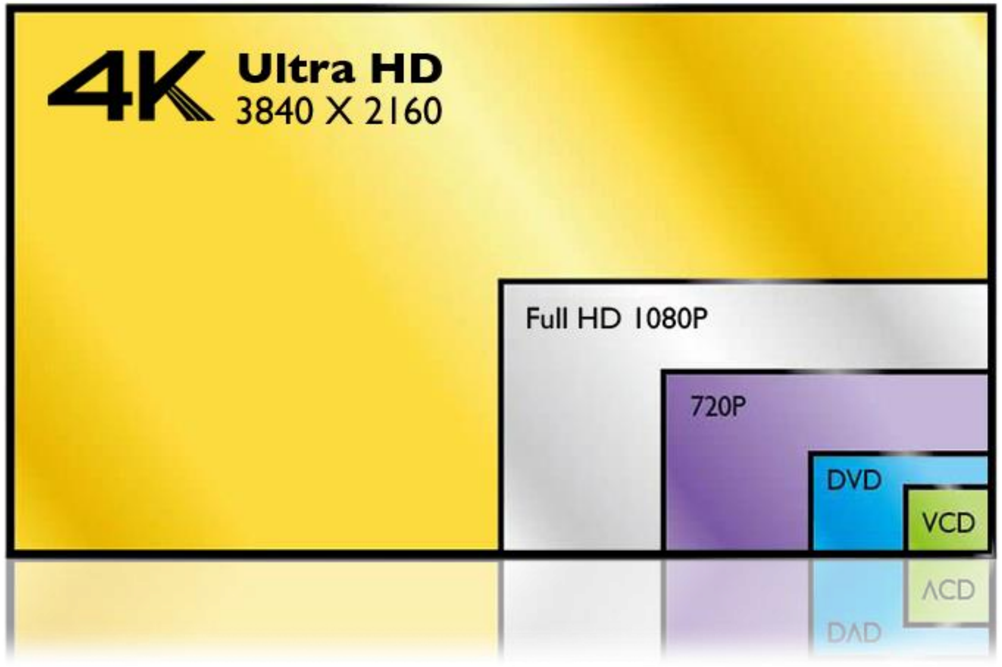
Definition ⇔ resolution



- Microprobe **150** X 100 mm @ 1 µm
  - 20 nm pixels possible
  - 5 nm steps coming soon
- Milliprobe 600 X 1200 mm @ 50 µm
  - 1 µm pixels are possible
- Gigapixel images are possible

Beyond 2D

100 Mpix ~ 1 day @ 1 ms			
Scan axis 1 (fast)	**Scan axis 2 (medium)**	**Scan axis 3 (slow)**	**Measurement modality**
10k X	10k Y		**High-definition imaging**
1k X	1k Y	100 Ene	**XANES imaging**
5.6k X	18k θ		**High-definition 2D fluorescence tomography**
316 X	316 Y	995 θ	**3D fluorescence tomography**
560 X	1.7k θ	100 E	**2D XANES tomography**

Tomography

Arabidopsis Thalania,
ipk1

Punshon, Lombi, *et al*
2011

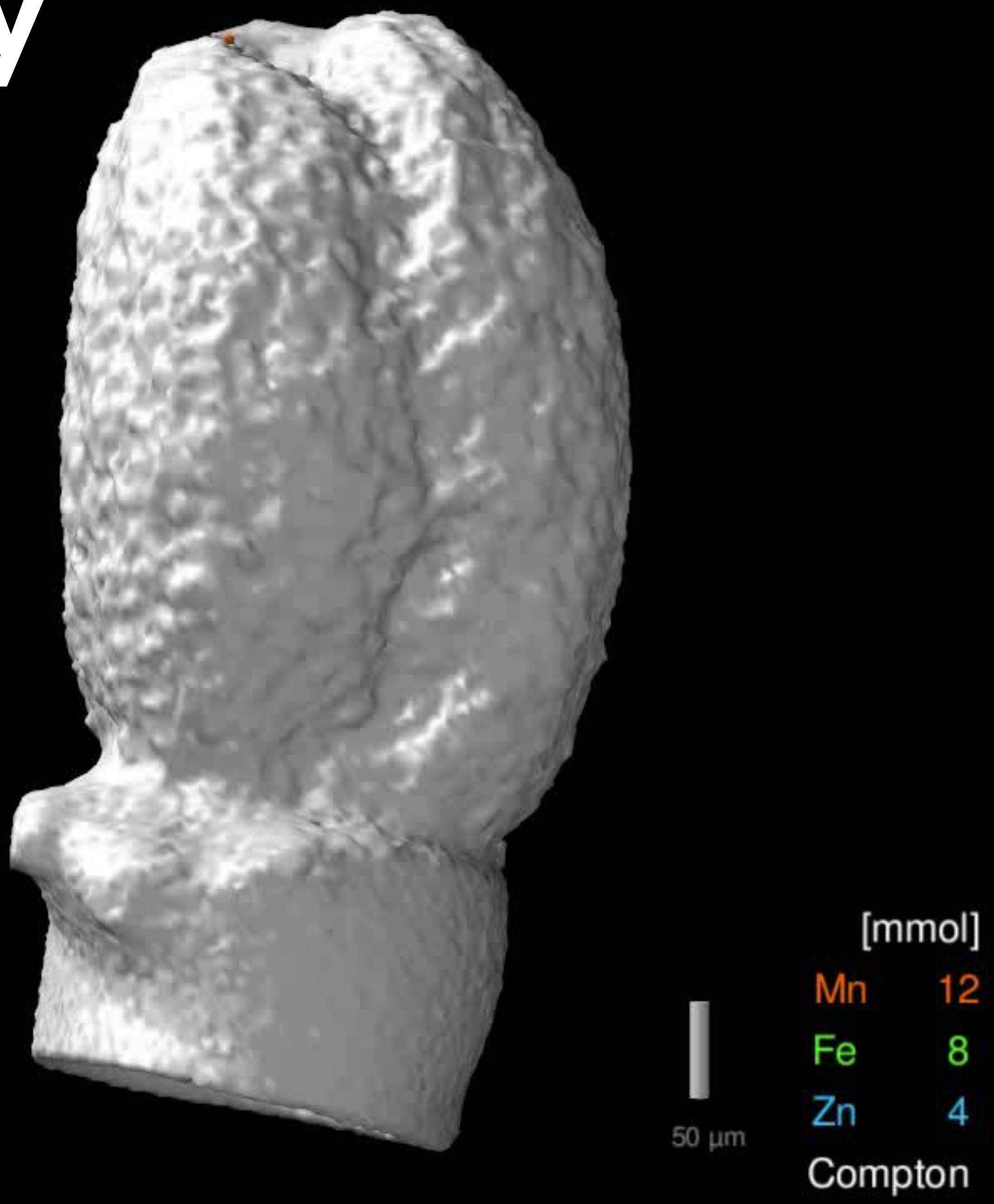
Δx = Δy = 2 µm

FoV = 600 * 700 µm
v = 768 µm / s
Dwell = 2.6 ms

Nangles = 100

7m 40 s / projection
12.8 hrs / series

Estimate ~ 2.1 hrs
with upgraded
motion + Maia at 90°



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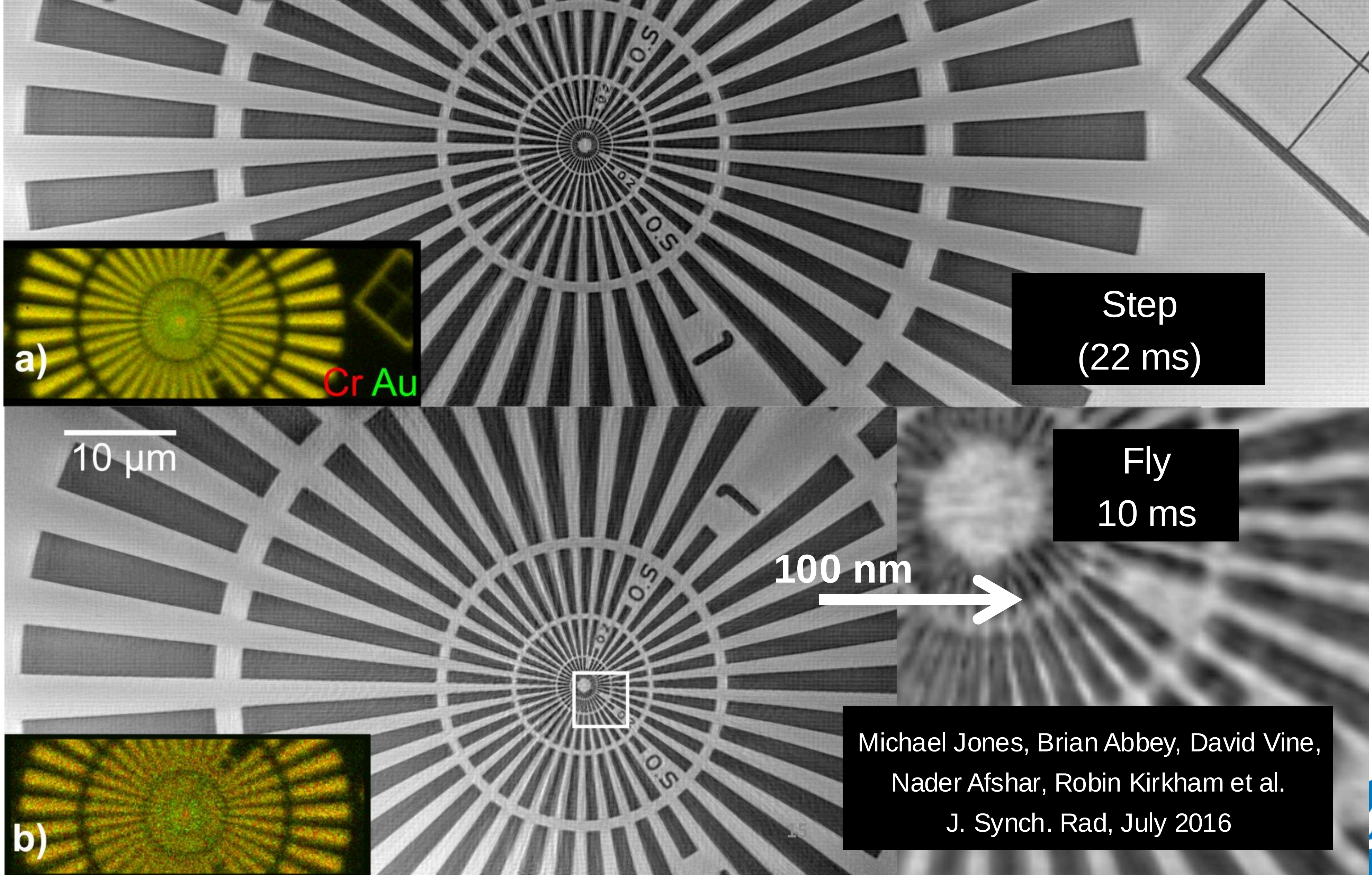
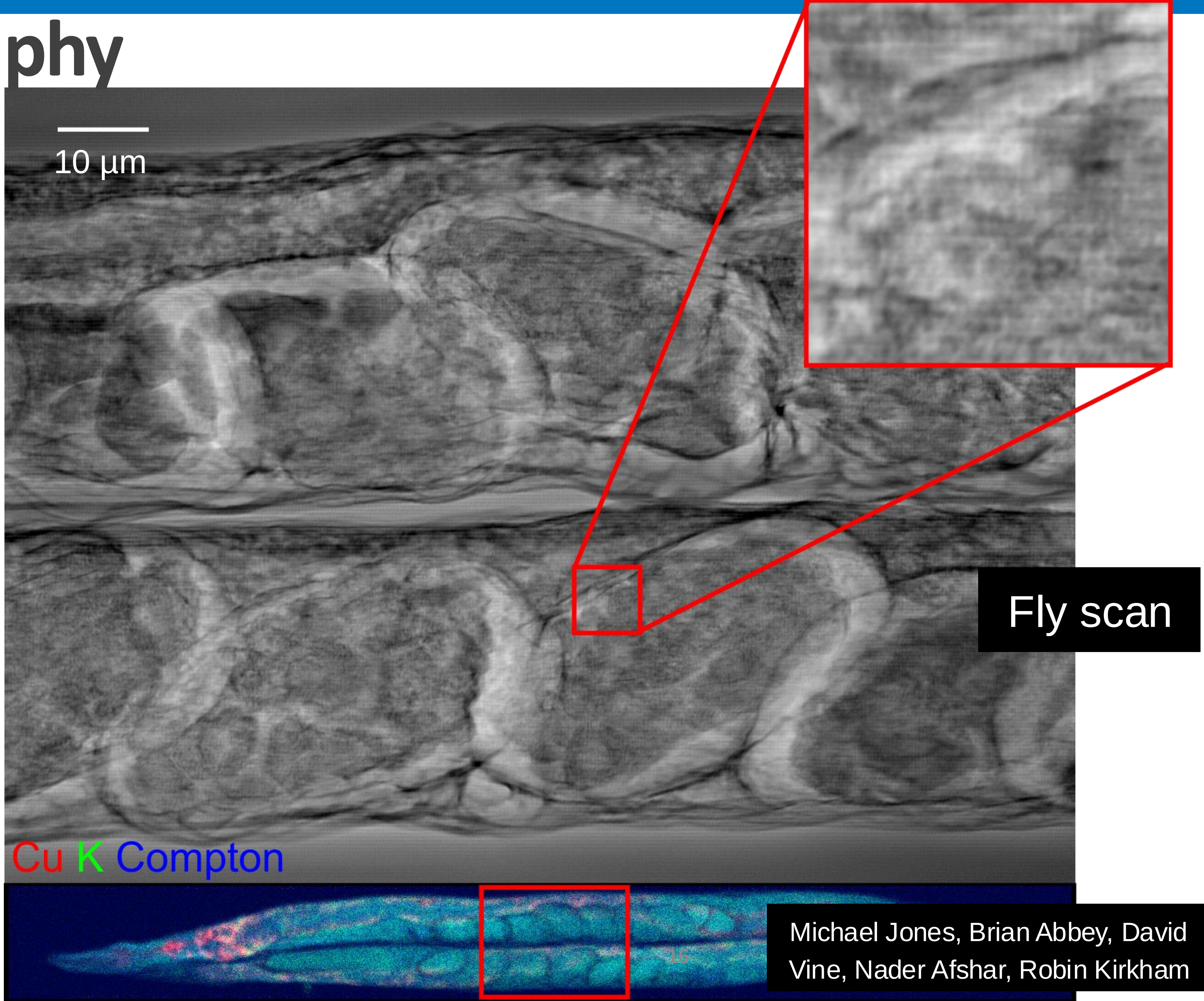
Ptychography



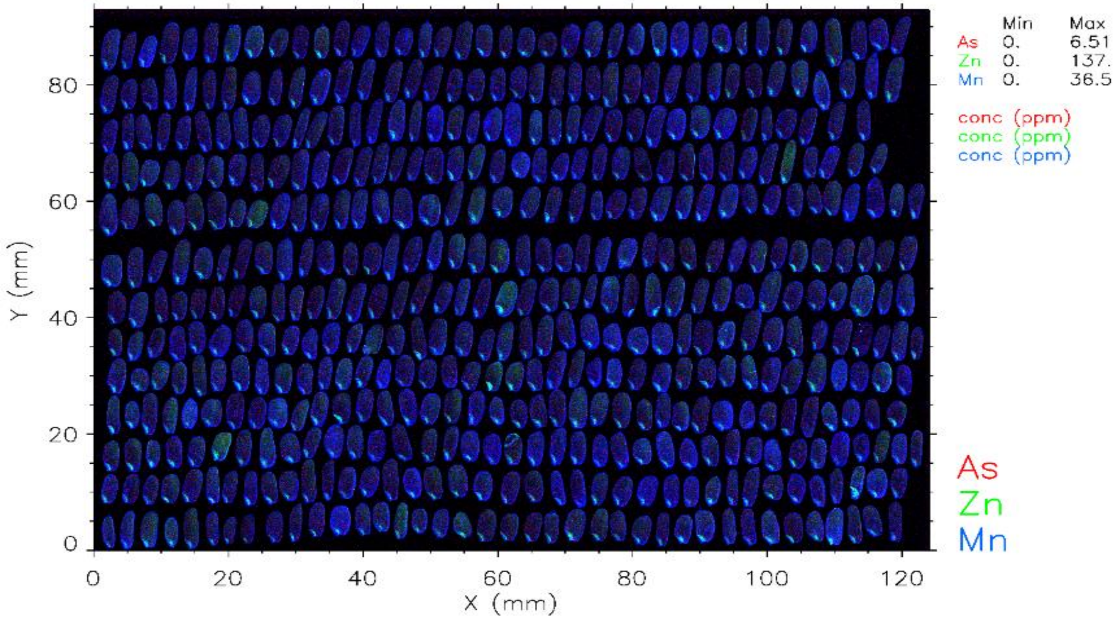
Ptychography



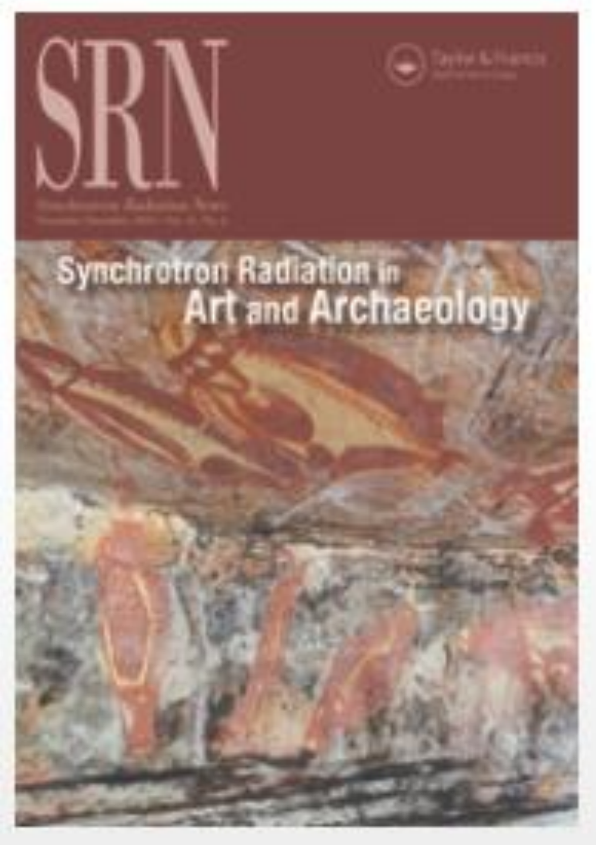
Michael Jones, Brian Abbey, David Vine, Nader Afshar, Robin Kirkham

Research examples

- Earth Sciences
- Environment
- Agriculture
- Life sciences
- Cultural heritage
- Art and archaeology, …



Un-published data courtesy P. Wang, P. Kopittke, (Uni. QLD) and E. Lombi (Uni. SA) ***494 rice seeds,*** *pixels, 6200 X 4640 28.8 M 20 µm pixels.*



Mineral wastes: Future mines

- **Challenges for mineral resources industry**

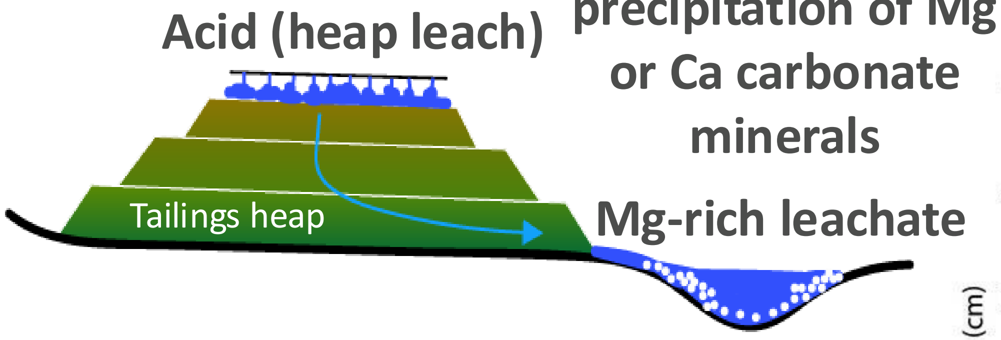
Jessica Hamilton

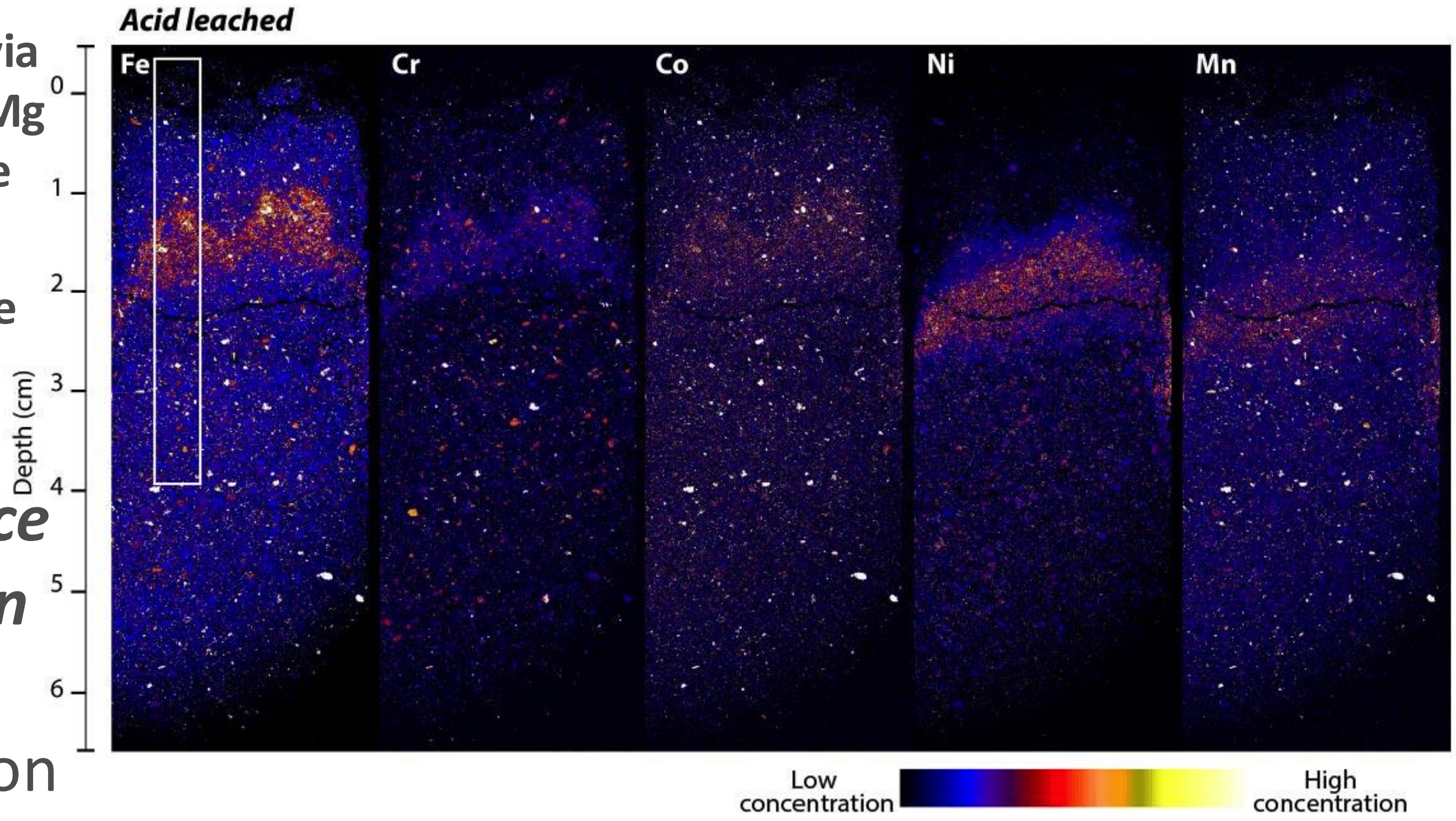
- meet increased demand
- operate more sustainably (and ethically)

- **Waste rock and tailings are future resources**

- weathering reactions in waste piles alter mineralogy & geochemistry
- can mobilise previously inaccessible metals
- Opportunity: harness these reactions & speed them with aim to re-mine
- Bonus: Ca- and Mg-rich rock types also suitable for carbon sequestration!

Carbon sequestration coupled with metal enrichment





Acid leaching also ***enriches trace metals at the pH neutralisation horizon***

- simulates laterite ore formation
- potentially re-minable zone

Hamilton et.al. Economic Geology **115**, 303 (2020)

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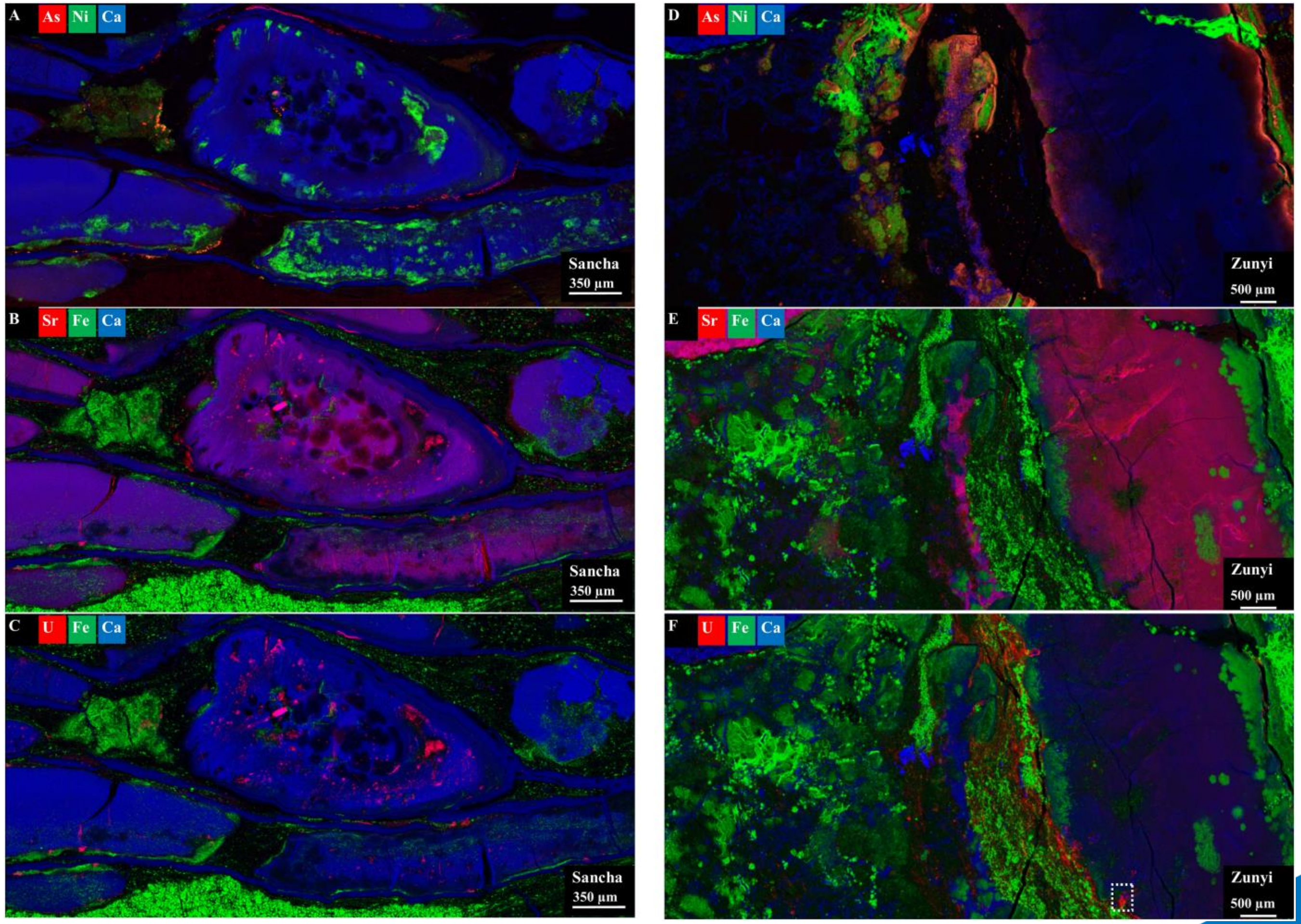
Micron-scale distribution of metals: Insights into local biologically driven redox disequilibrium

- South China Cambrian shales
- A thin organic-rich layer contains exceptional concentrations Mo, Ni, Se, Re, Os, As, Hg, Sb, Ag, Au, Pt, Pd, U.
- A rare opportunity to study the interface between metals and biogenic material.
- Highlights how biogenic activity can induce micron-scale variations in redox conditions.



A. Pagès, S. Barnes, S. Schmid, C. Ryan, D. Paterson, C. MacRae, J. Laird, M. Le Vaillant, H. Fan and Hanjie Wen. Chemical Geology **528,** 119283 (2019)

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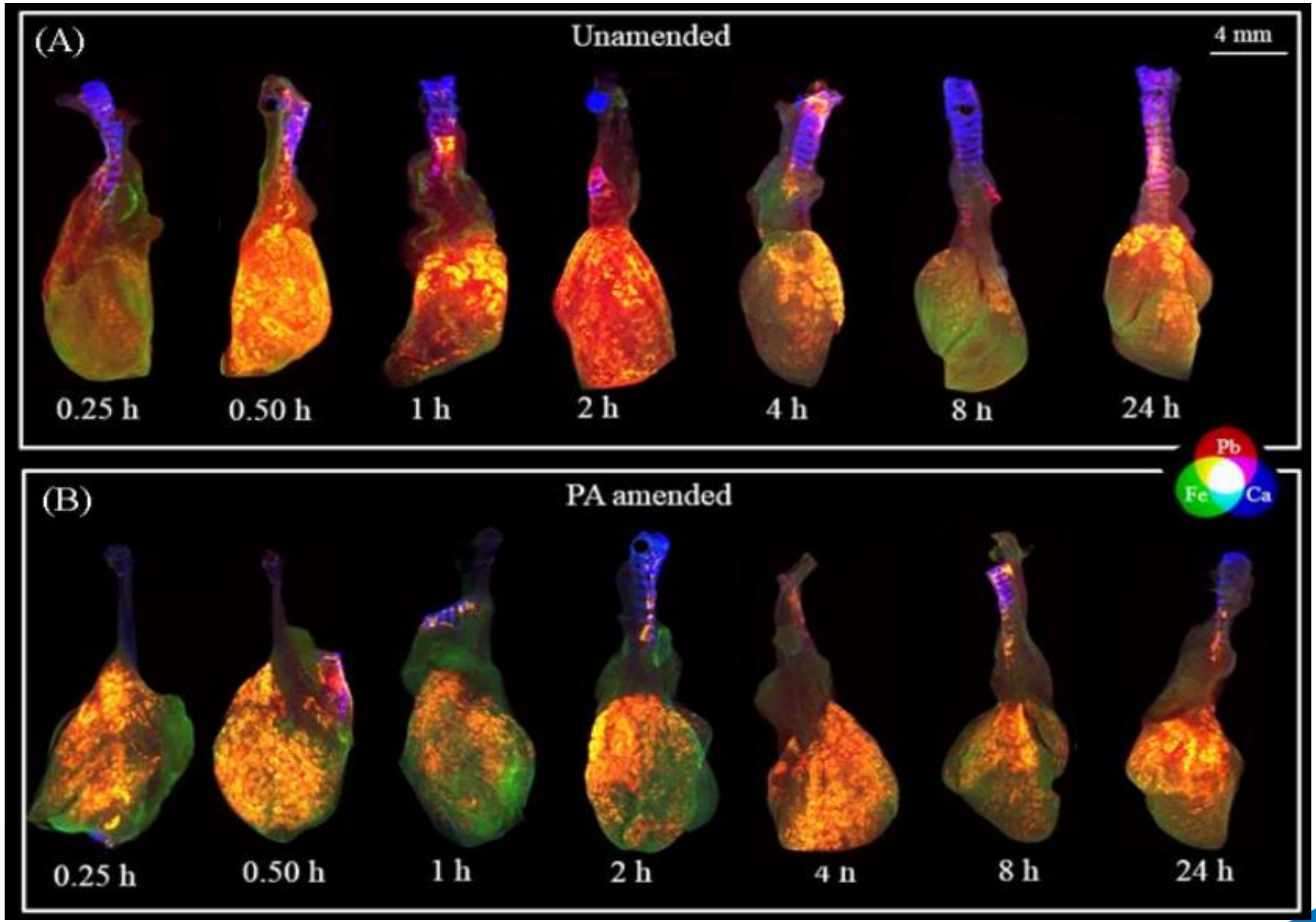
Lead exposure reduction via inhalation pathways using phosphate amendments

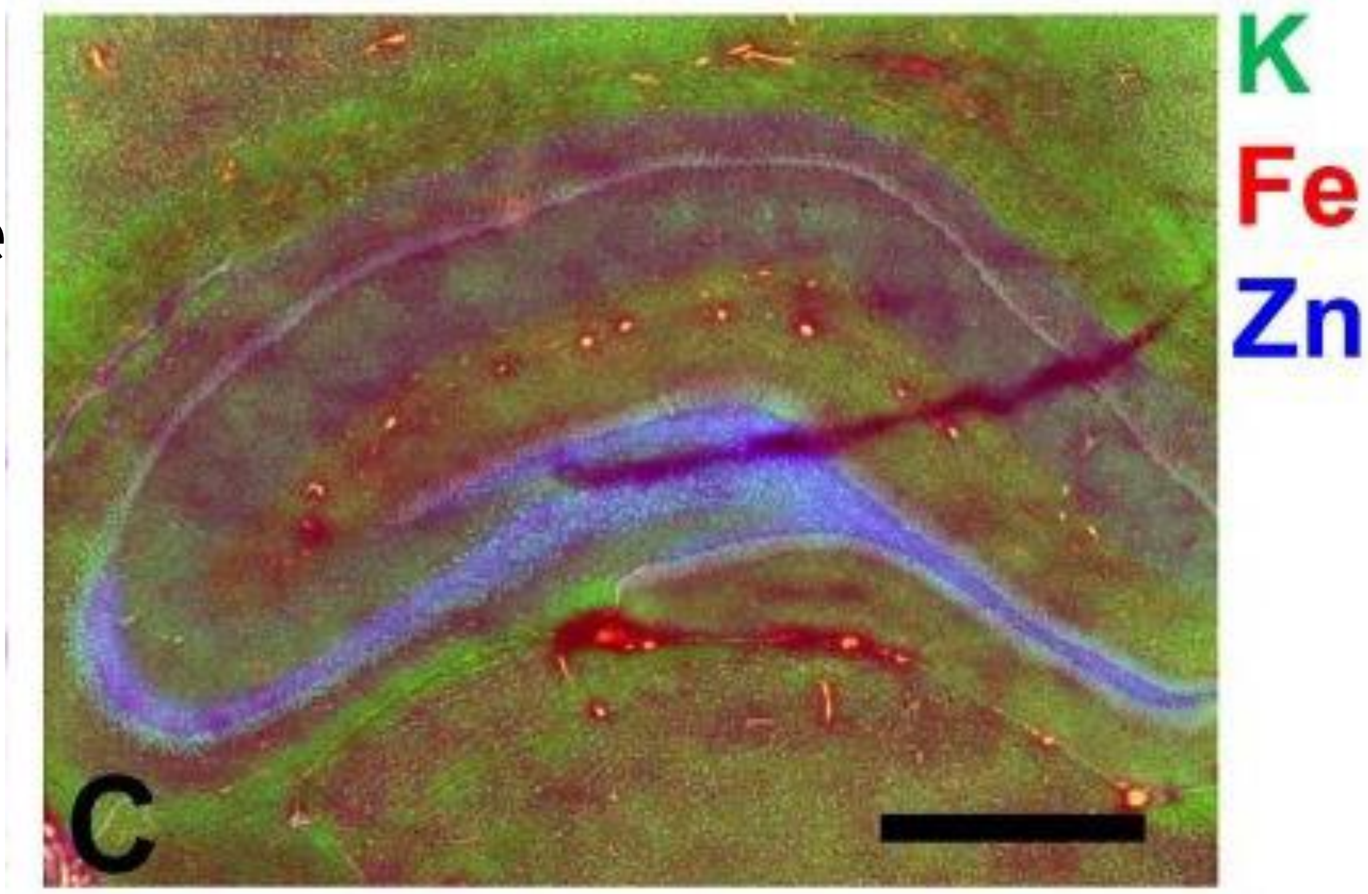
- Elemental map using XFM in mice lungs exposed to unamended and phosphoric acid (PA) amended Broken-Hill dust.



F Kastury, E Smith, E Doelsch, E Lombi, M Donnelley, P Cmielewski, D Parsons, K Scheckel, D Paterson, M de Jonge, C Herde, A Juhasz. Environmental Science & Technology. 53(17) 2019.

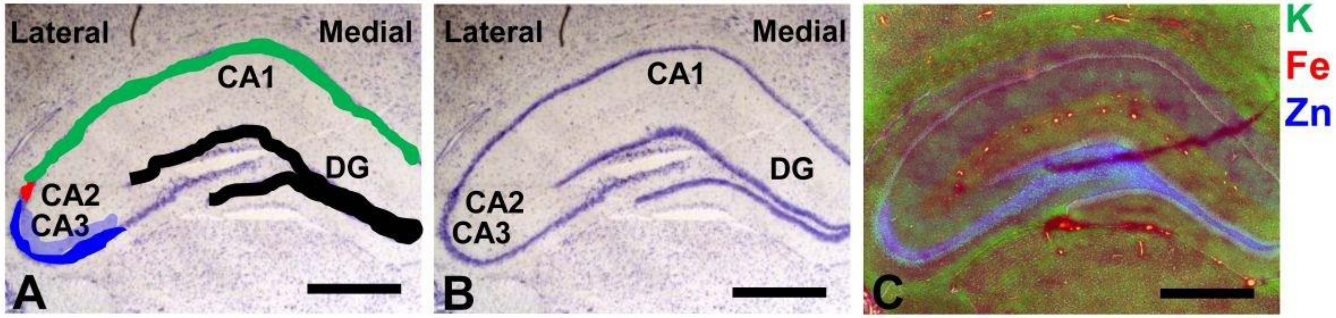
Life sciences research capabilities

- **X-Ray Fluorescence Microscopy**
  - Metals in biology
  - Diabetes
  - Neurodegenerative disease



XFM: Elemental content of neuronal cells

- A unique combination of sensitivity, resolution, and penetration make X-ray Fluorescence Imaging ideally suited to study trace elemental distributions in the biological context
- Characterisation of the elemental content within neuronal cell layers of hippocampal sub-regions of mice and rats.
- Direct, label-free metal quantification, *in situ* within *ex vivo* brain tissue sections



Cresyl violet histology (A, B) and XFI tri-colour elemental maps of K, Fe, Zn (C) of hippocampus in a representative rat. The major hippocampal sub-regions, CA1, CA2, CA3, DG, and lateral to medial orientation, are annotated in A and B, with location of neurons in each subregion colour coded in A (CA3 = blue, CA2 = red, CA1 = green, DG = black). Neurons in CA3, CA2 and CA1 are pyramidal neurons, neurons in DG are granule cells. The dendritic layer of the CA3 region (the mossy Fibres), known to be rich in a pool of labile or chelatable Zn, is shaded in partially transparent blue, in A. Scale bar = 500 µm.

Staff involved – Martin de Jonge (XFM=> Nanoprobe)
Collaboration with Mark Hackett (Curtin University)

Hackett et al., Metallomics 11, 151 (2019)

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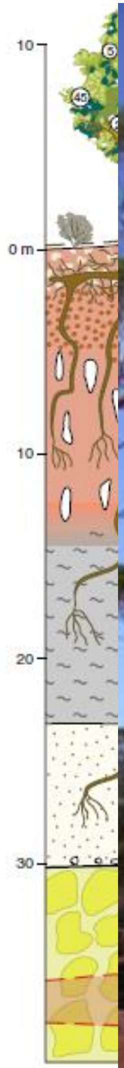
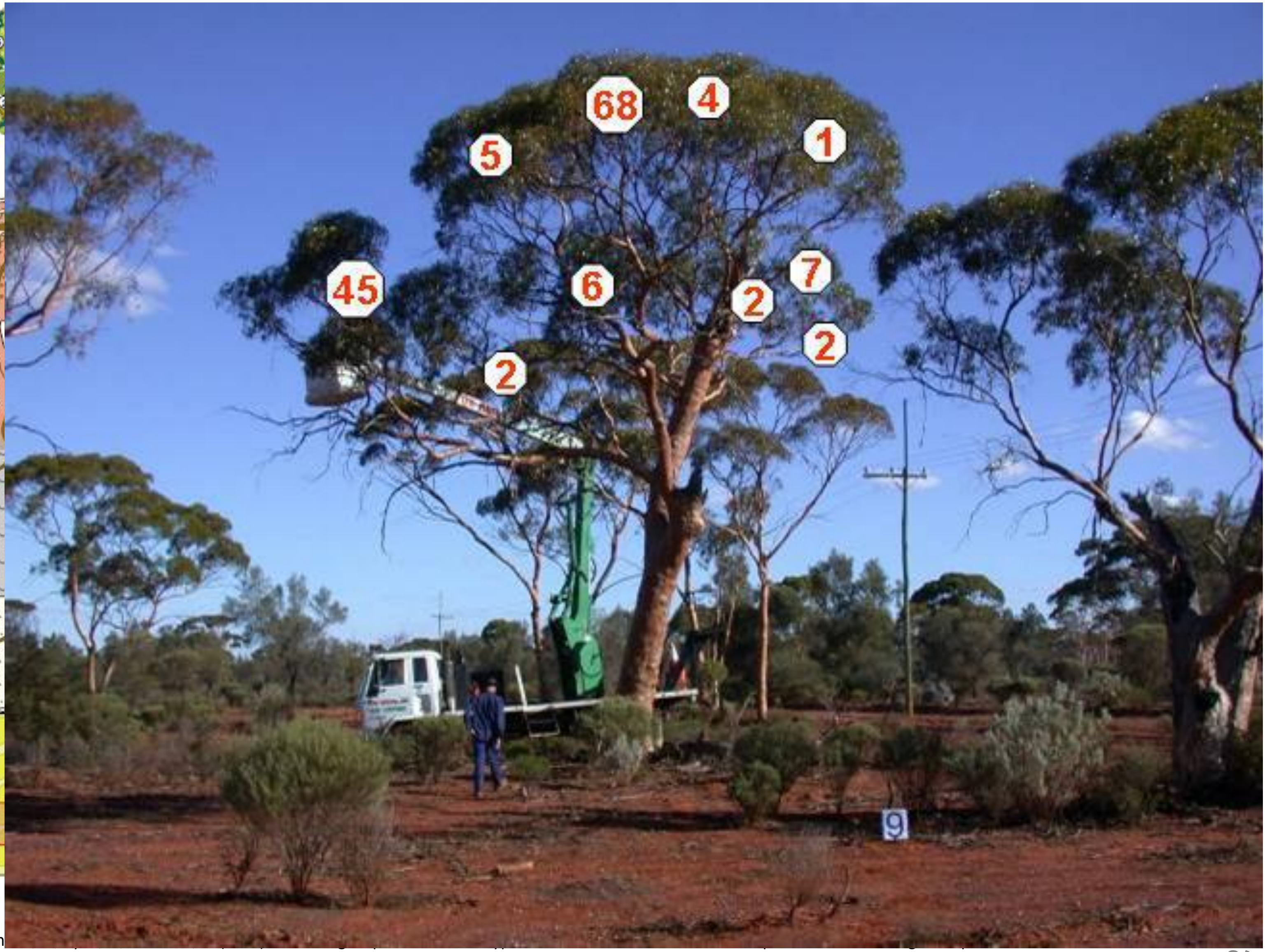
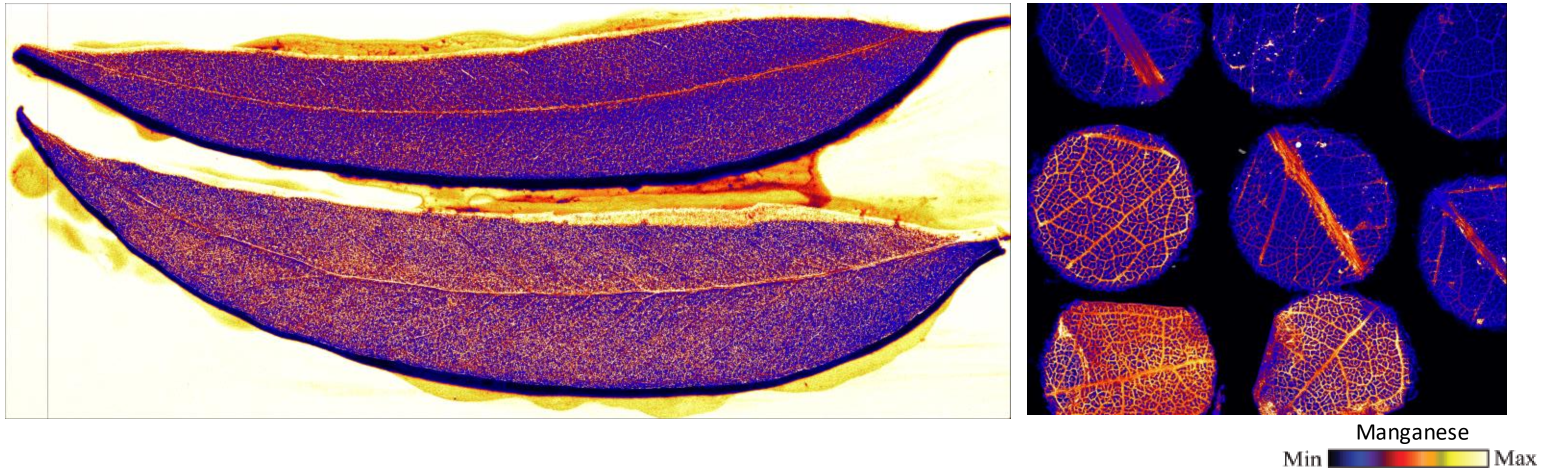
Can gold grow on trees?

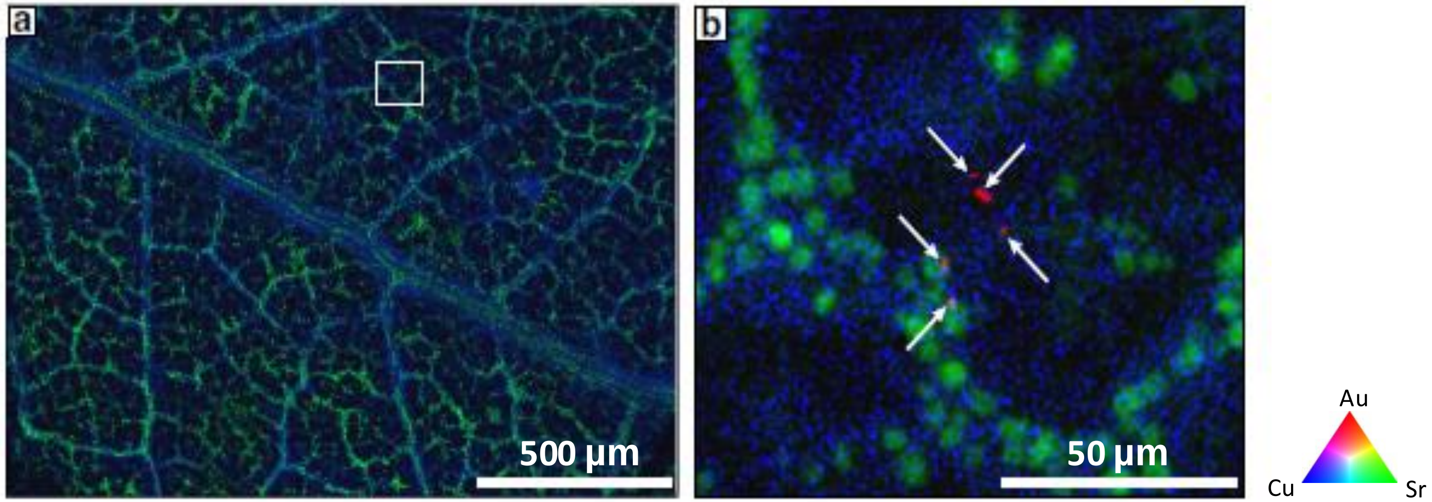




1. Lintern, M., An

Natural gold particles in Eucalyptus leaves



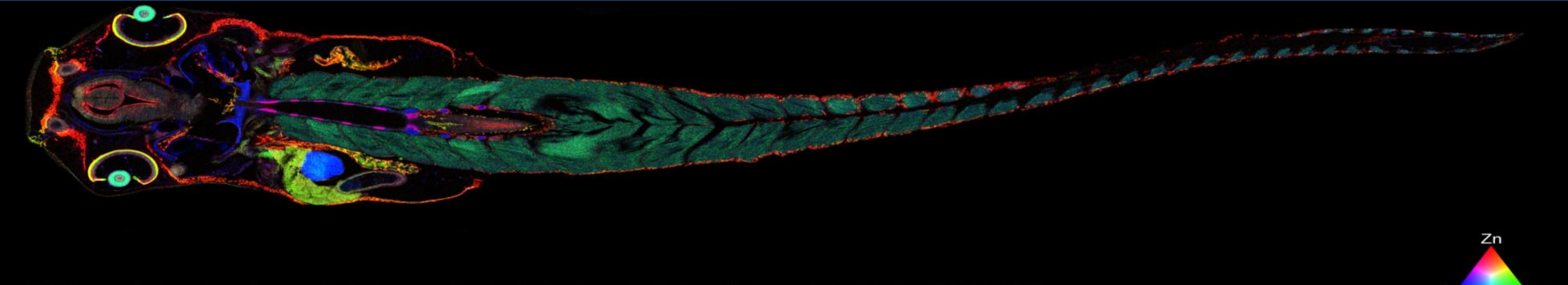


1. Lintern, M., Anand, R., Ryan, C., Paterson, D. (2013). "Natural gold particles in Eucalyptus leaves and their relevance to exploration for buried gold deposits." Nature Communications 4:2614
2. http://www.csiro.au/Portals/Media/Gilding-the-gum-tree-scientists-strike-gold-in-leaves.aspx, accessed 26/11/2013

Needle in a haystack searches

Finding 1-micron gold particles in gum leaves is equivalent to …
finding single sugar grains in 1 metre deep soil
across the Melbourne Cricket Ground field

Questions?



SXFM image of a *Limnodynastes peronii* tadpole exposed to dissolved selenium (Se^{IV}) - Lanctôt, Cresswell, Lombi, Bennett (XFM 11607)

Selenium bioaccumulation on micron scale

Synchrotron-based imaging reveals the fate of selenium in striped marsh frog tadpoles

Chantal M. Lanctôt, Tom Cresswell, Enzo Lombi, William W. Bennett

Environmental Science & Technology **55**, 11848-11858 (2021).

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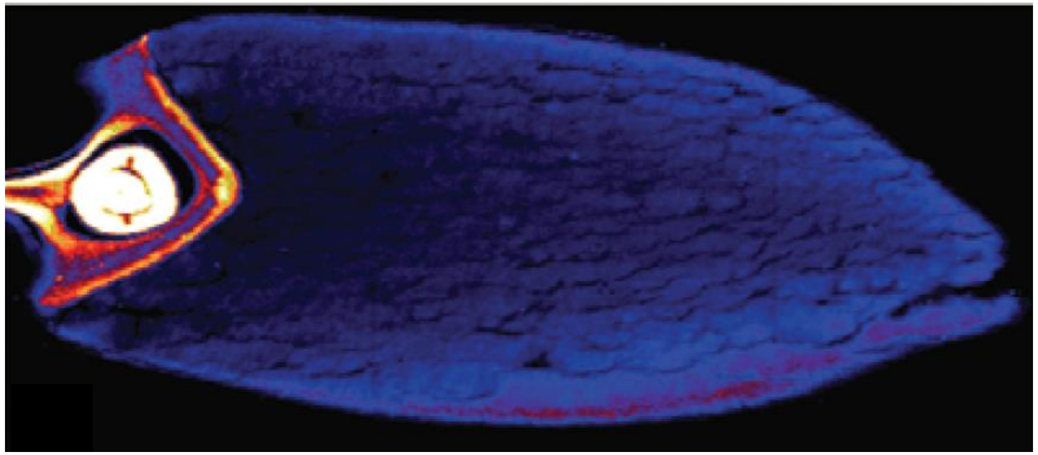
Future improvements



- Instrumentation
  - Higher incident energy and flux across entire energy range with Double Multilayer Monochromator
    - {being installed at the XFM beamline this week}
  - More efficient Germanium based XRF detector
- Data processing
  - Tomography – automated processing pipeline
  - Ptychography fast parallel processing

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Cadmium hyperaccumulator
Noccaea caerulescens

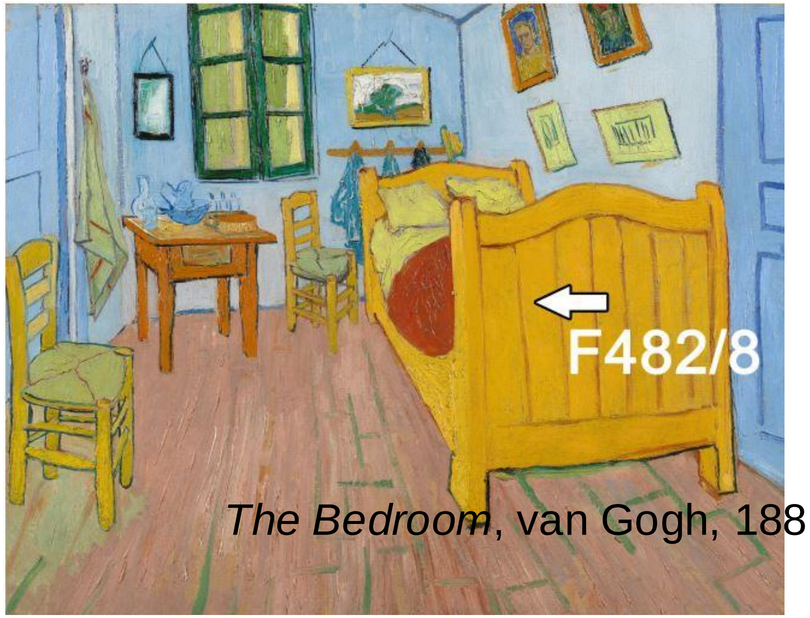
- Cadmium distribution in <u>whole live plant</u>
- High energy capabilities
  - >Cd and Ag K edges

Antony van der Ent,
Peter Kopittke,
Peng Wang,
University of Queensland.

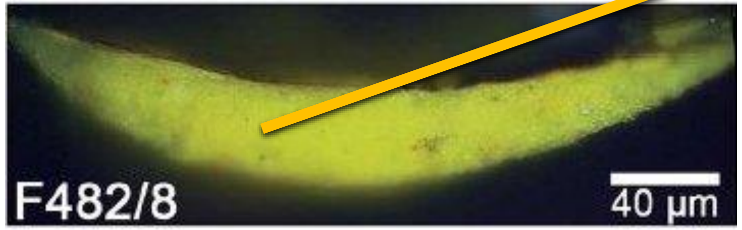
Micro-XANES

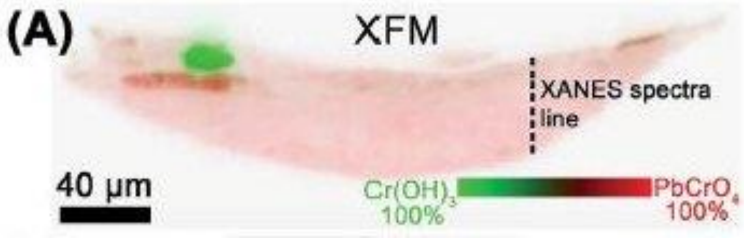
Darkening of chrome yellow pigments

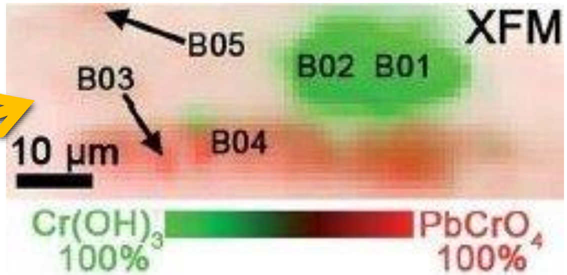
Cr (VI) yellow $\xrightarrow{\text{photo-reduction}}$ Cr (III) brown

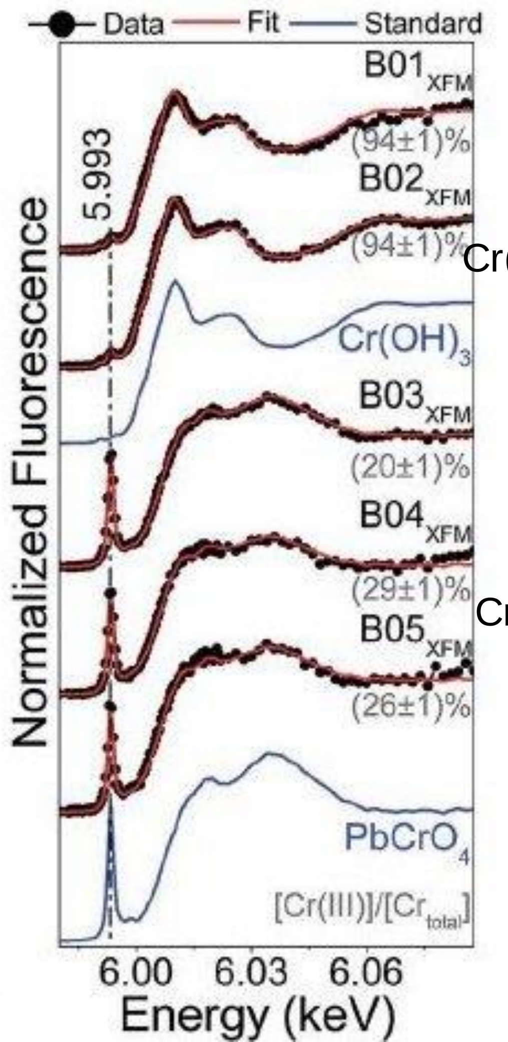


The Bedroom, van Gogh, 1888







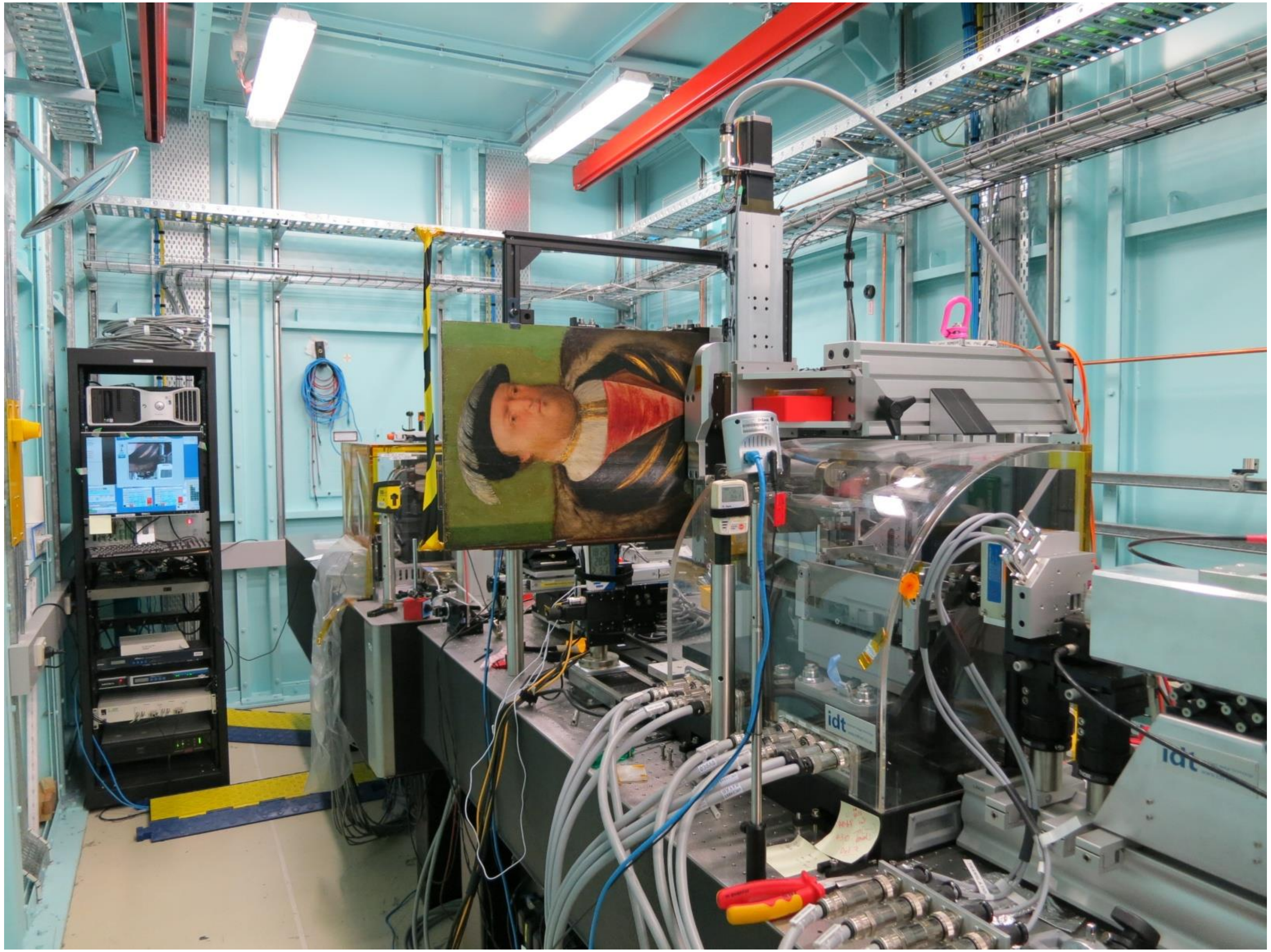


Stack of 126 maps measured across the Cr edge

0.5 ms dwell per 1 µm pixel

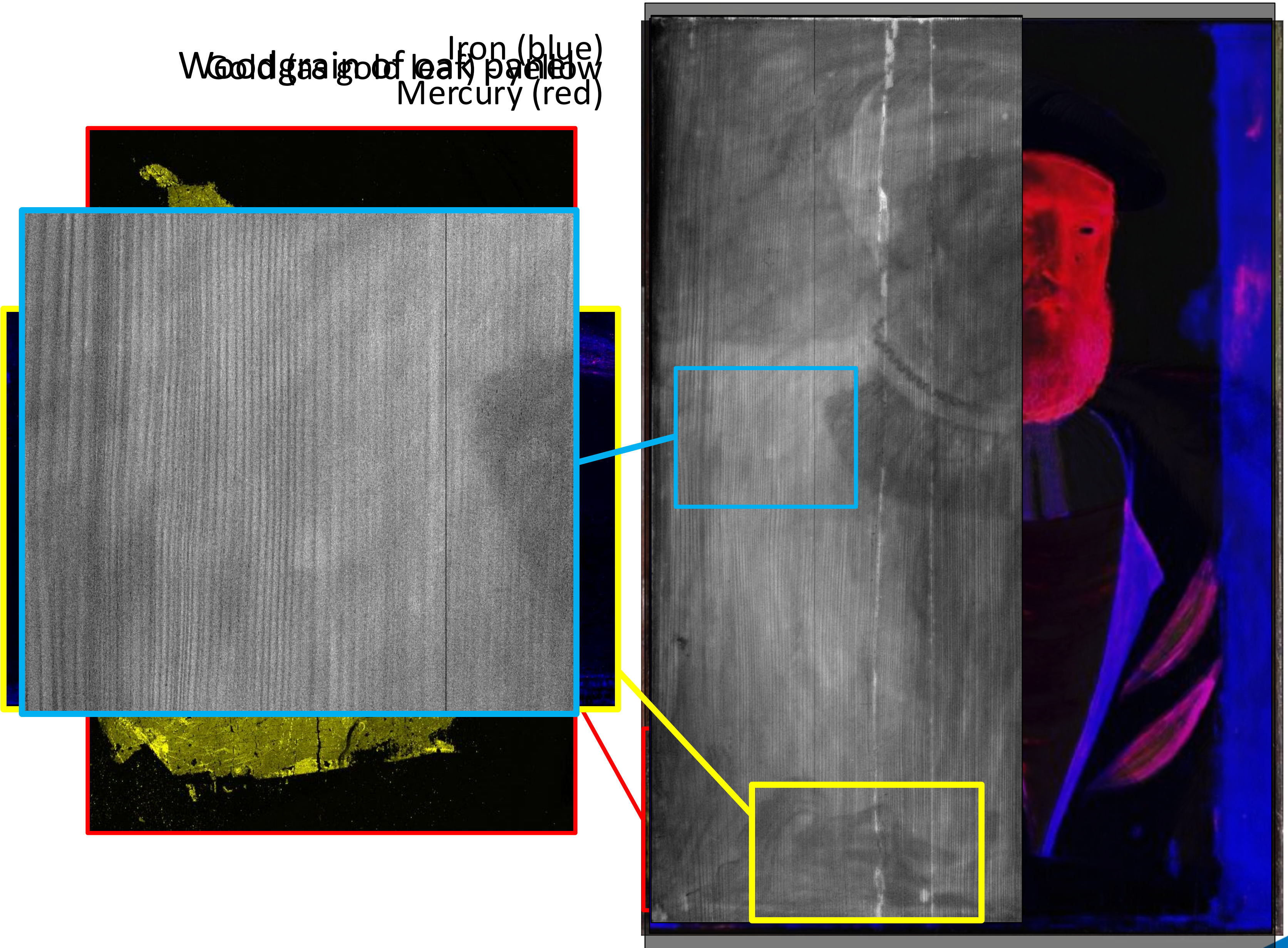
Monico et al. JAAS (2015)

Henry VIII: Art Gallery of NSW



Henry VIII: Art Gallery of NSW

Iron (blue)
Wood grain of oak panel
Gold (as gold leaf) yellow
Mercury (red)



Restoration – an example

Before treatment

Mercury Image

After restoration

Paula Dredge, Simon Ives, AGNSW

Naturally Occurring Radioactive Materials (NORM) scale in the ocean Science informing decommissioning strategies

Australia has an enormous future liability in decommissioning.

Estimated at >AUD$27bn over the next 50 years (Wood Mackenzie 2016).

Examples of 1.5 km of pipe being removed and cleaned at a cost of US$4 million.

External facilities and collaborators

中国科学院大学
University of Chinese Academy of Sciences

MONASH University

CSIRO

THE UNIVERSITY OF MELBOURNE

THE UNIVERSITY OF QUEENSLAND
AUSTRALIA

UNIVERSITY OF PLYMOUTH

UNIVERSITY OF WOLLONGONG AUSTRALIA

NCRIS
National Research Infrastructure for Australia
An Australian Government Initiative

LA TROBE UNIVERSITY

UNIVERSITY of OTAGO
Te Whare Wānanga o Otāgo
NEW ZEALAND
SAPERE AUDE

University of St Andrews

Griffith UNIVERSITY

University of South Australia

University of Kent

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