The BRIGHT future of X-ray Spectroscopy at the Australian Synchrotron

UoM Chem. Dept. Inorg. Chem. Seminar
Chemistry Department, University of Melbourne

Dr Simon James (sjames@ansto.gov.au)

MEX Beamline Scientist

Science. Ingenuity. Sustainability.

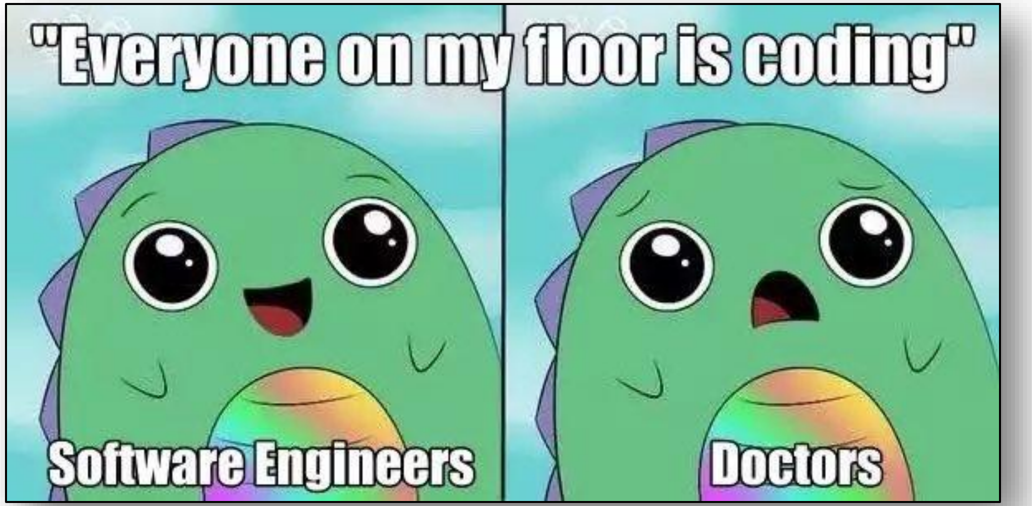
What's the plan?

1. *What is X-ray Spectroscopy?*
2. *Introducing MEX 1 and 2*
3. *Mechanics of Beamtime*

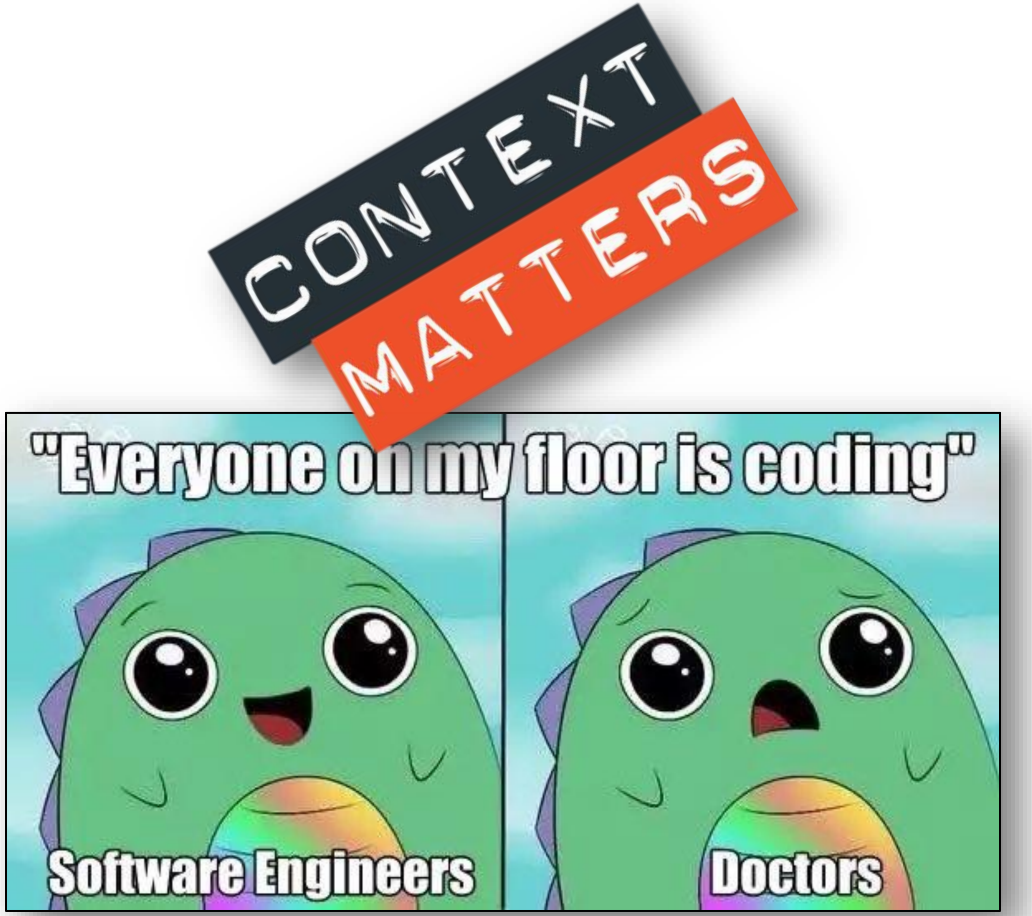
What’s the plan?

1. What is X-ray Spectroscopy?
2. Introducing MEX 1 and 2
3. Mechanics of Beamtime

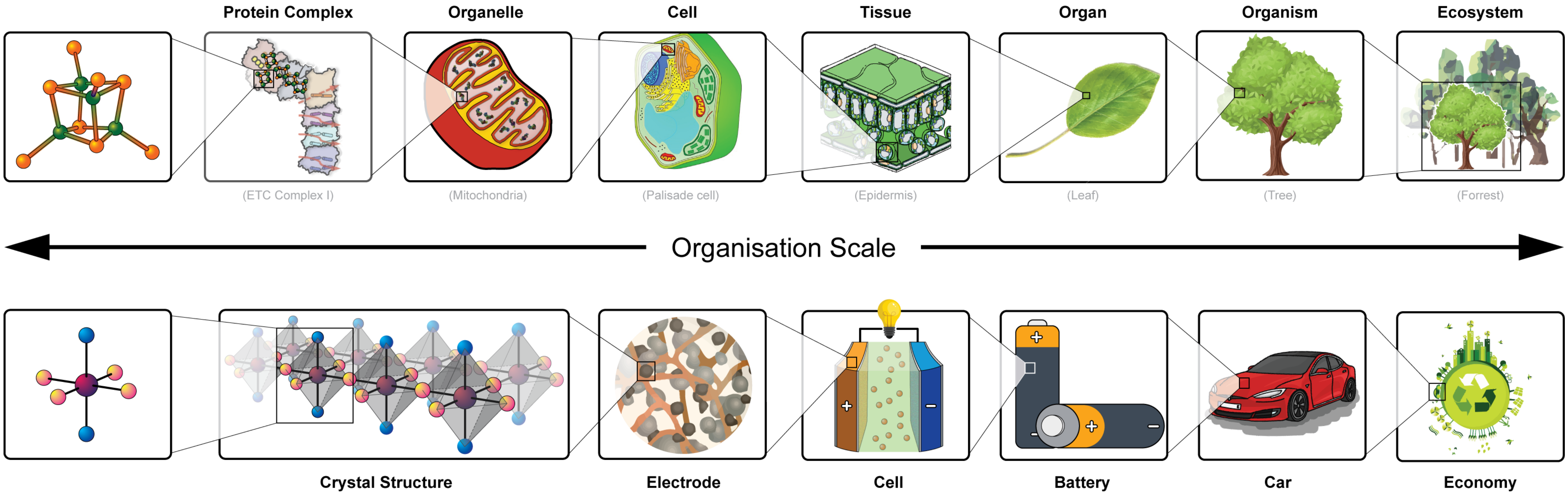
1. X-ray Spectroscopy (XAS) | X-rays and matter



1. X-ray Spectroscopy (XAS) | X-rays and matter

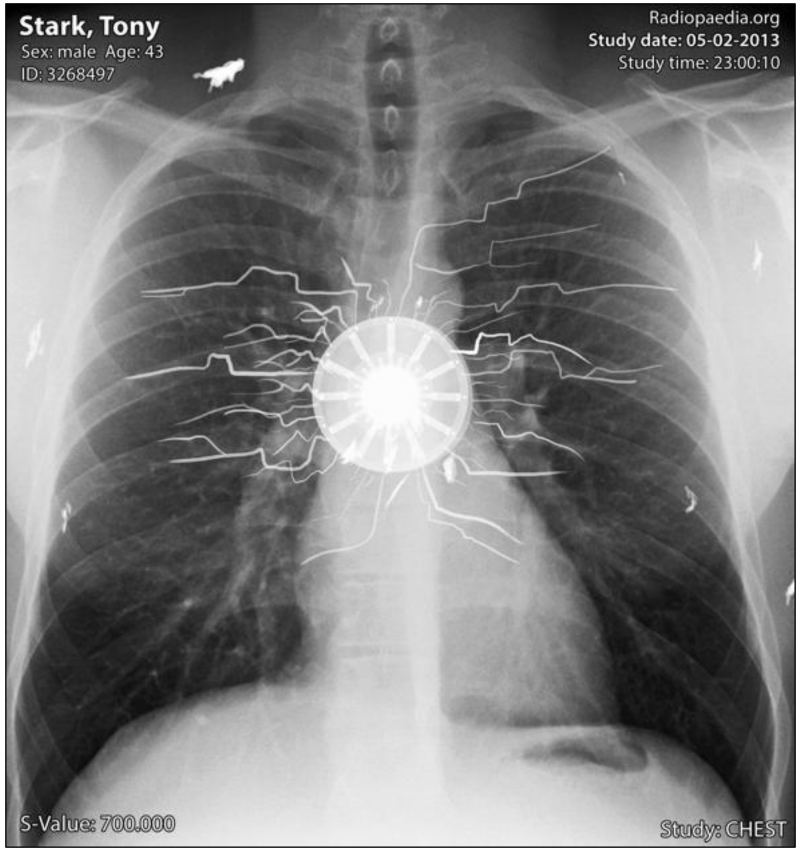


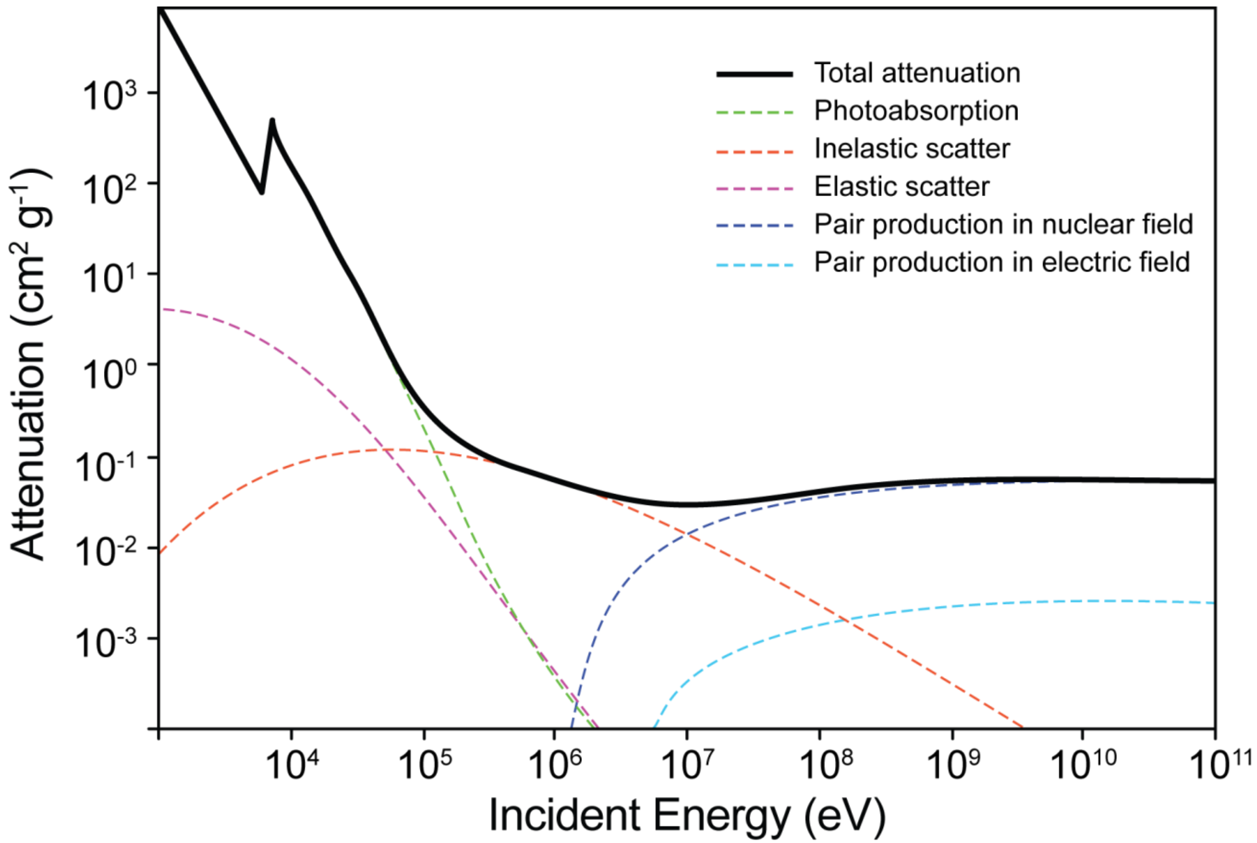
1. X-ray Spectroscopy (XAS) | Chemistry in Context



X-ray absorption spectroscopy (XAS) provides access to elemental composition, localization and chemical speciation **in context**

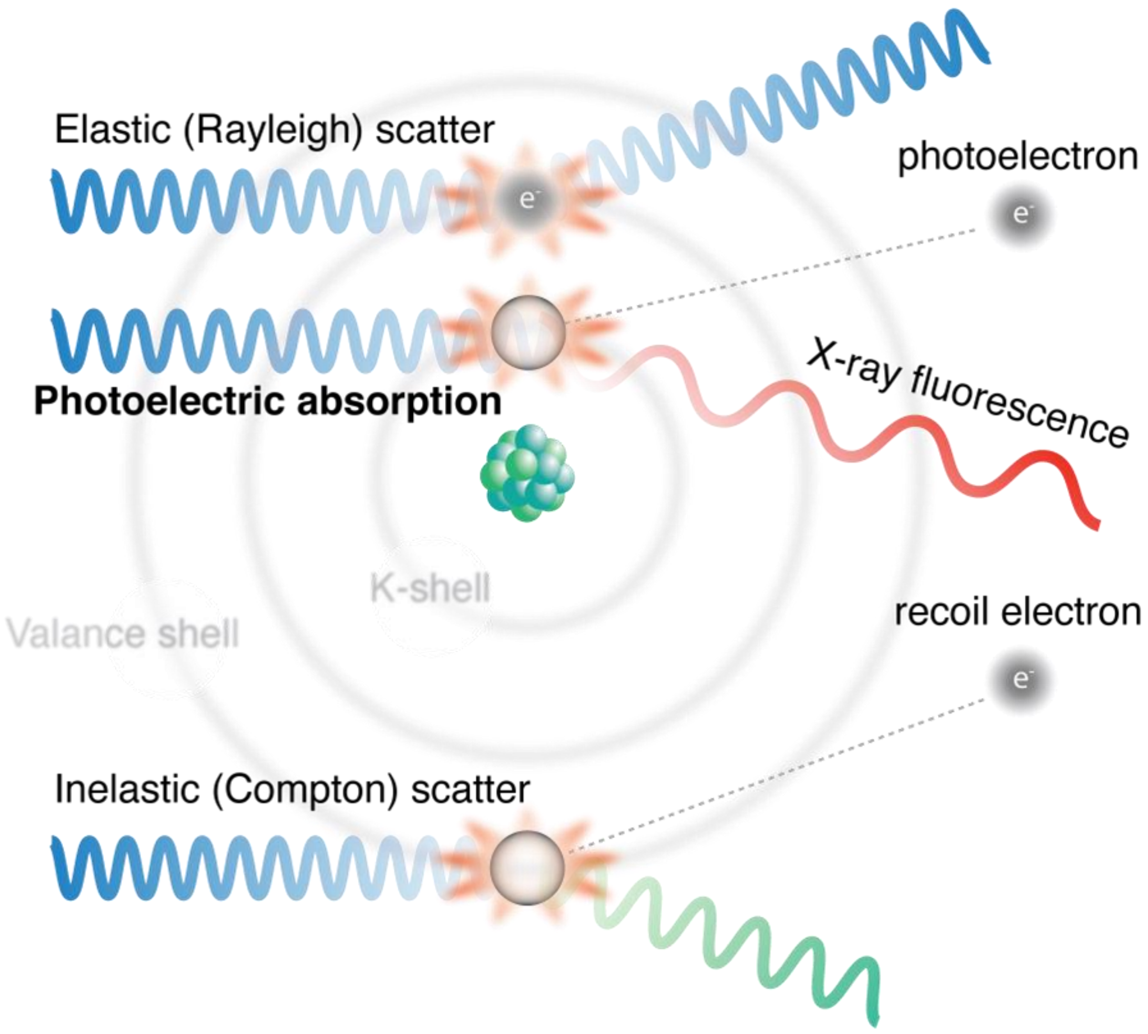
1. X-ray Spectroscopy (XAS) | X-rays and matter





X-rays interact with matter through a variety of mechanisms.
XAS is (essentially) concerned with only one – ***Photoelectric absorption***

1. X-ray Spectroscopy (XAS) | Photoelectric absorption



- Dominant interaction mechanism at energies < 50 keV.
- X-ray energies are similar to binding energies of core-level electrons
- Probability is maximum when the energy of the incident photon is equal to or just greater than the binding energy of an electron.
- X-ray wavelengths similar to atomic spacing in ordered materials

1. X-ray Spectroscopy (XAS) | Photoelectric absorption

- We are primarily concerned with the *photoabsorption coefficient* (μ)
- X-ray absorption is a transition between two quantum states;

Interaction term

$$\mu(E) \propto |\boxed{\langle i|}\boxed{H}\boxed{|f\rangle}|^2$$

Initial state
(X-ray + core electron)

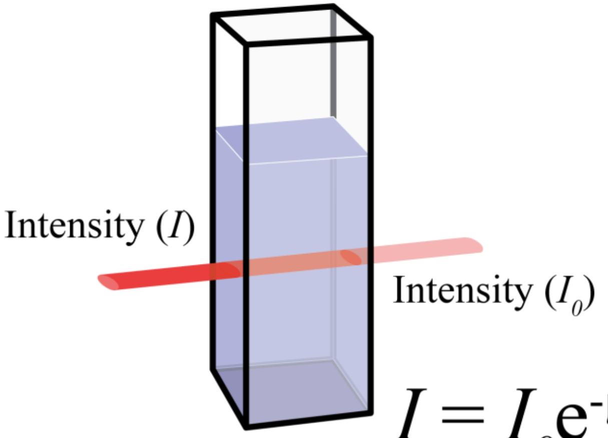
invariant to neighbours

Final state
(core hole + photoelectron)

Sensitive to neighbouring atoms

Enrico Fermi (1943)

Beer-Lambert Law

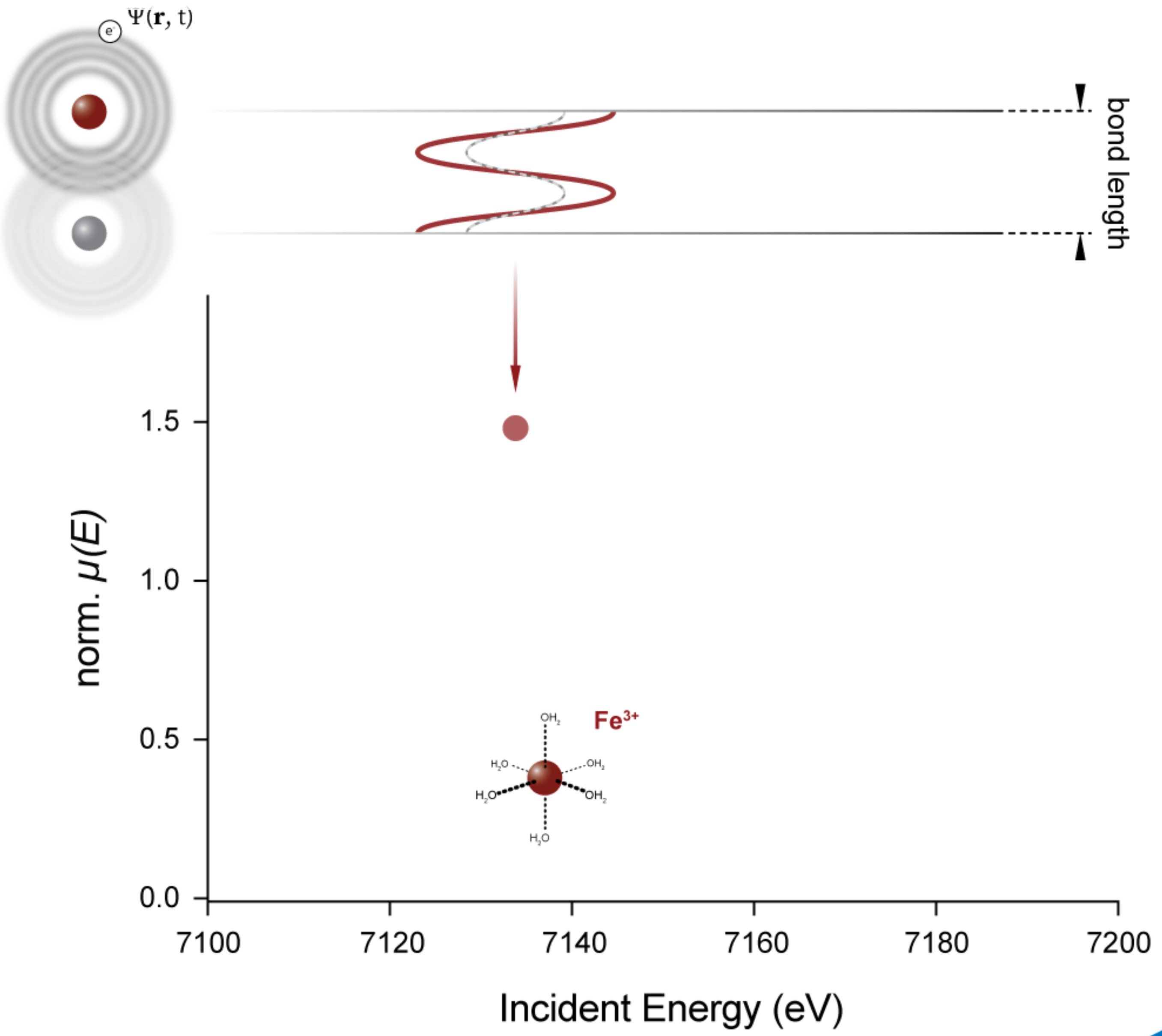


$$I = I_0 e^{-\mu x}$$

***Photoabsorption* will be likely to occur if the coupling between the initial and final states is stronger.**

1. X-ray Spectroscopy (XAS) | Photoelectric absorption

- Ejected photoelectron scatters off neighboring atoms.
- Scattered photo-electron interferes with itself modulating photoabsorption.



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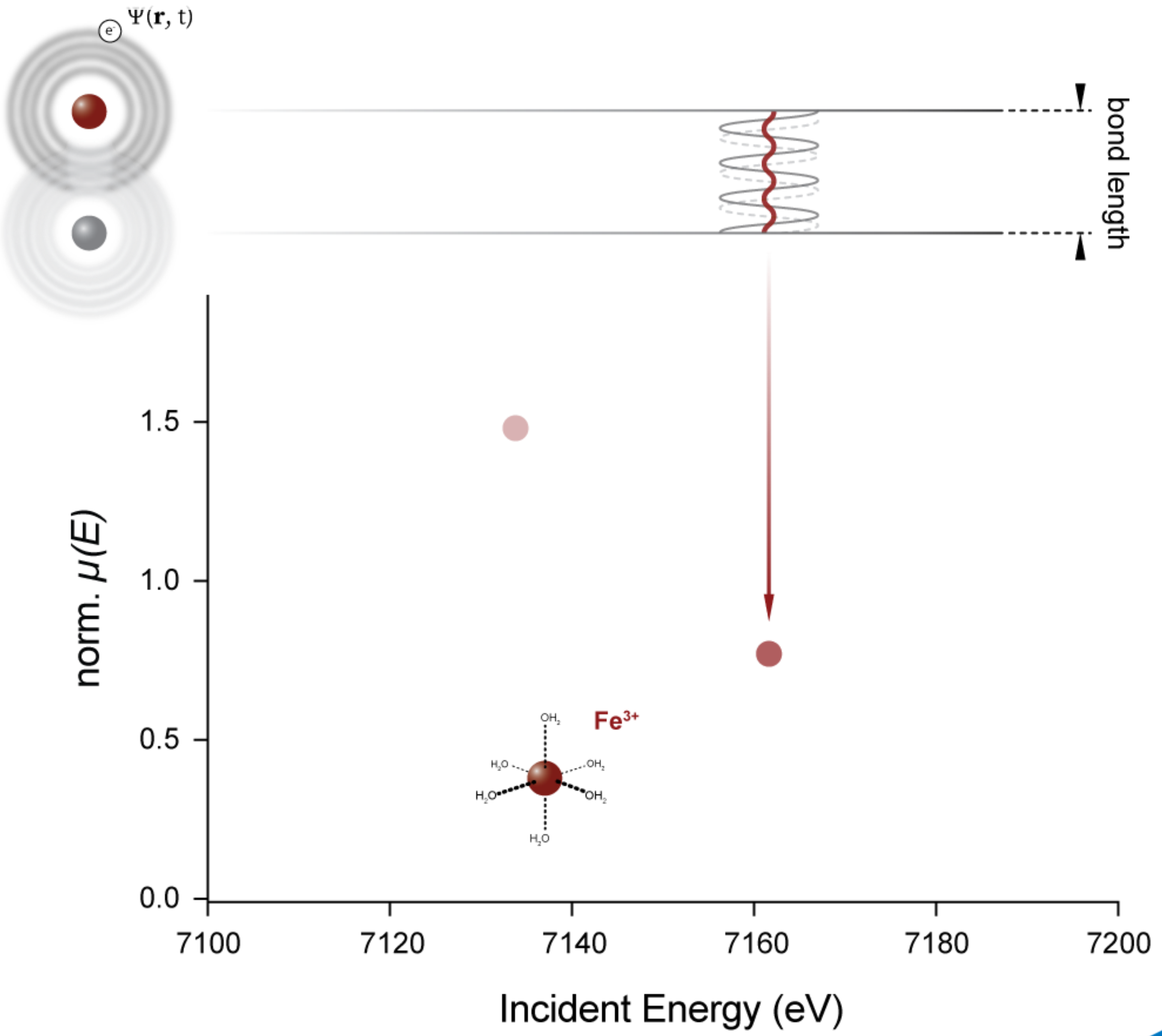

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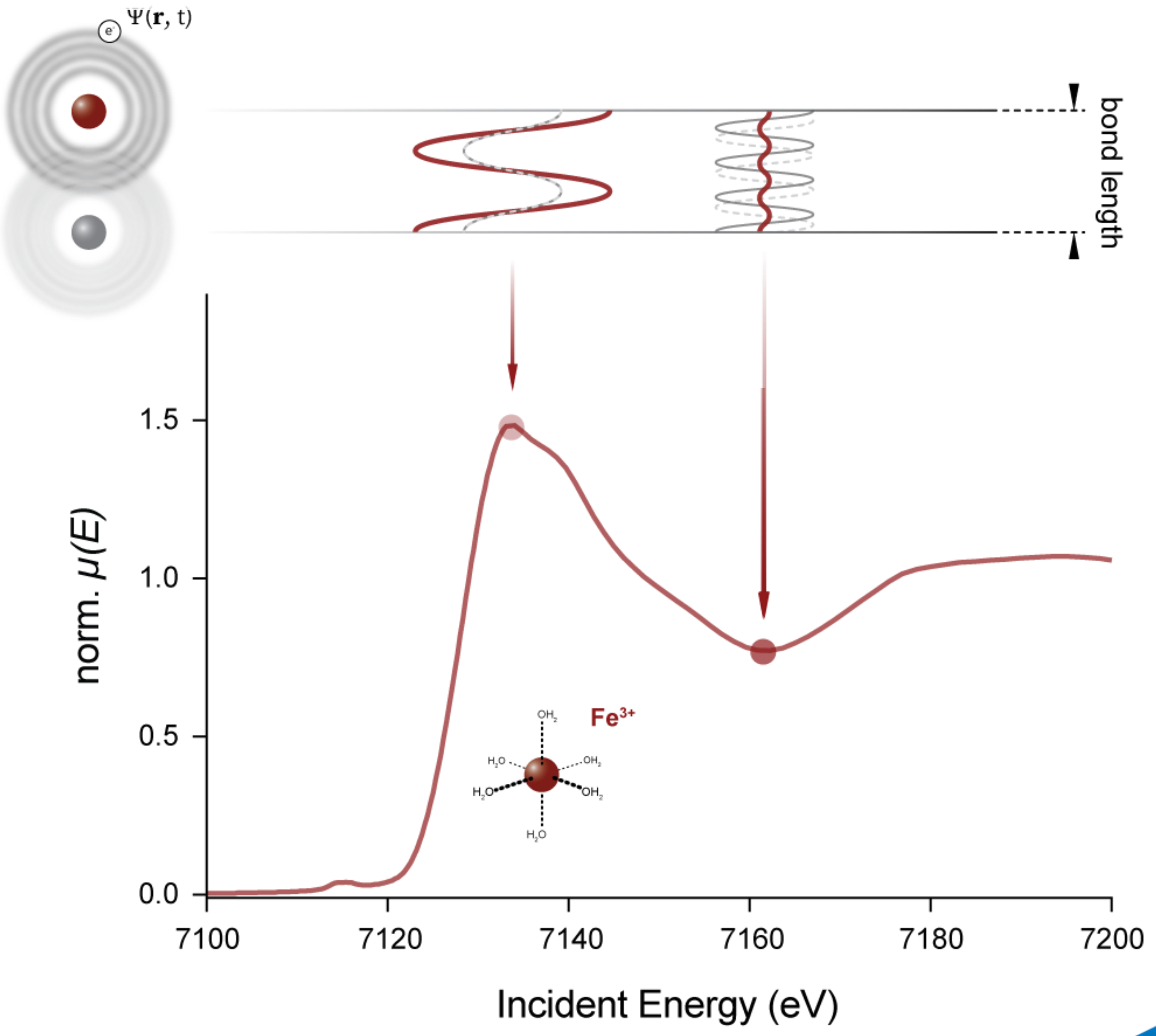
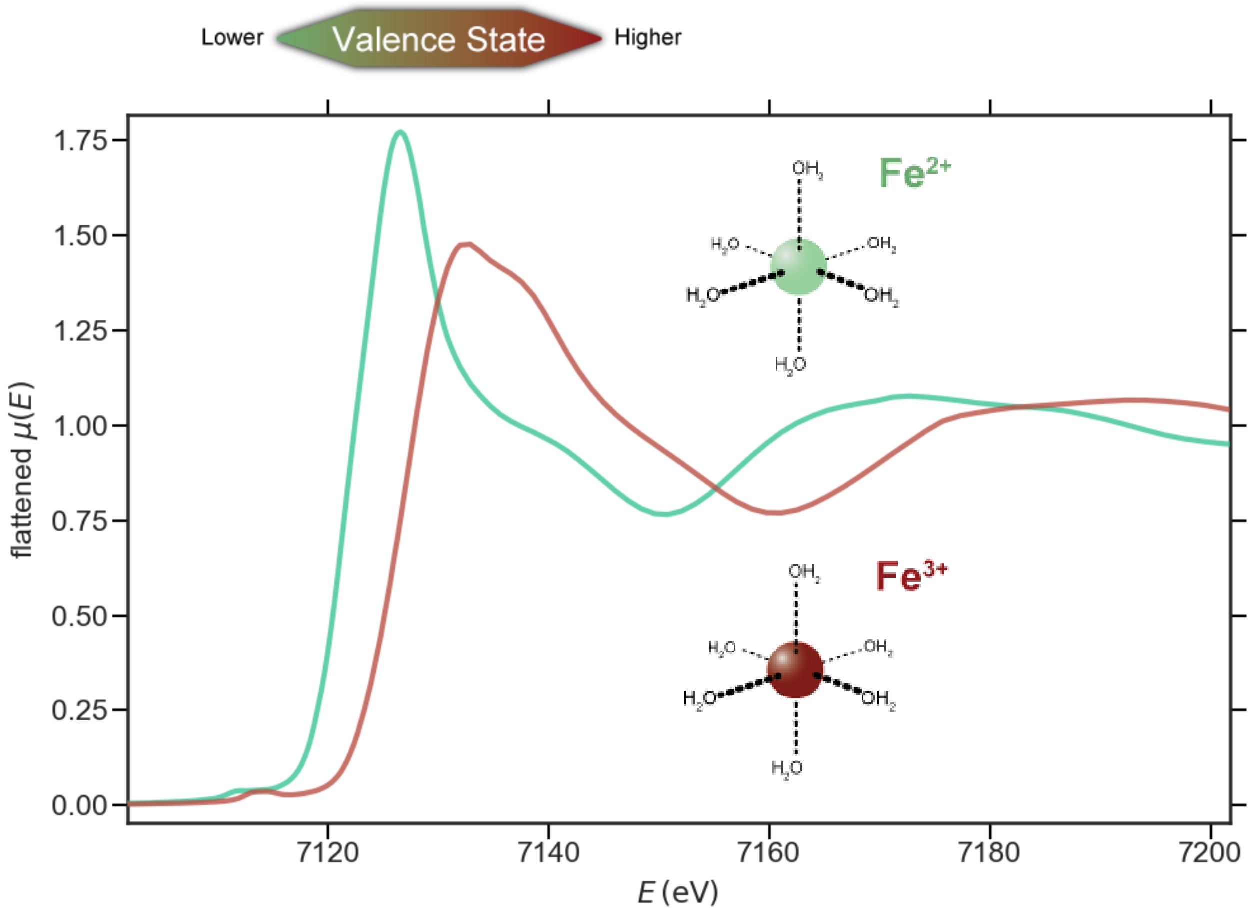


1. X-ray Spectroscopy (XAS) | Electronic Insights (XANES)

- Near edge structure (**XANES**) reveals information on the valency and symmetries of the absorbing atom.



Edge shift and positions of main peaks can determine valence state.

"Fingerprint" chemical species.

Pre-edge peaks can be modeled with orbital and crystal field theory

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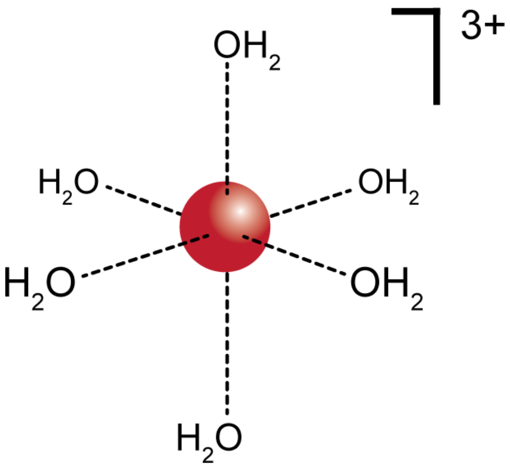

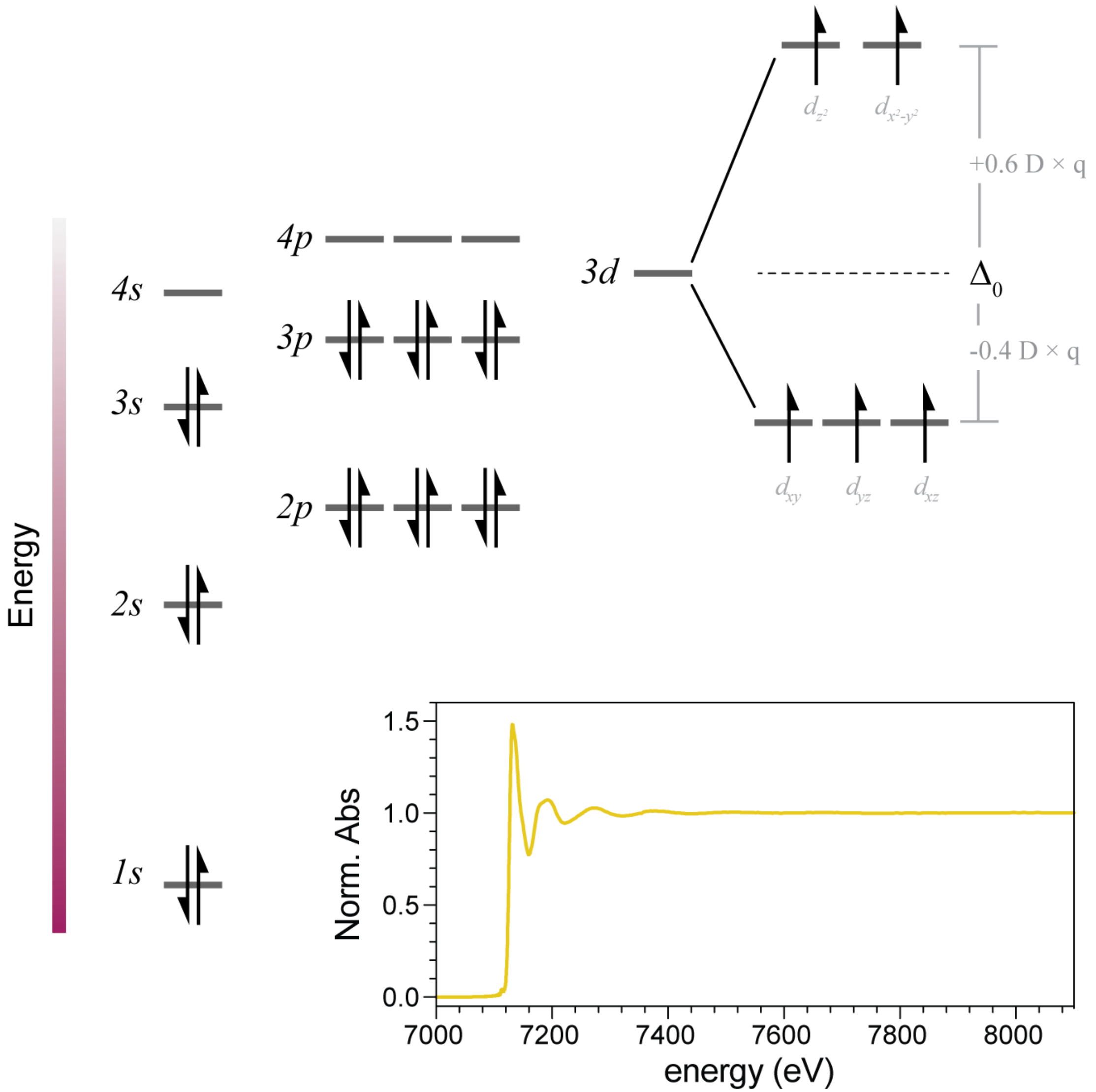

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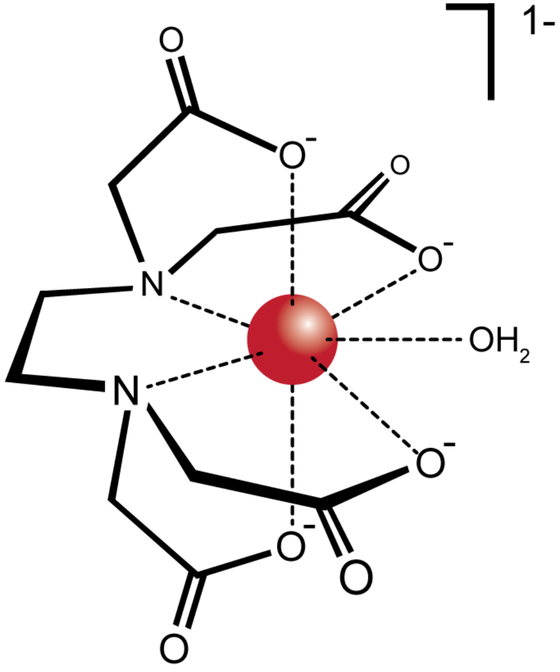

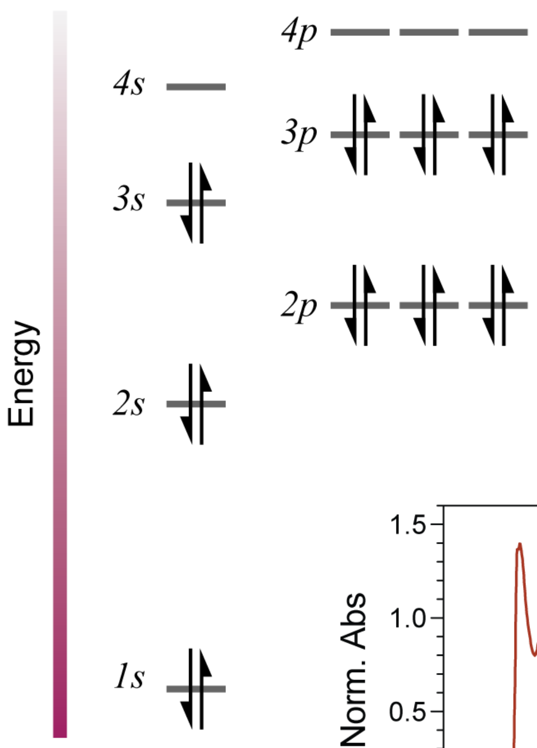

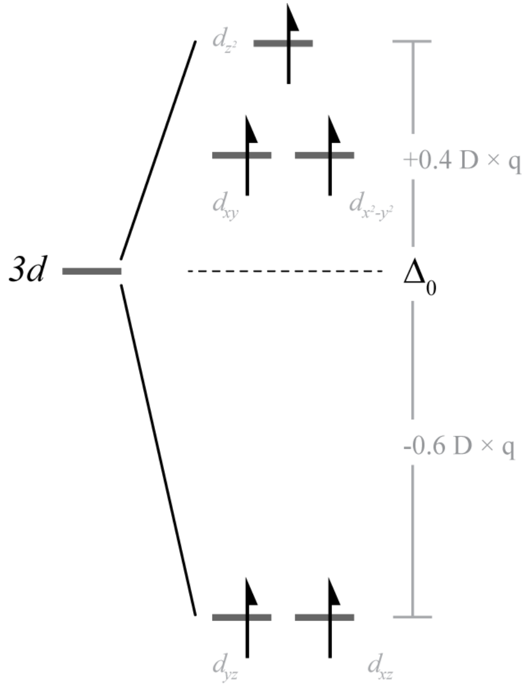

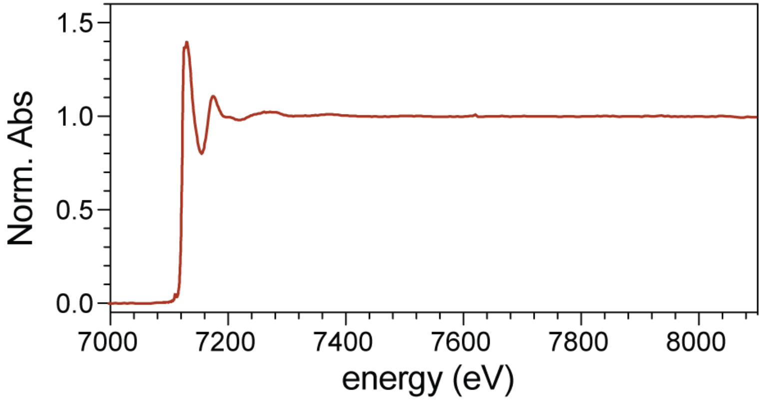

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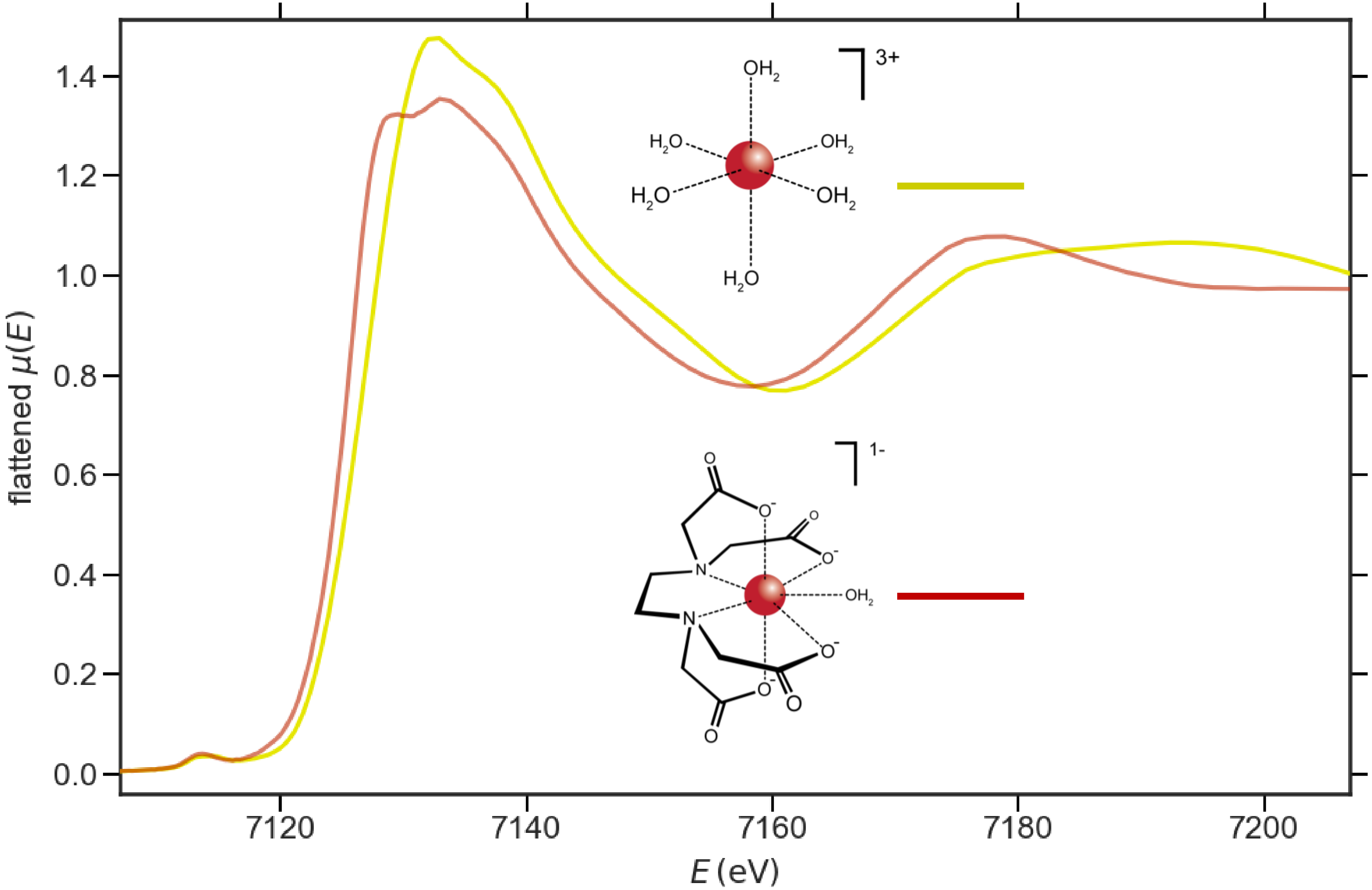

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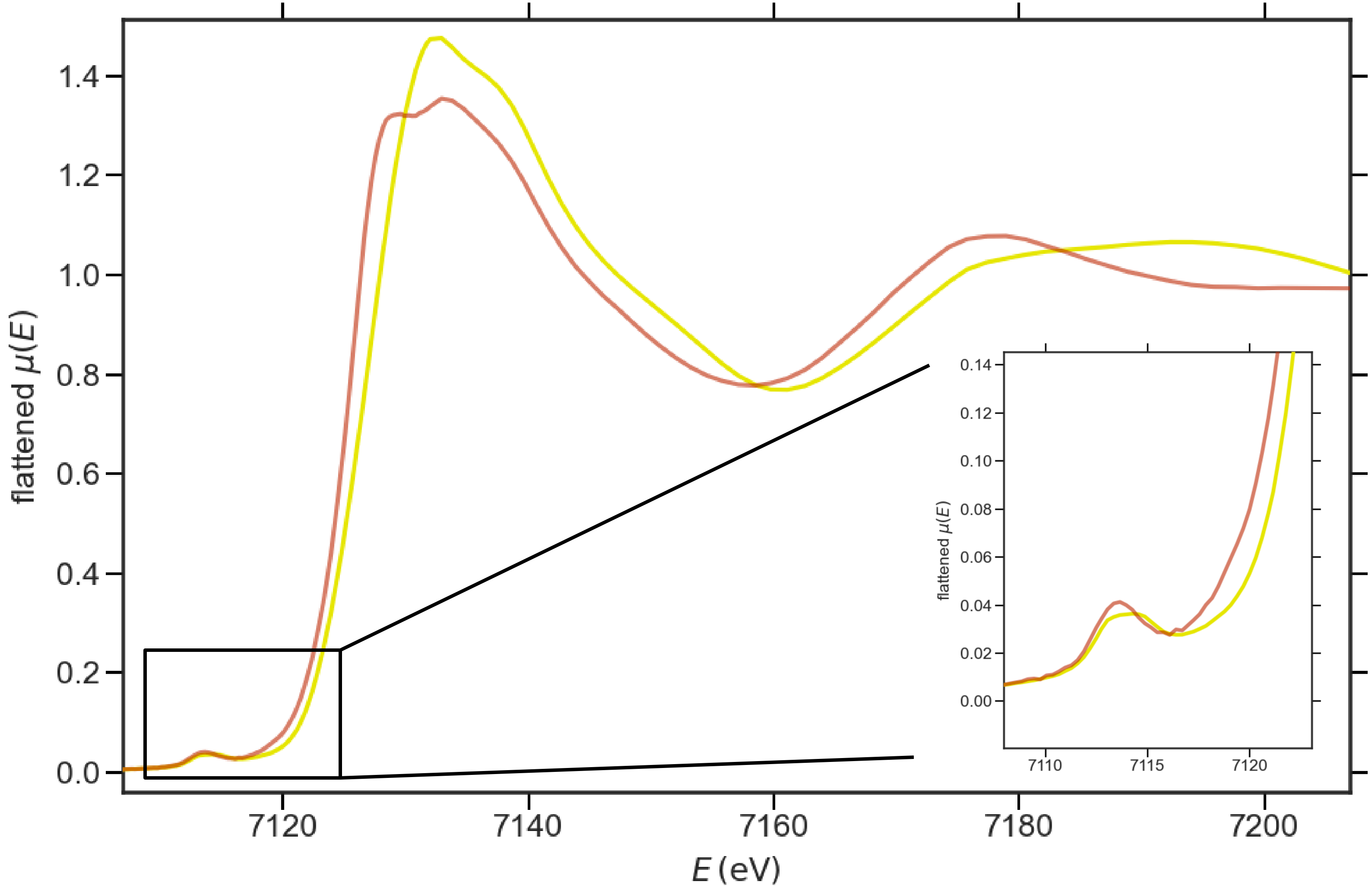

- In a 1st row transition metals, a K-edge transition implies a *s* → *p* like transition;
  - For Octahedral coordination site is centrosymmetric implying no *p*-*d* mixing (only weak quadrupole transitions)
  - *p*-*d* mixing becomes possible with distortion from octahedral point symmetry
  - tetrahedral site symmetry, largest pre-edge peaks

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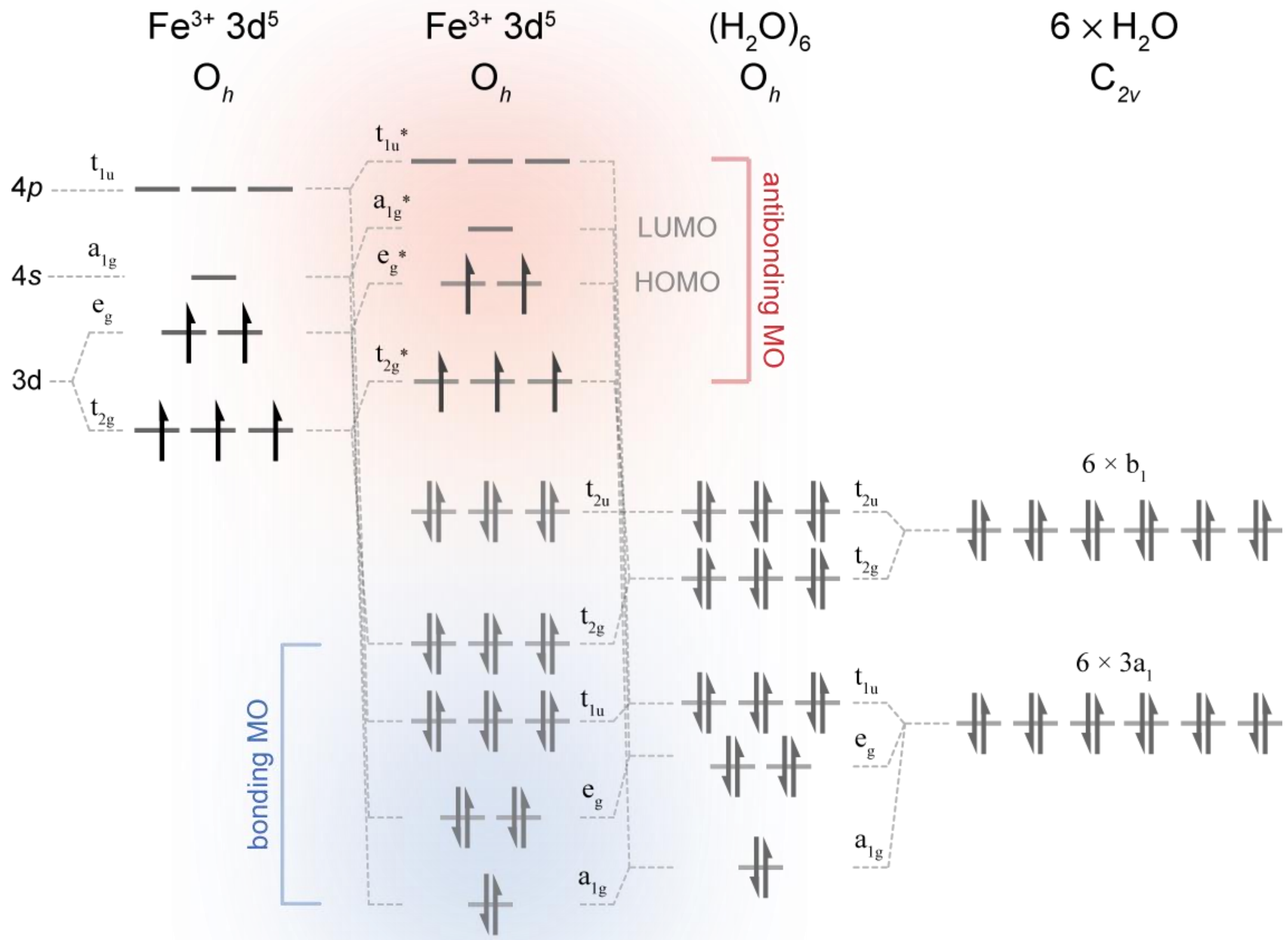
1. X-ray Spectroscopy (XAS) | Electronic Insights (XANES)



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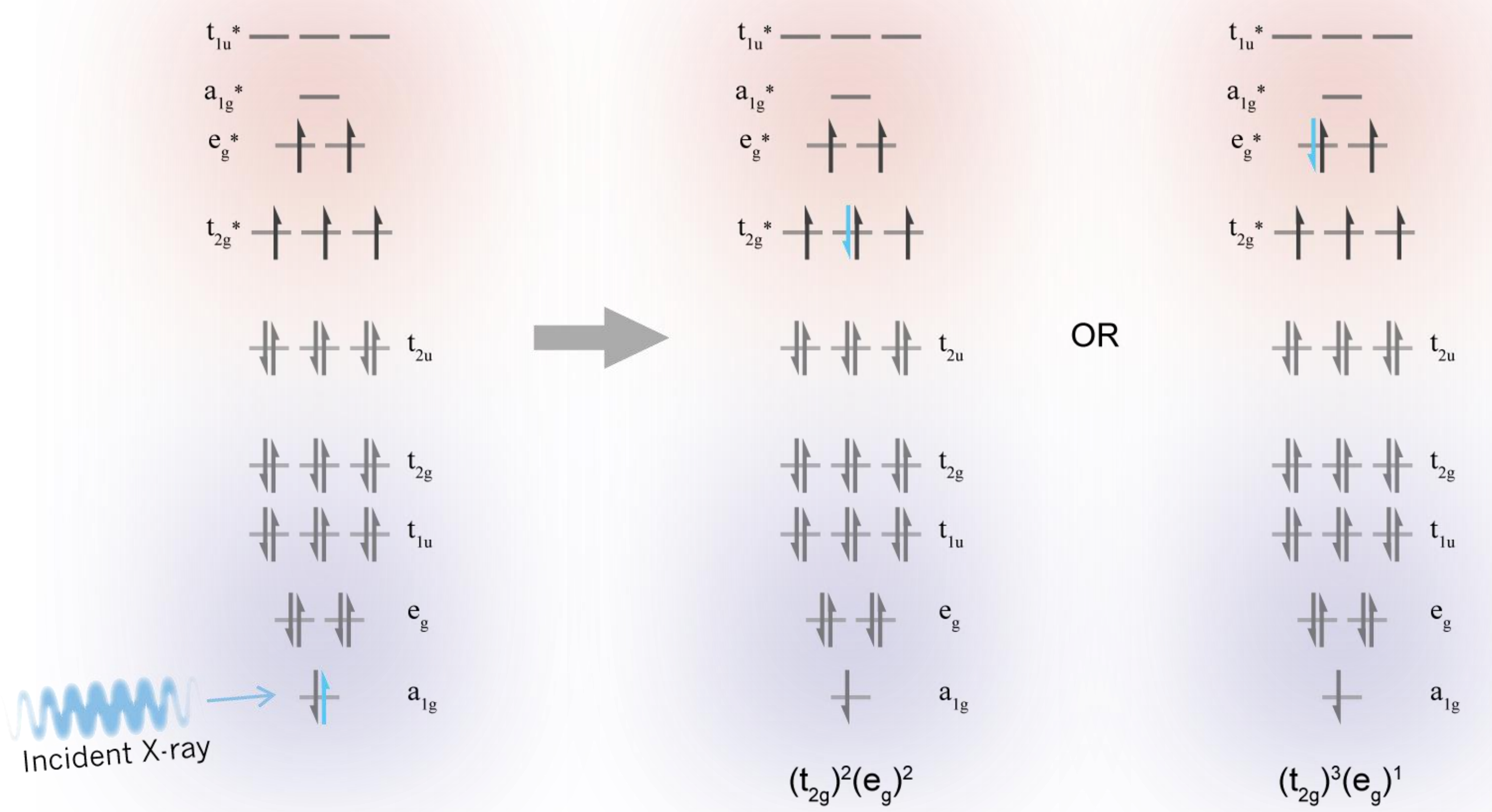

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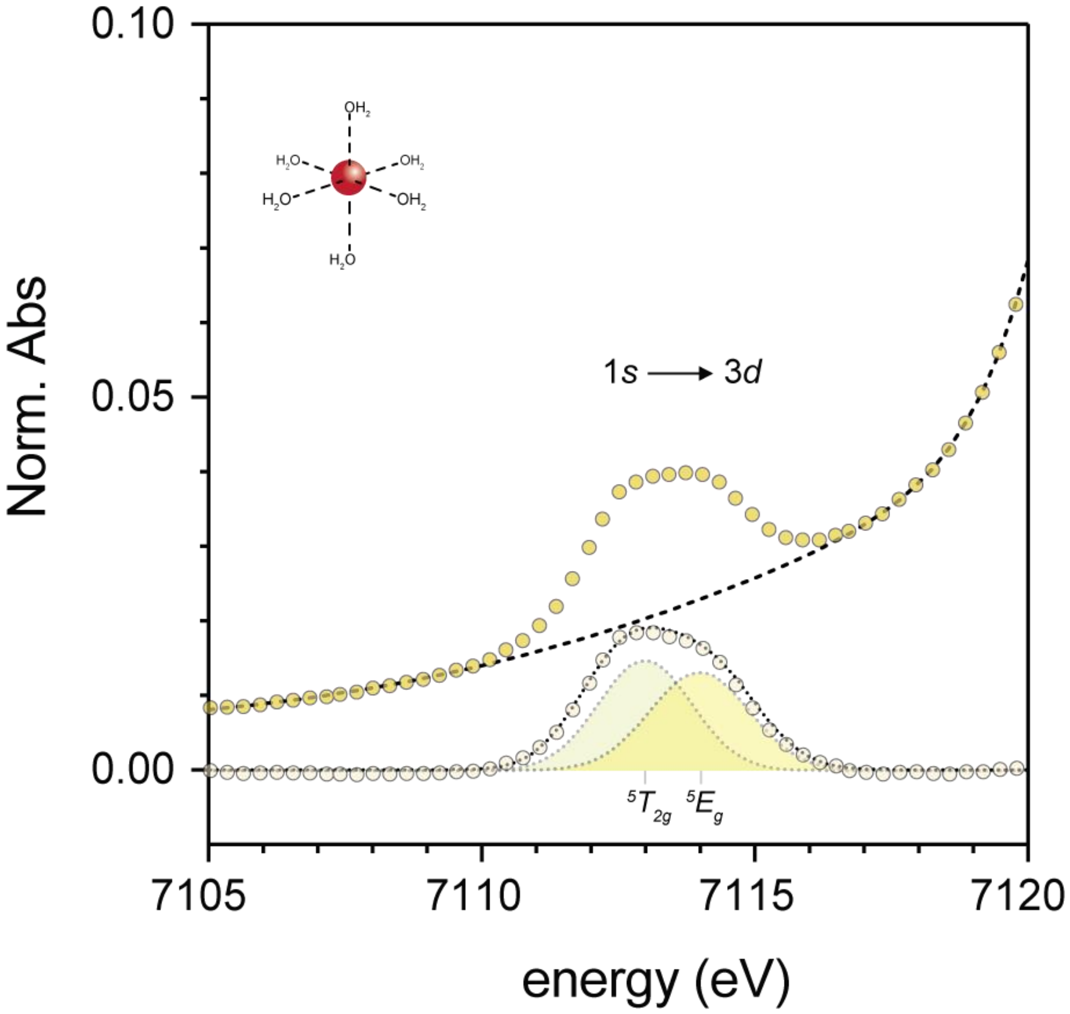


- Only mechanism available for the 1s→3d feature in centrosymmetric O_h complexes is the allowed electric quadrupole transition.

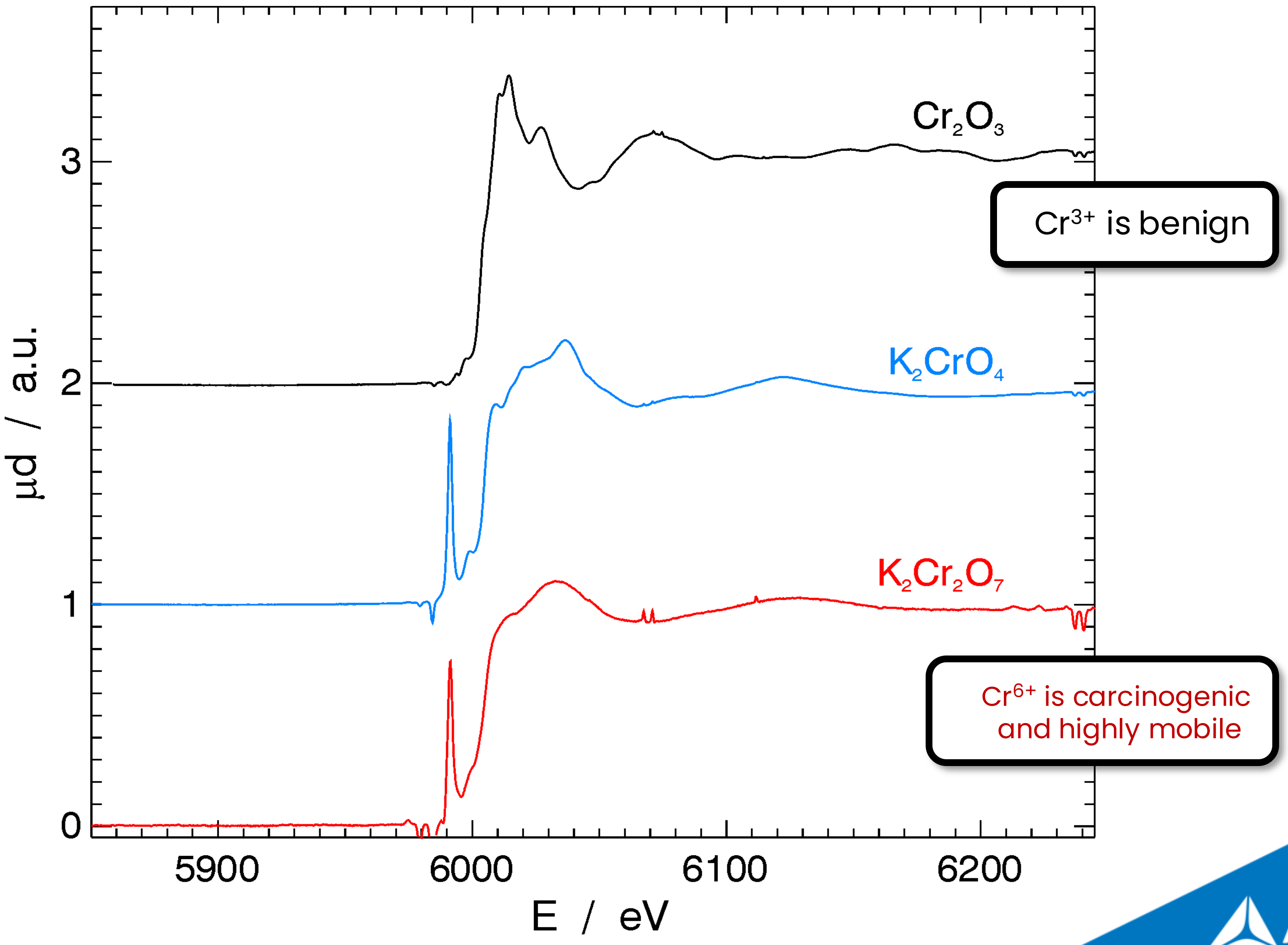
- Coupling of the holes in $(t_{2g})^2(e_g)^2$ and $(t_{2g})^3(e_g)^1$ configurations give a $^5T_2$ and a ^5E_g excited state.

- Therefore, an octahedral high-spin ferric complex will show two pre-edge features with an approximate electric quadrupole intensity ratio of 3:2

1. X-ray Spectroscopy (XAS) | Environmental Science

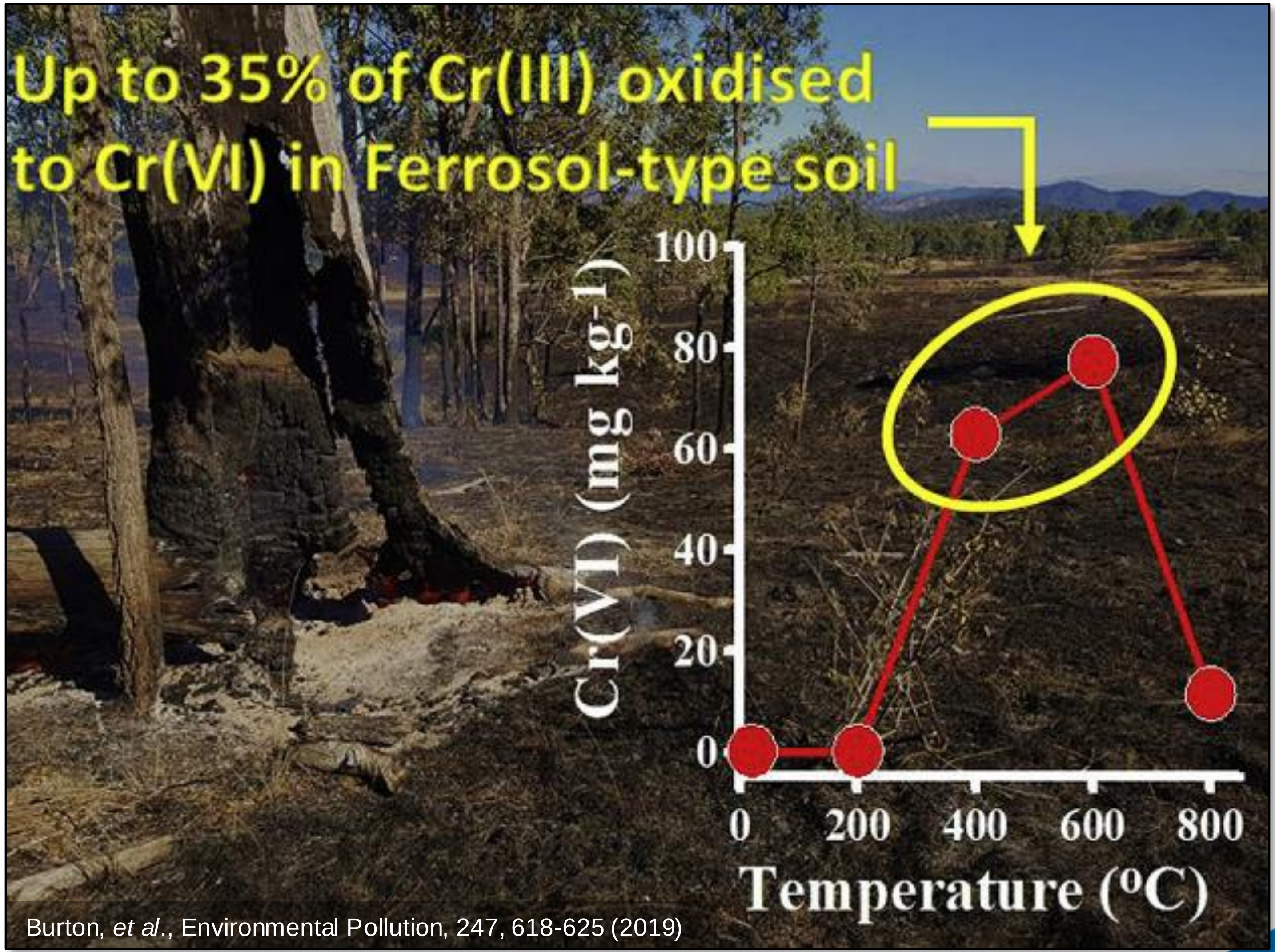
- During bushfires, soil temperatures of 100 – 700 °C are common.
- Fe-oxide minerals scavenge trace metals in soils.
- Cr^{3+} is benign, while Cr^{6+} is carcinogenic and highly mobile.

Burton, *et al*., Environmental Pollution, 247, 618-625 (2019)



1. X-ray Spectroscopy (XAS) | Environmental Science

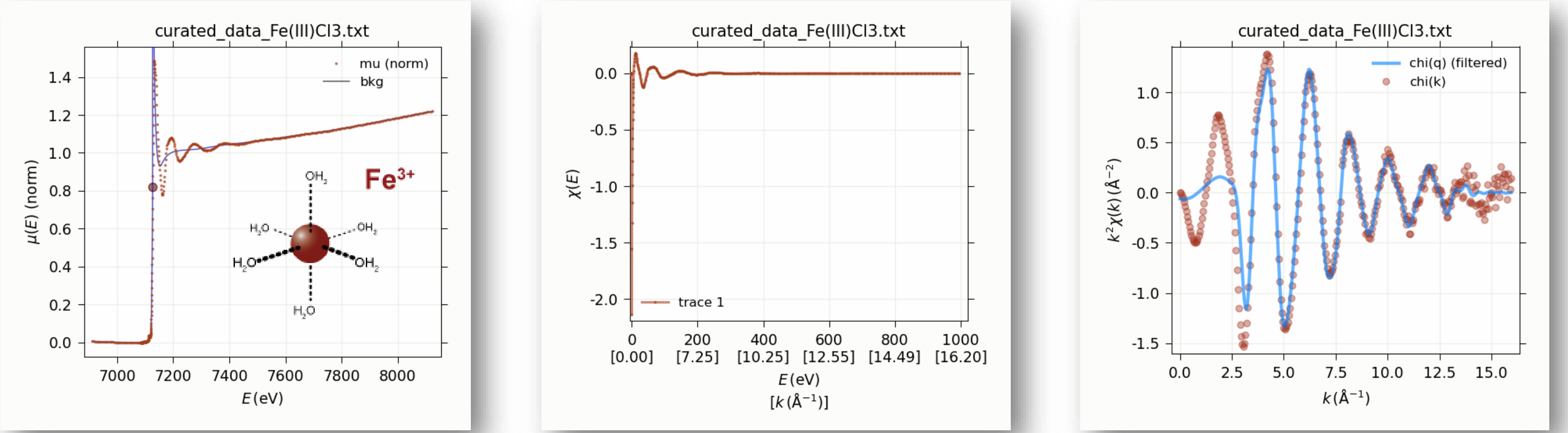
- Intensity of the pre-edge peak can be used to quantify Cr^{6+}.
- Bushfires cause oxidation to Cr^{6+} in Fe-oxides.
- Environmental risk of Cr^{6+} runoff into waterways.



Burton, *et al.*, Environmental Pollution, 247, 618-625 (2019)

1. X-ray Spectroscopy (XAS) | Geometrical Insights (EXAFS)

- Extended X-ray Absorption Fine Structure (**EXAFS**) reveals geometric information on distribution and identify of nearest neighbors.



EXAFS Equation

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-\left(\frac{2R_j}{\lambda(k)}\right)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

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1. X-ray Spectroscopy (XAS) | Geometrical Insights (EXAFS)

[Cu-Cu] Bond Length
(metallic copper, fcc)

Expected values

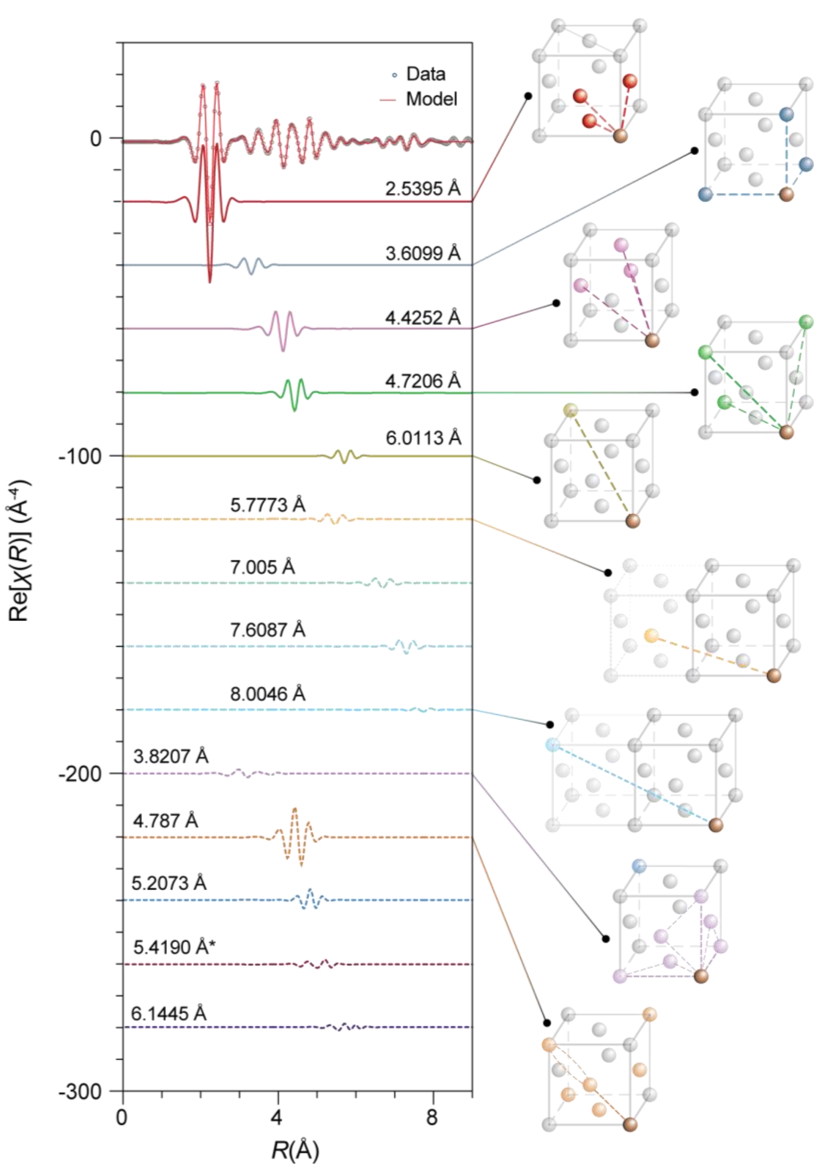
R = **2.542** ± 0.003 Å

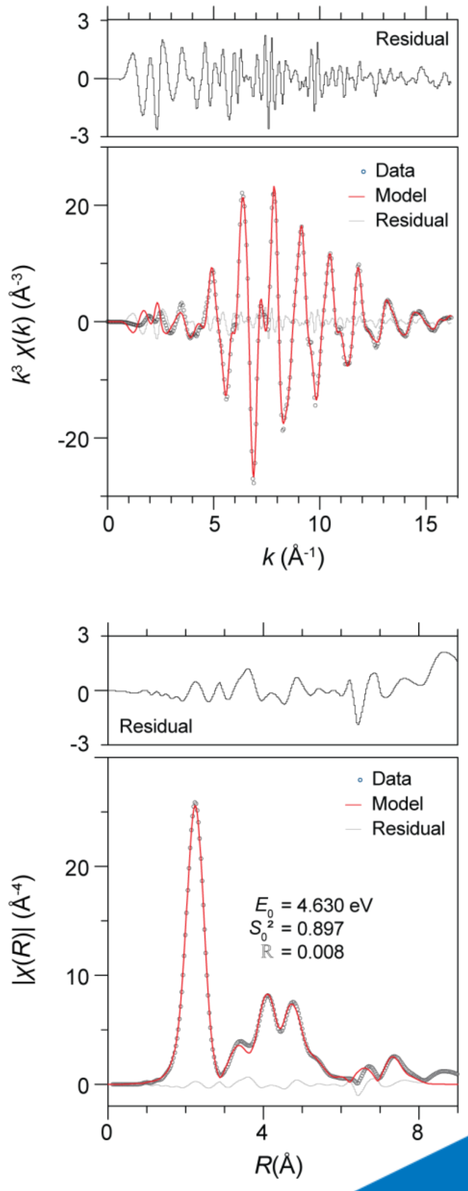
σ^2 = 0.008670 ± 3.078×10^{-4} Å^2

Fitted values

R = **2.542** ± 0.002 Å

σ^2 = 0.009001 ± 2.460×10^{-4} Å^2





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1. X-ray Spectroscopy (XAS) | Bringing it all together

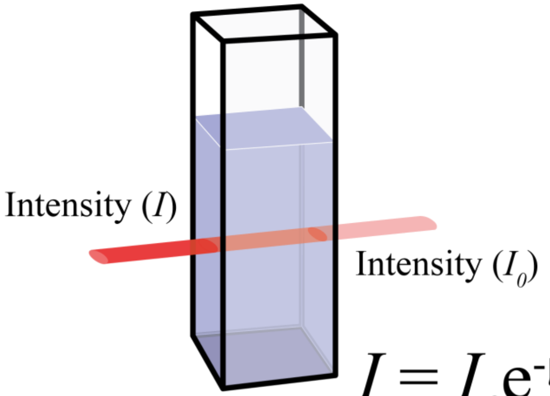
X-ray Absorption Spectroscopy (XAS) – *NO LONG-RANGE ORDER REQUIRED*

Analytical technique for determining the local geometric and/or electronic structure of matter.

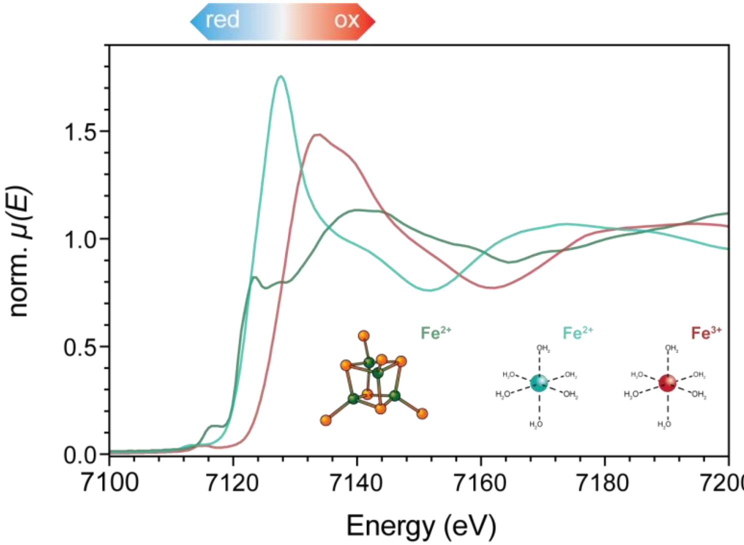
Use XAS when you need;

Element-specificity

Sensitivity to the 'bulk'



$$I = I_0 e^{-\mu x}$$



Sensitivity to the local chemical environment

What's the plan?

1. What is X-ray Spectroscopy? ✓

2. Introducing MEX 1 and 2

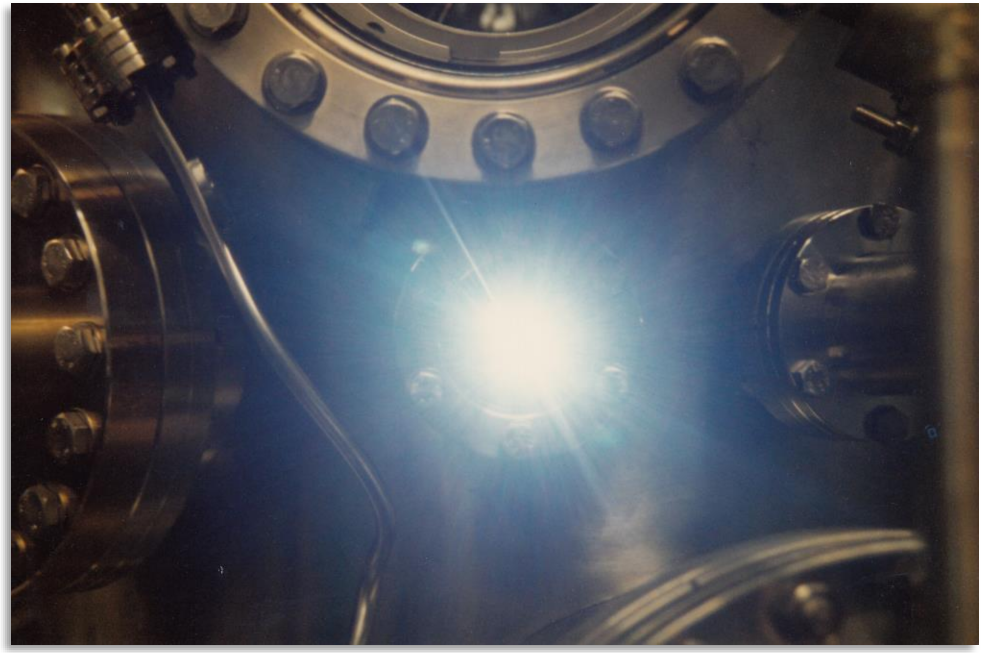
3. Mechanics of Beamtime

4. XAS, worms and ischemia

2. Introducing MEX 1 and 2 | Synchrotron Radiation

Synchrotron radiation |

A charged particle moving on a curved trajectory in a magnetic field radiates energy. At relativistic velocities (a whisker below 299,792,458 m sec^{-1}) it results in synchrotron radiation.



Synchrotron radiation reflecting from a terbium crystal at the Daresbury Synchrotron Radiation Source (UK), 1990.

Brilliance

units = sec^{-1} mm^{-2} mr^{-2} (0.1%BW)

60 W light bulb
10^6 photons

Sun
10^{10} photons

3rd generation synchrotron
10^{16} photons

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2. Introducing MEX 1 and 2 | The Australian Synchrotron

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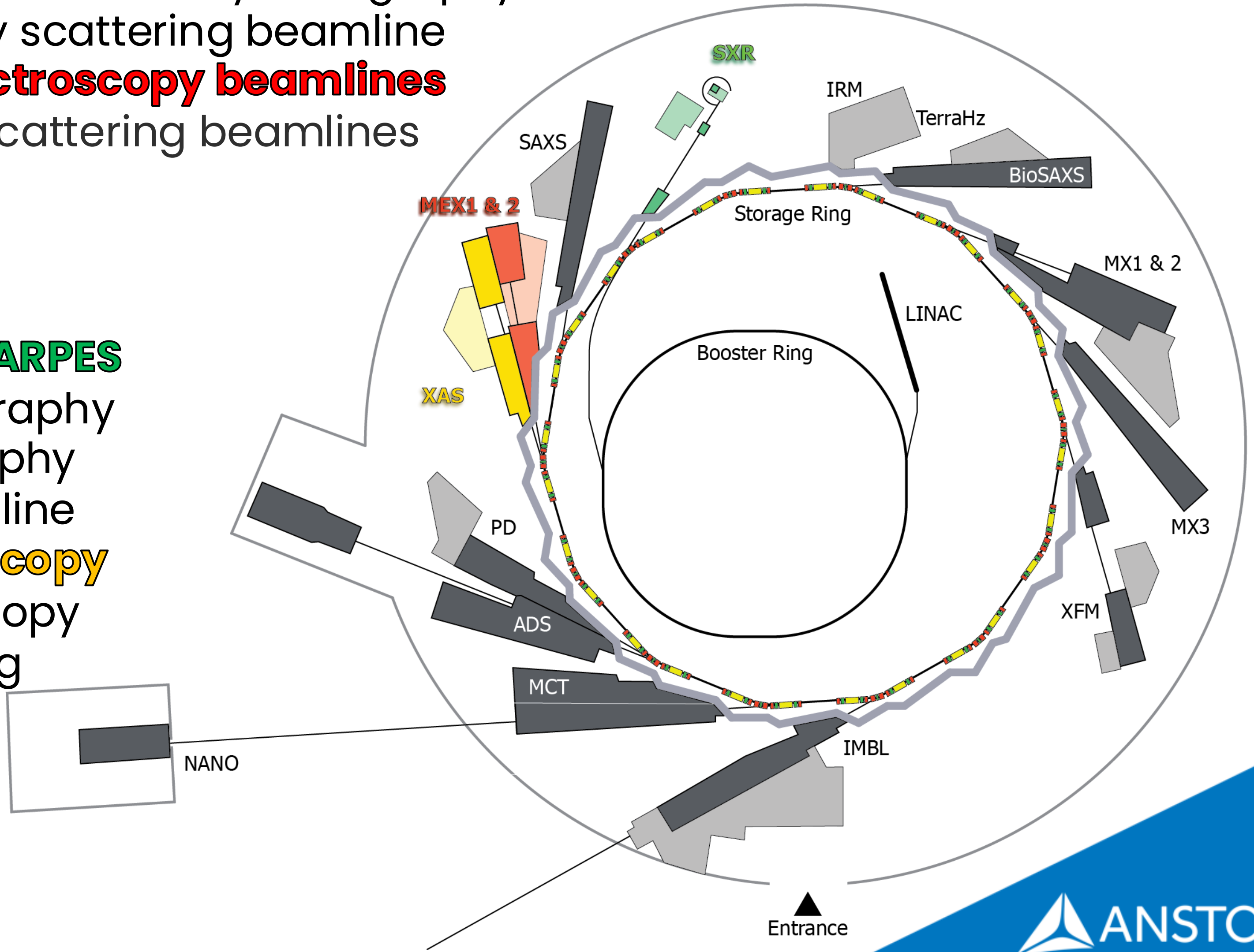
2. Introducing MEX 1 and 2 | The Australian Synchrotron

- **BRIGHT Beamlines**
  MX3: High-Performance Macromolecular Crystallography beamline
  BioSAXS: Biological small angle X-ray scattering beamline
  MEX 1 & 2: Medium Energy X-ray Spectroscopy beamlines
  ADS 1 & 2: Advanced Diffraction and Scattering beamlines
  NANO: Nanoprobe beamline

- **Existing Beamlines**
  SXR: Soft X-ray Spectroscopy / ARPES
  MX 1: Macromolecular Crystallography
  MX 2: Micro-focused Crystallography
  IMBL: Imaging and Medical Beamline
  XAS: X-ray Absorption Spectroscopy
  XFM: X-ray Fluorescence Microscopy
  SAXS/WAXS: Small/Wide Angle Scattering
  IRM: Infrared Microspectroscopy
  THz: THz / Far-IR Spectroscopy
  PD : Powder Diffraction



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2. Introducing MEX 1 and 2 | FIRST LIIIIIIIIIIIIIIIIIIIIIIIGHT!

First Light
Sunday 12th June 2022

Dr Emily Finch

Dr Chris Glover
(*Lead Scientist*)

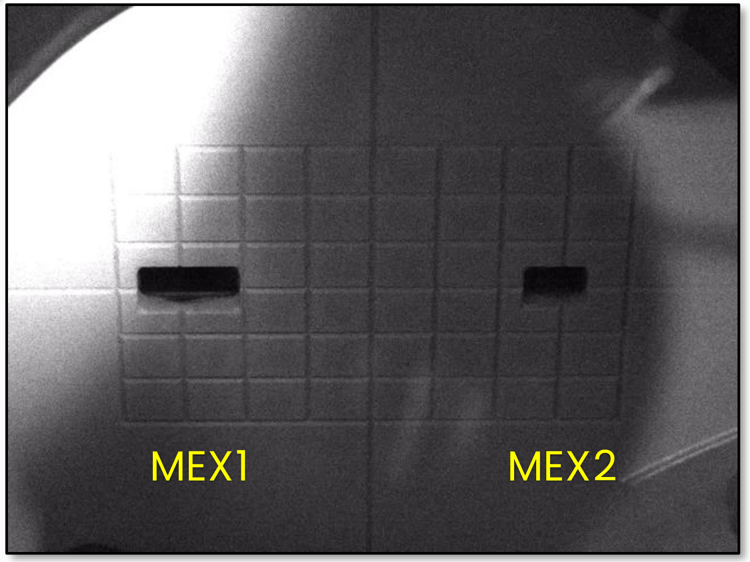
Dr Jeremy Wykes

Dr Jess Hamilton
(XAS)

Dr Simon James

Dr Valerie Mitchell
(XAS)

Dr Krystina Lamb



First light!

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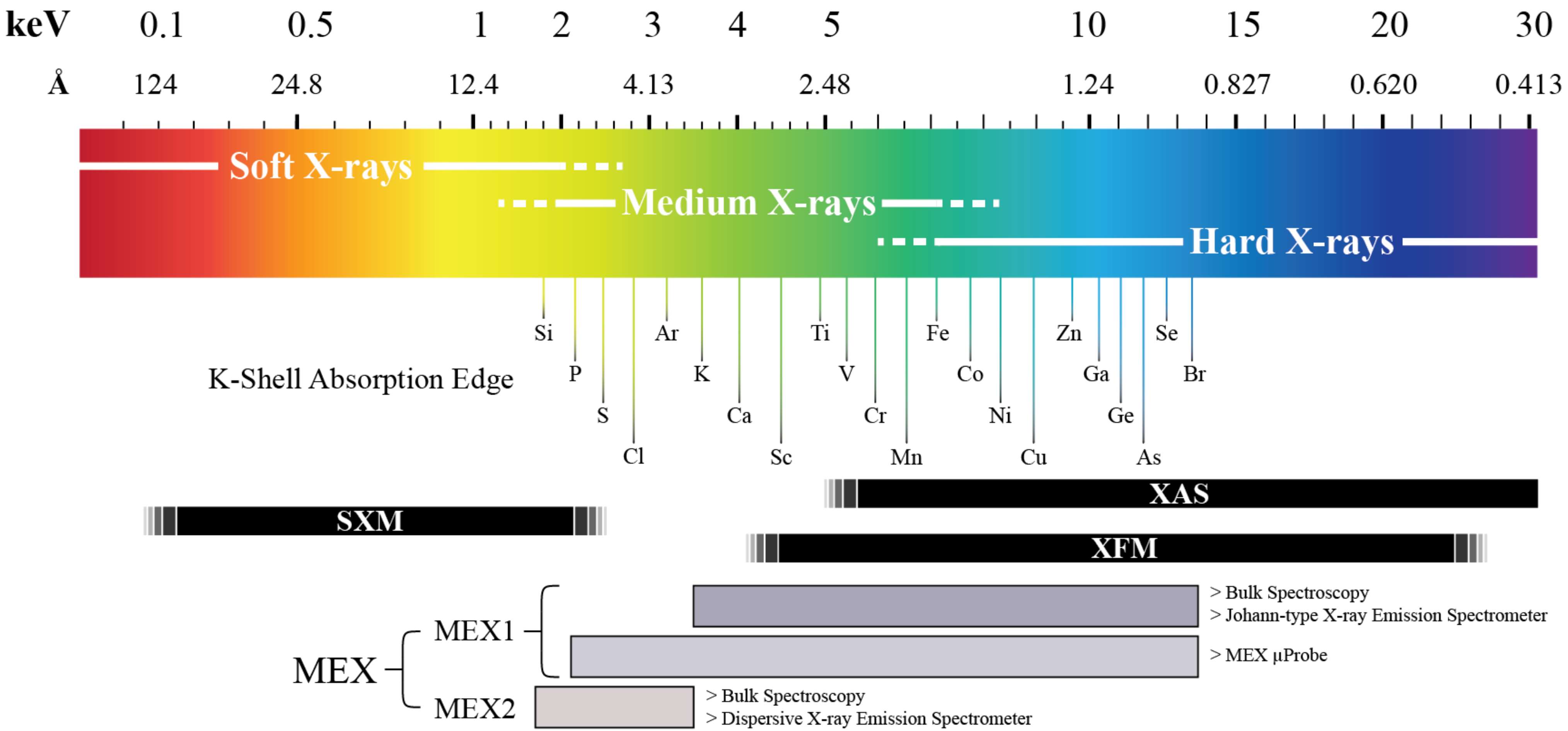
2. Introducing MEX 1 and 2 | Complimentary Capabilities



- Designed for experimental flexibility, MEX complements and extends the suite of X-ray spectroscopy techniques available at the Australian Synchrotron.
- The MEX-1 and MEX-2 beamline utilizes the same bend magnet source but operate independently.

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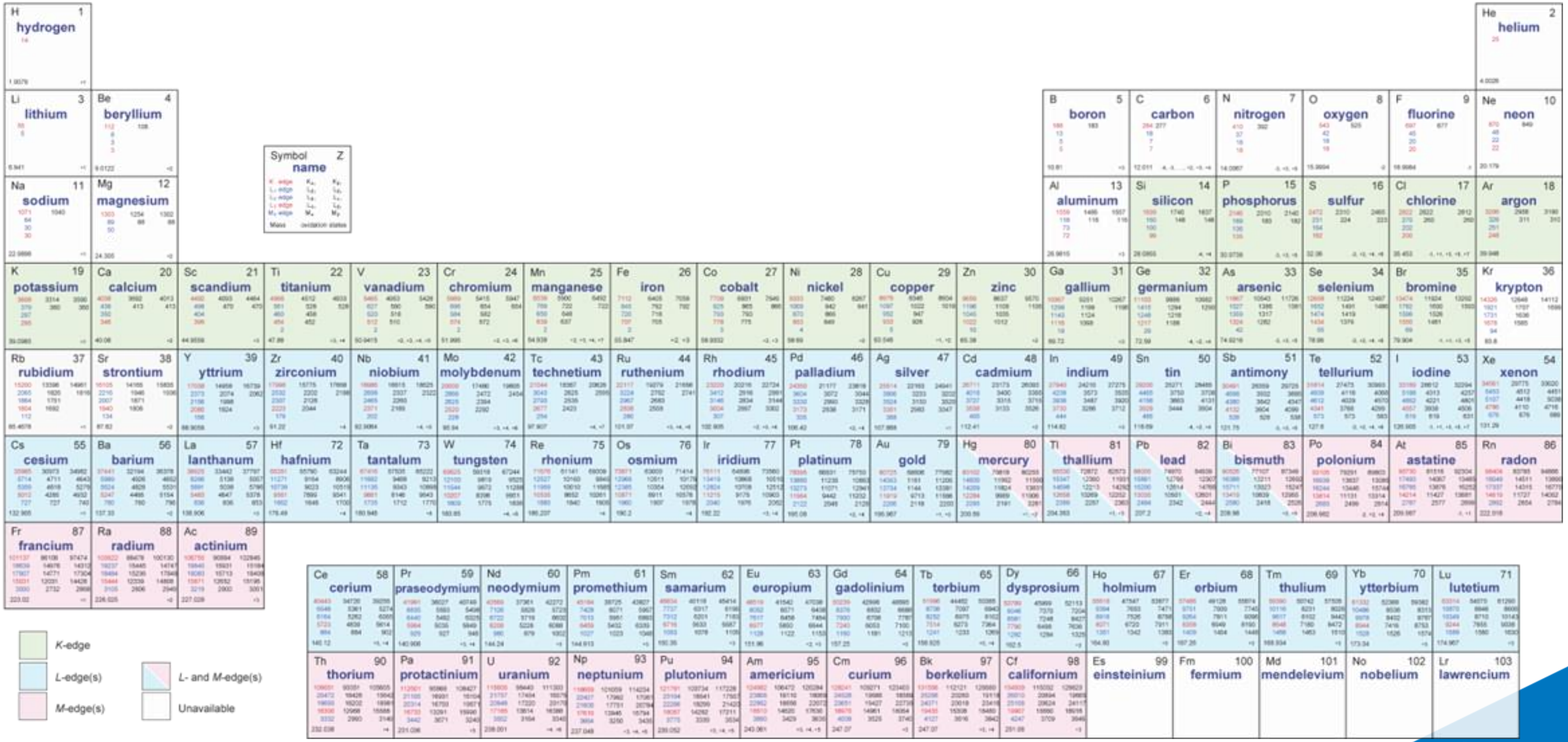
2. Introducing MEX 1 and 2 | See anything you like?



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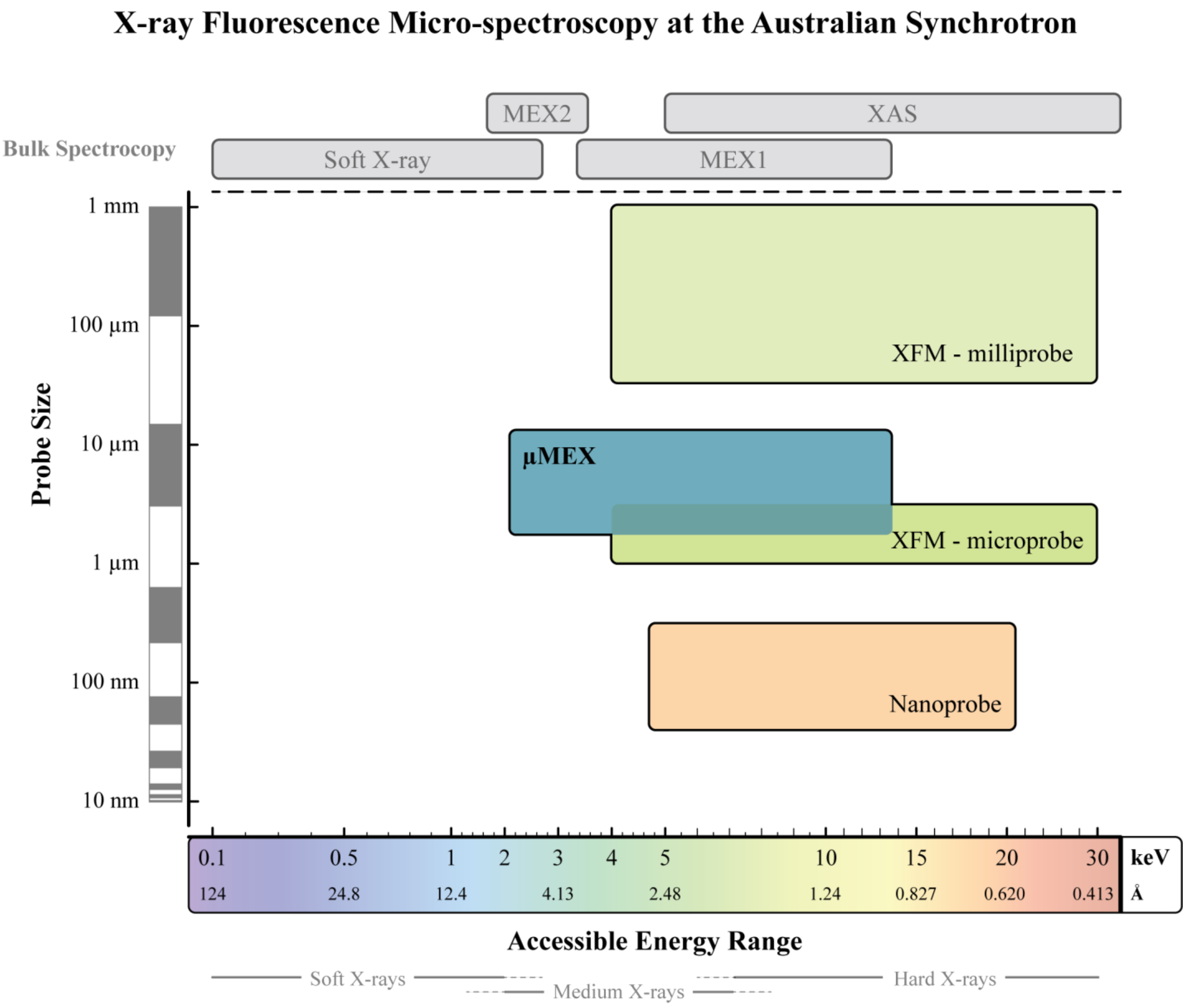
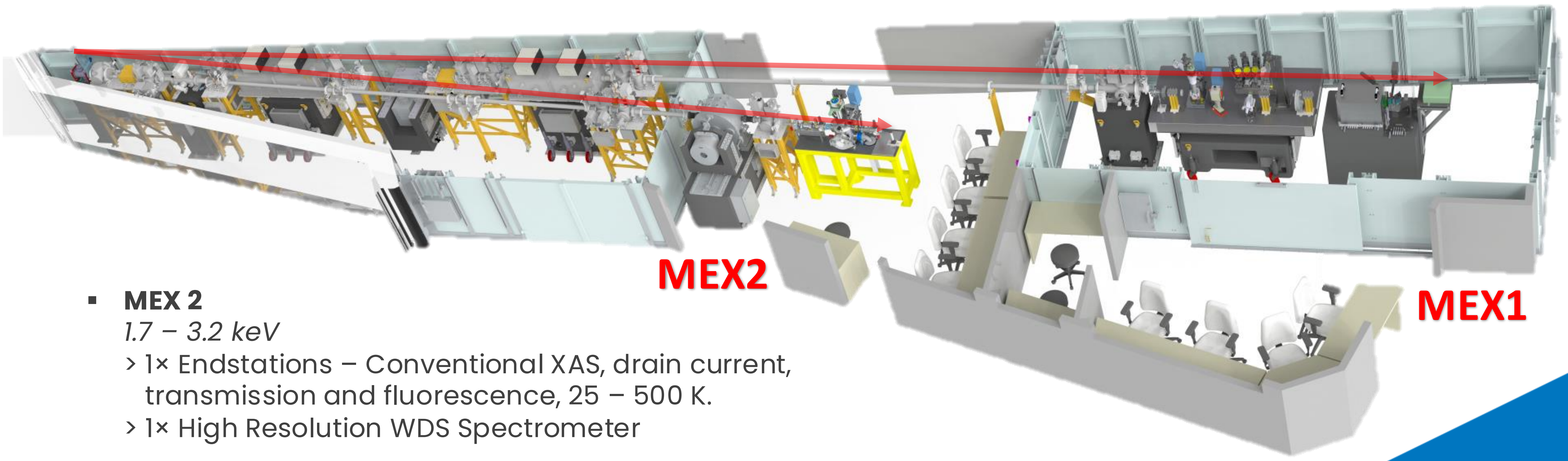


2. Introducing MEX 1 and 2 | Lots of kit… Not much space.

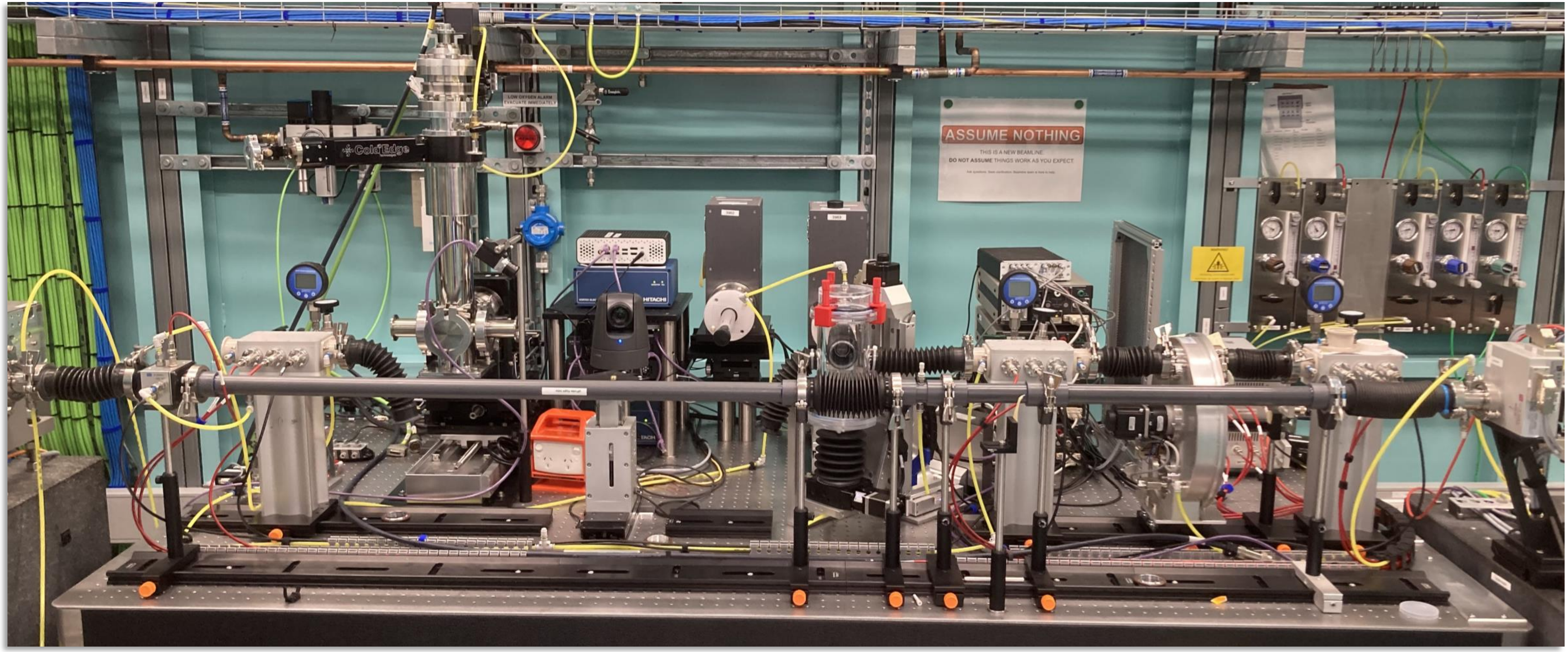
- **MEX 1**
  3.4 – 13.6 keV
  > 2× Endstations – Conventional XAS, transmission and fluorescence, 25 – 500 K.
  > 1× High-Resolution WDS Spectrometer – 5 crystal Johann-type spectrometer.

  2.1 – 13.6 keV
  > 1× microspectroscopy – Scanning X-ray Fluorescence microprobe, 80 – 500 K.



- **MEX 2**
  1.7 – 3.2 keV
  > 1× Endstations – Conventional XAS, drain current, transmission and fluorescence, 25 – 500 K.
  > 1× High Resolution WDS Spectrometer

2. Introducing MEX 1 and 2 | MEX1 First looks



MEX1 Bulk Spectroscopy

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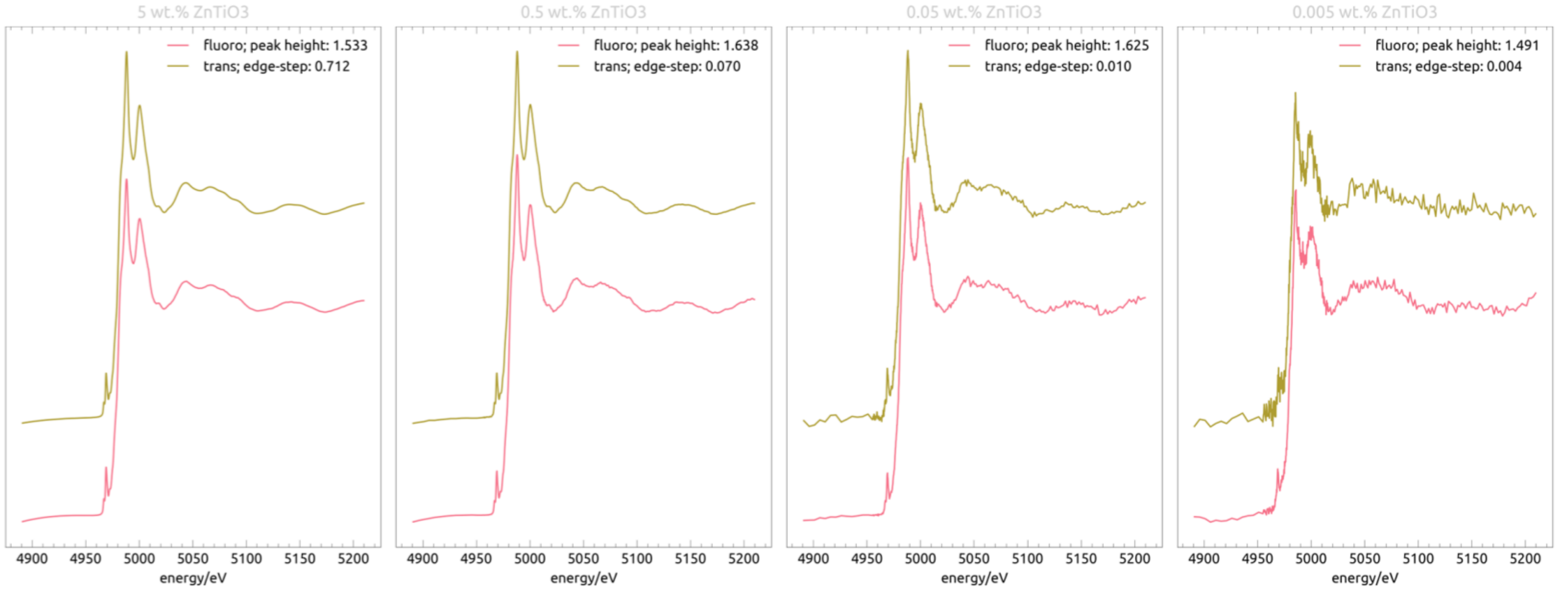
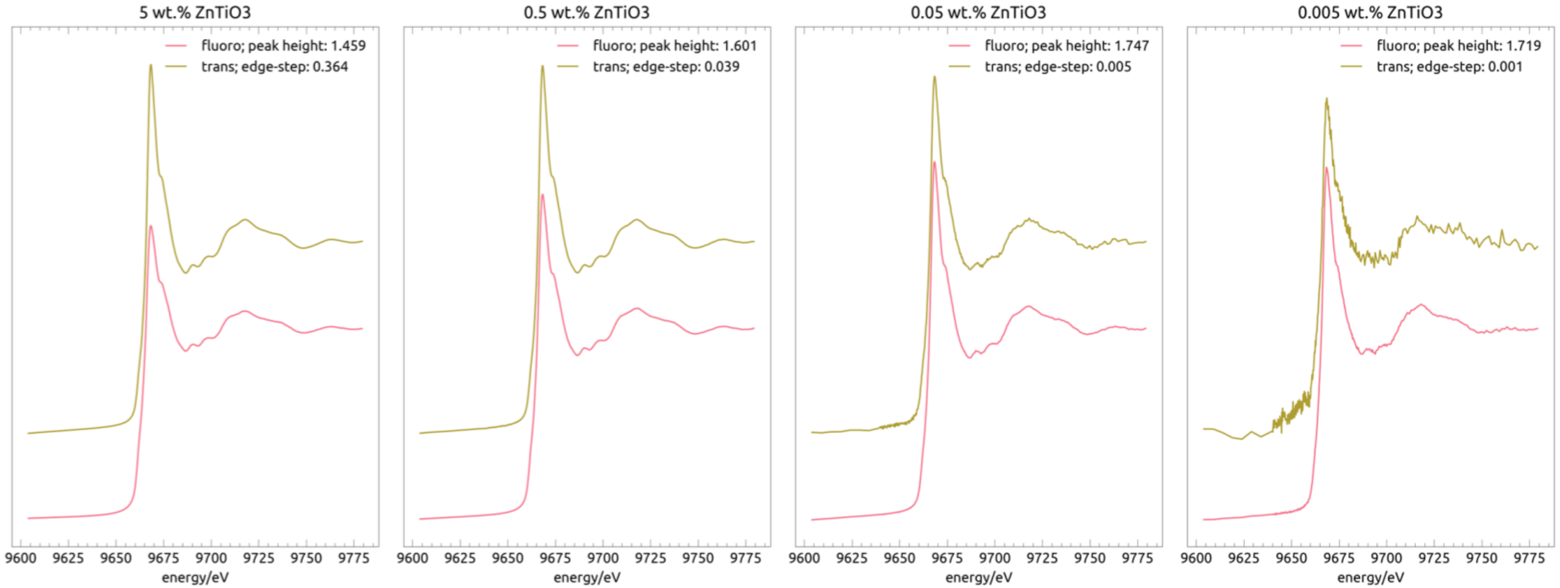
2. Introducing MEX 1 and 2 | MEX1 First looks

Data courtesy of
Dr Jeremy Wykes

Ti XANES
K edge = 4.966 keV



Zn XANES
K edge = 9.659 keV



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2. Introducing MEX 1 and 2 | MEX2 First looks

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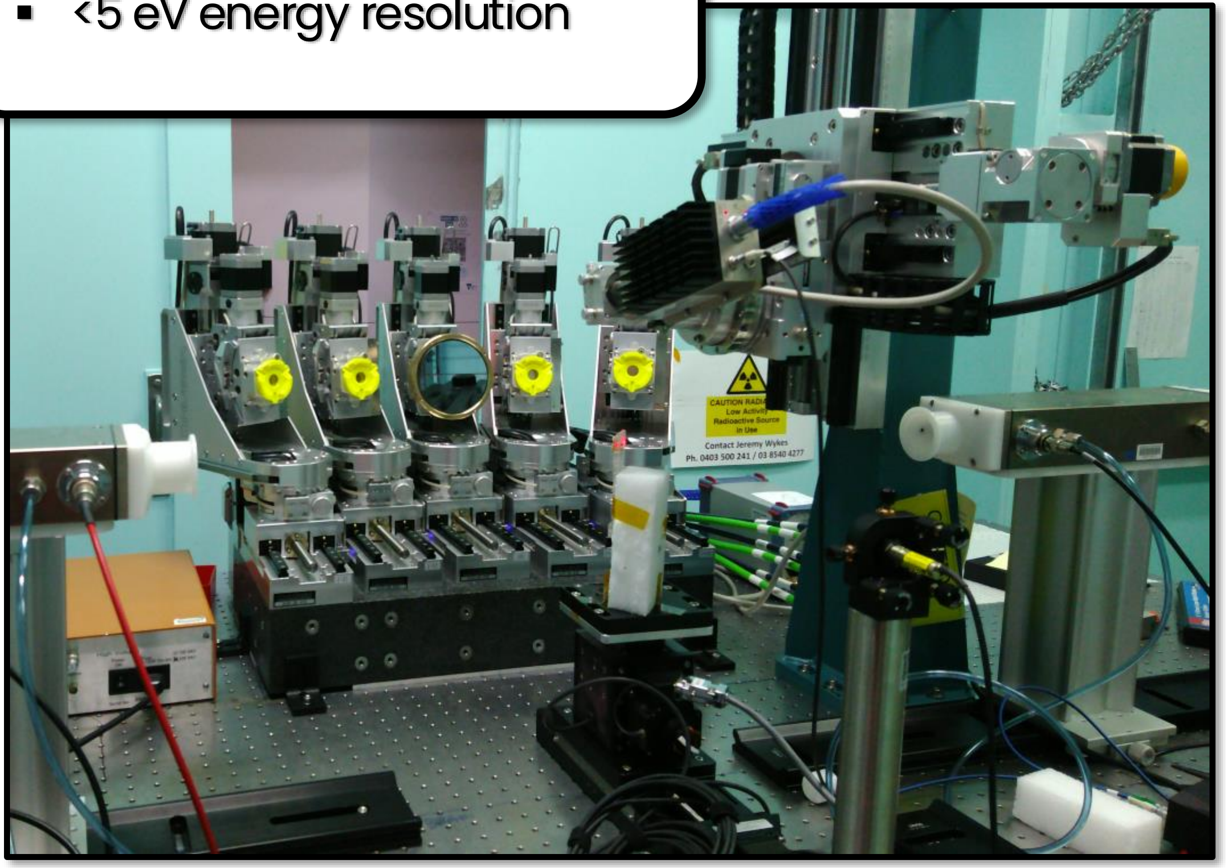
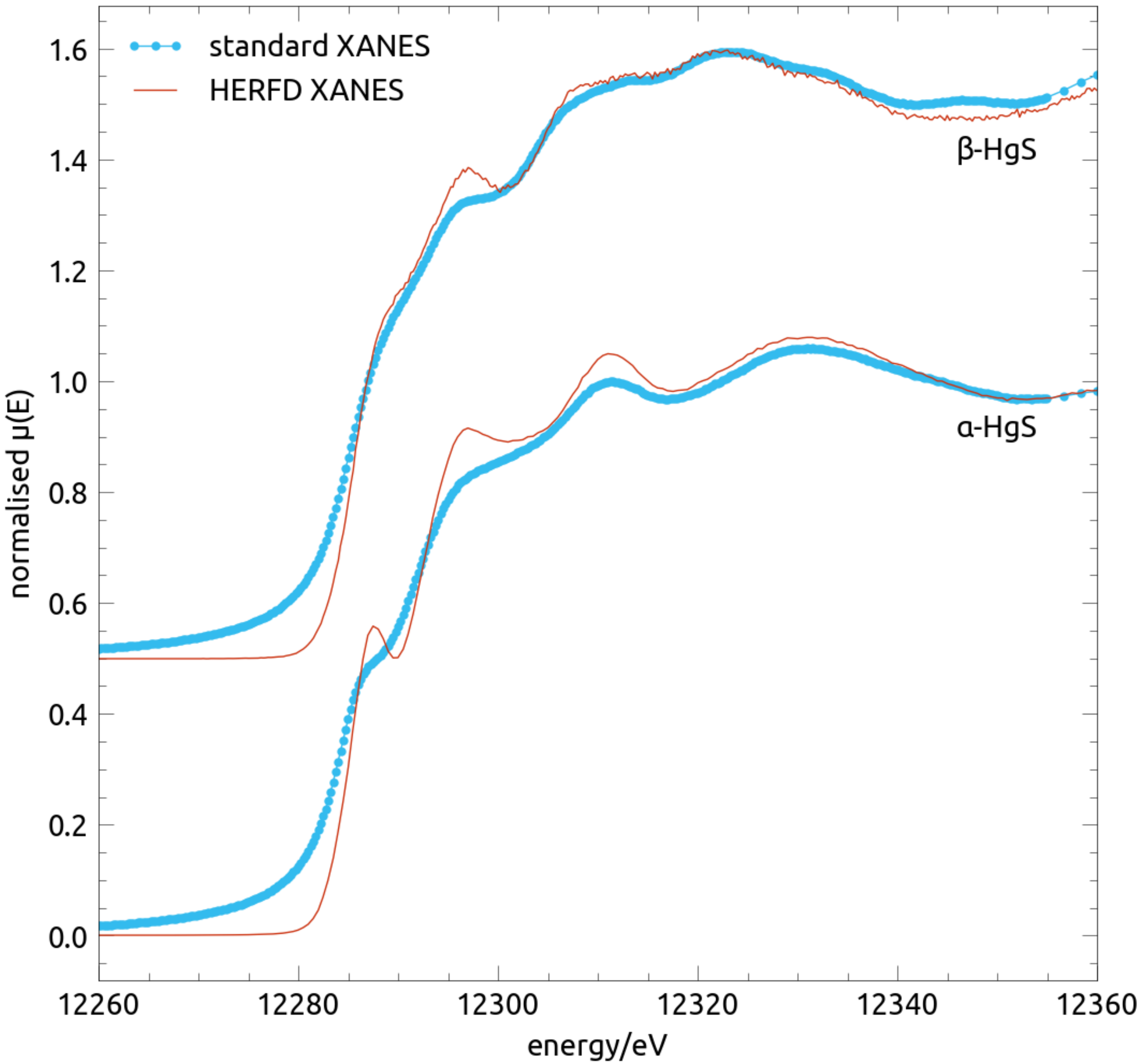
2. Introducing MEX 1 and 2 | What's next? HERFD-XAS

- 50 cm Rowland circle
- <5 eV energy resolution

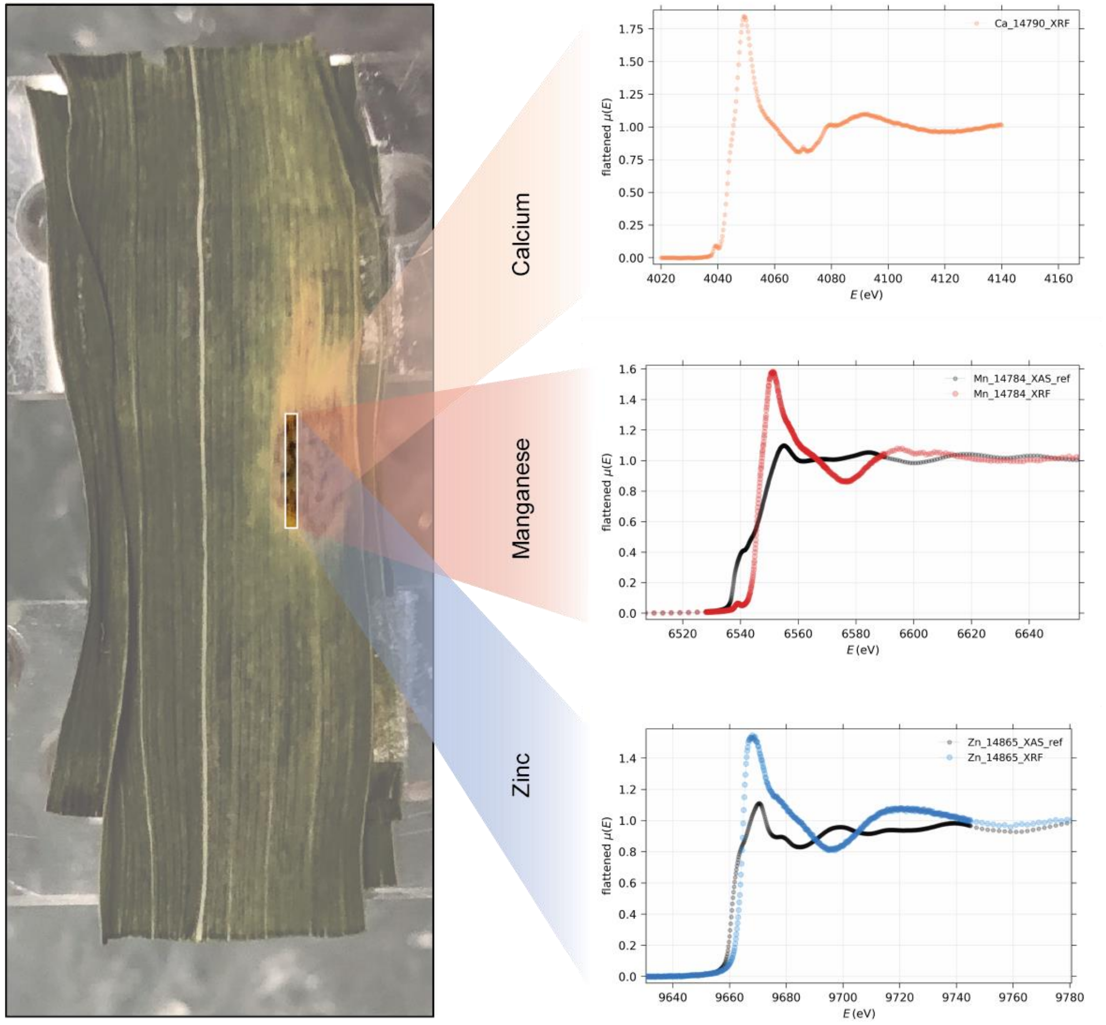




2. Introducing MEX 1 and 2 | What's next? μXAS

Microspectroscopy

	Specification
Spot	> Tuneable, routine 3 – 20 μm.
Flux	> 10^8 - 10^{10} photon sec^{-1} in spot
Harmonic Rejection	> Yes. Rh stripe and bare Si.
Sample environment	> Pressure: Ambient. > Atmosphere: > 95% (v/v) $He_{(g)}$. > Temp: 80 – 500 K (Cryostream)
Scan Range	> Horizontal: ≥ 90mm. > Vertical: 100 mm.
Scan Velocity	> 0.05 – 5 mm sec^{-1} (PVT scanning)
Detectors	> Ion Chambers (IC_{KB}, IC_0 and IC_1). > 3-Element Vortex (90° to the beam). > Pilatus 200K (transmission)*.
Sample Alignment	> Various optical light cameras.



Data courtesy of Meg Willians and Dr Mark Hackett, Curtin University.

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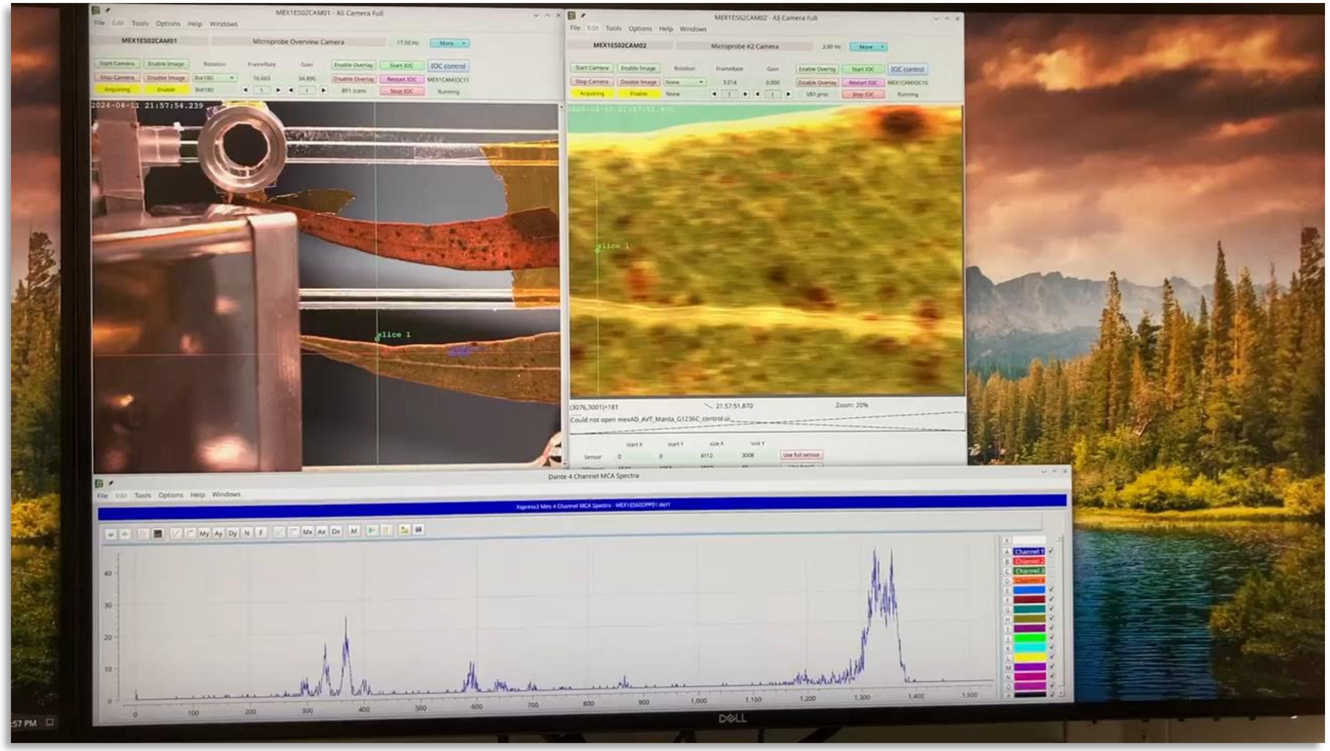


2. Introducing MEX 1 and 2 | ... and a big thanks to...

Design and Build
Scientists
Chris Glover (*Lead Scientist*)
Jeremy Wykes
Simon James
Emily Finch
Valerie Mitchell
~~Krystina Lamb~~
Bruce Cowie
Pria Ramkissoon (new starter)

Engineers
~~Mohamed Elrabiey (Project Manager)~~
~~Adrian Hawley (Project Manager)~~
Renata Lippi (Project Manager)
Ben Pocock (Mechanical)
Ben Baldwinson (Controls)
Letizia Sammut (Scientific Software)

Beamline Advisory Committee

Peter Lay (Chair)	University of Sydeny, NSW
Mark Hackett	Curtin University, WA
Peter Kopittke	The University of Queensland, QLD
Andrew Berry	Australian National University, ACT
Rosalie Hocking	Swinburne University of Technology, VIC
Serena DeBeer	Max Planck Institute for Chemical Energy Conversion, Germany

Selected Images and Data

Mark Hackett	Curtin University, WA
Zhiguang Xiao	University of Melbourne

Many other engineers, technicians, store people and administrators

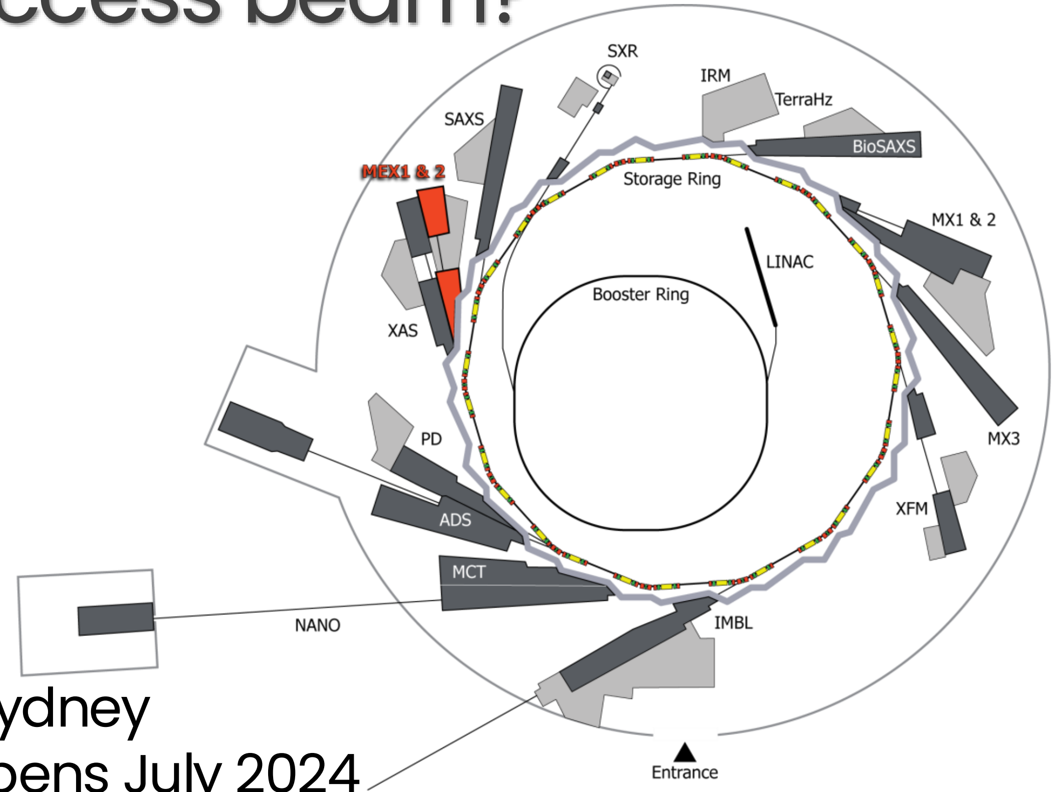
What's the plan?

1. *What is X-ray Spectroscopy?* ✓

2. *Introducing MEX 1 and 2* ✓

3. *Mechanics of Beamtime*

3. Beamtime Mechanics | How to access beam?



Contact your friendly beamline scientists

Merit-based (expectation to publish)

- all 10 operational beamlines
- BRIGTH beamlines; for Funders - incl. University of Sydney
- 3 proposal rounds per year; R1 2025 (next round) opens July 2024

Commercial (no expectation to publish)

- paid-for, any time

Preferred Access

- BRIGHT beamlines; for Funders – incl. UoM *e.g.* MEX2 Round 2 2024, 9 shifts (3 days)

3. Beamtime Mechanics | How to access beam?

Merit Access – Proposal round deadlines

Dates subject to change

2023-2: User beamtime late May to August

2023-3: User beamtime September to December

2024-1: User beamtime late January to early May 2024

	Key dates
Call for proposals opens	4 July 2023
Call for proposals closes	25 July 2023
Users notified	From mid-October 2023
Beamlines	Australian Synchrotron

2024-2: User beamtime late May to August 2024

2024:3 User beamtime September to December 2024

3. Beamtime Mechanics | Useful information

- https://asuserwiki.atlassian.net/wiki/spaces/UO/overview

- https://www.ansto.gov.au/facilities/australian-synchrotron

Simon James: sjames@ansto.gov.au
Beamline Team: as-mex@ansto.gov.au

Thank You

ANSTO

What's the plan?

1. *What is X-ray Spectroscopy?* ✓

2. *Introducing MEX 1 and 2* ✓

3. *Mechanics of Beamtime* ✓

4. XAS, worms and ischemia

Ischemia

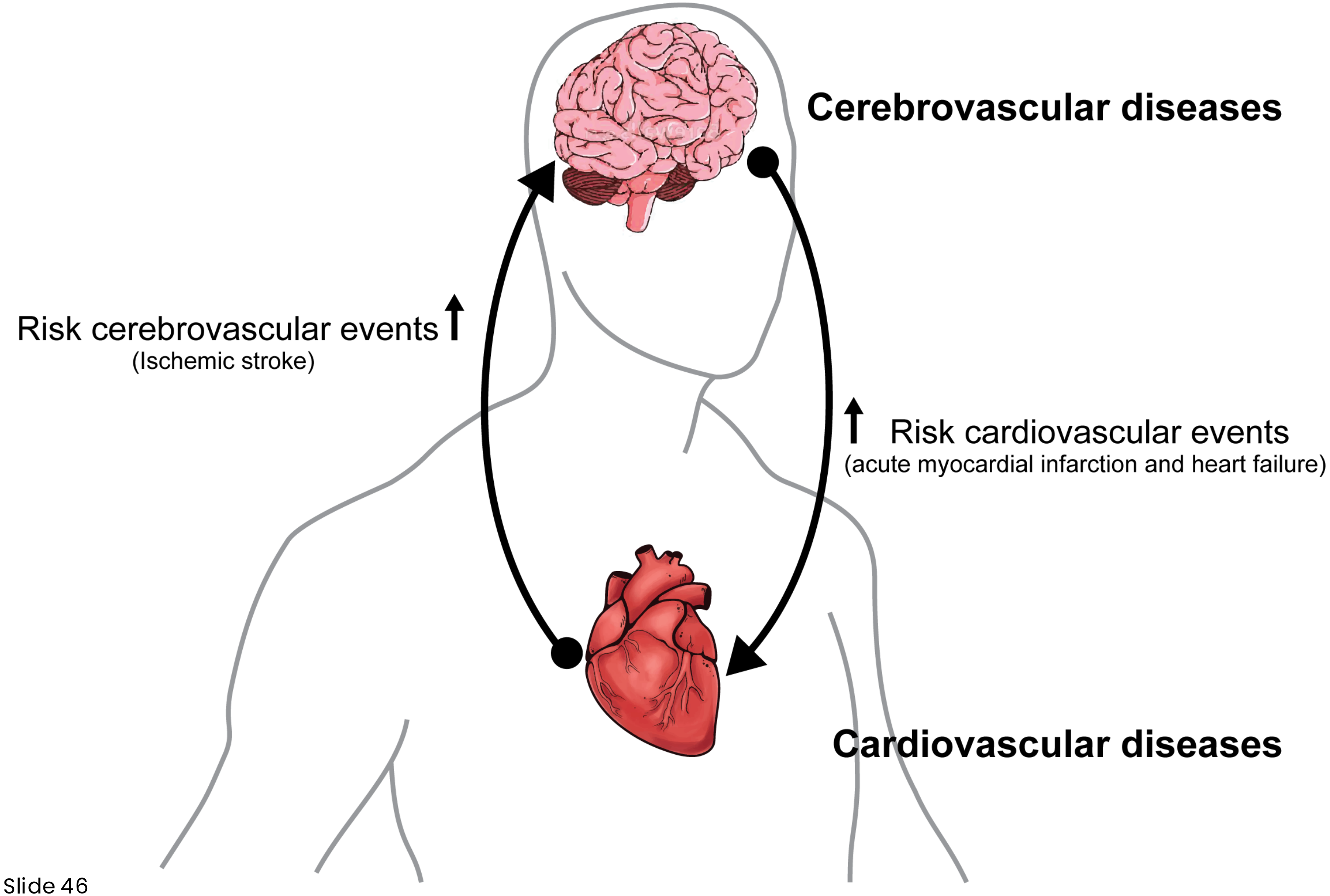
Greek *iskhaimos* (ἴσχαιμος) – "staunching blood"

From *iskho* (ἴσχω), "keep back, restrain" and *haima* (αἷμα) "blood".

4. XAS, worms and ischemia | CVD

Cerebrovascular and cardiovascular disease(s) (CVDs)

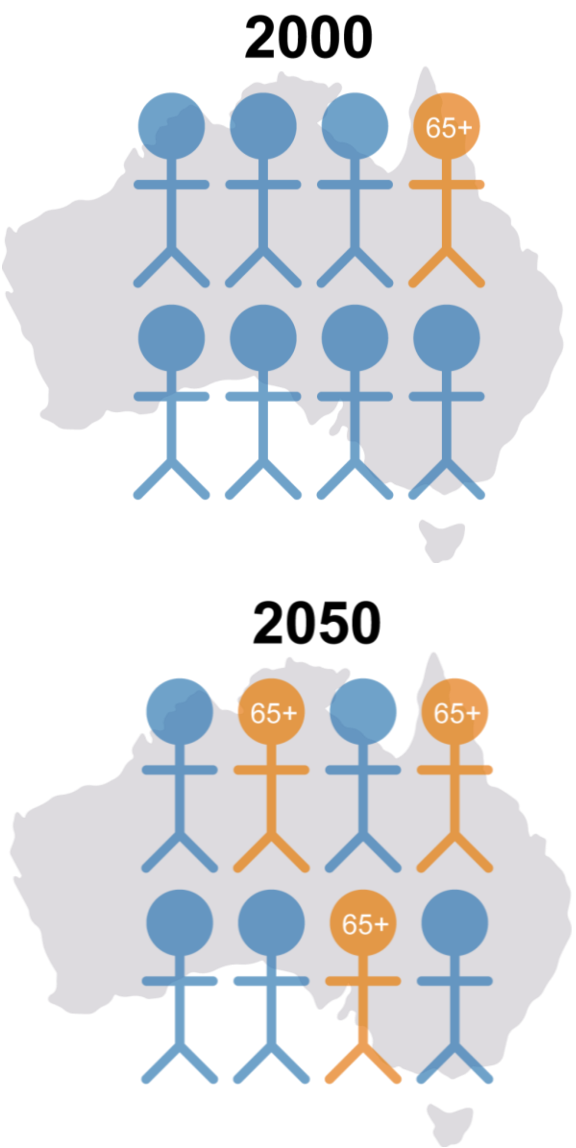
- Includes stroke and acute myocardial infarction (heart attack).

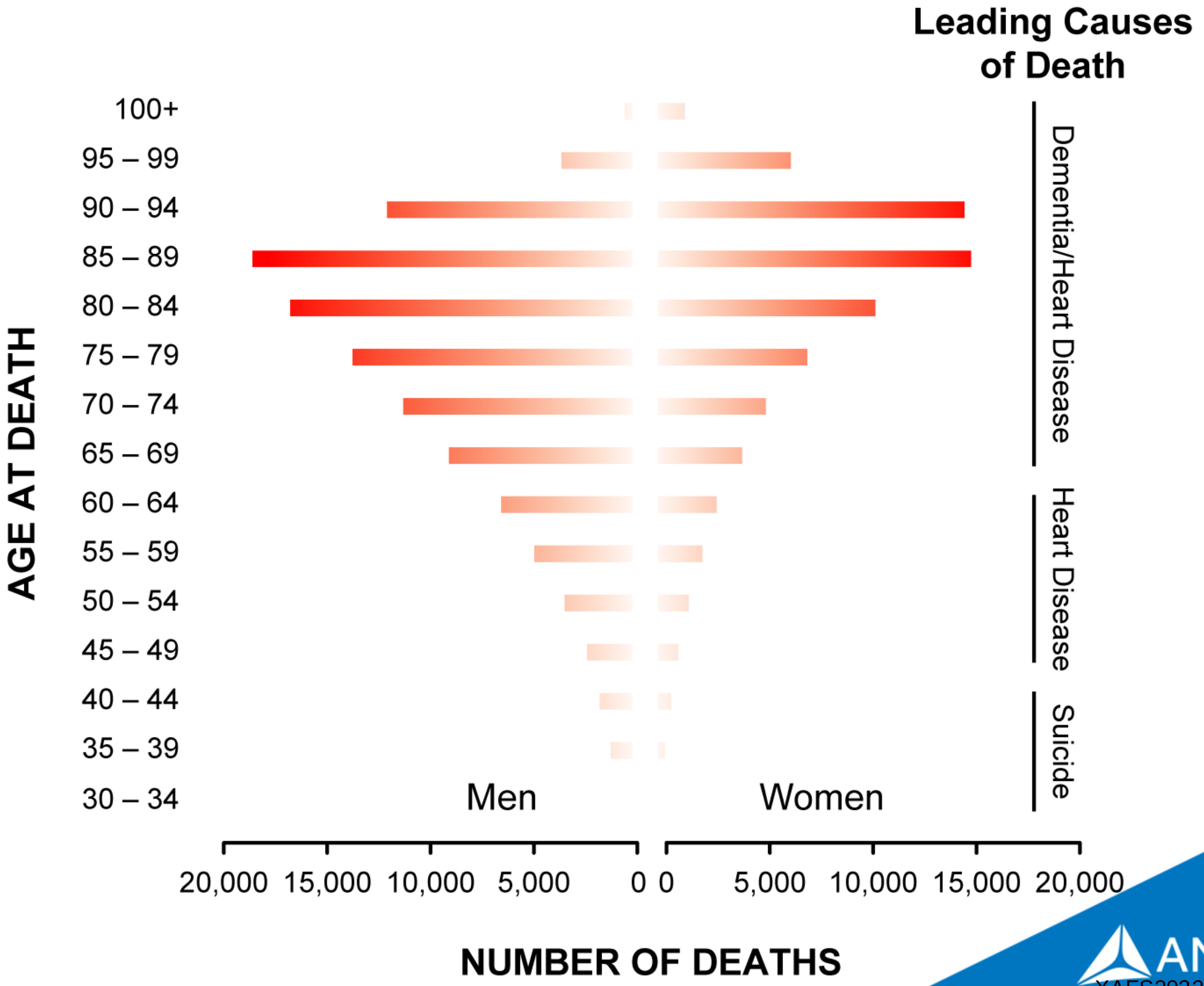


Share risk factors and common pathophysiological mechanisms.

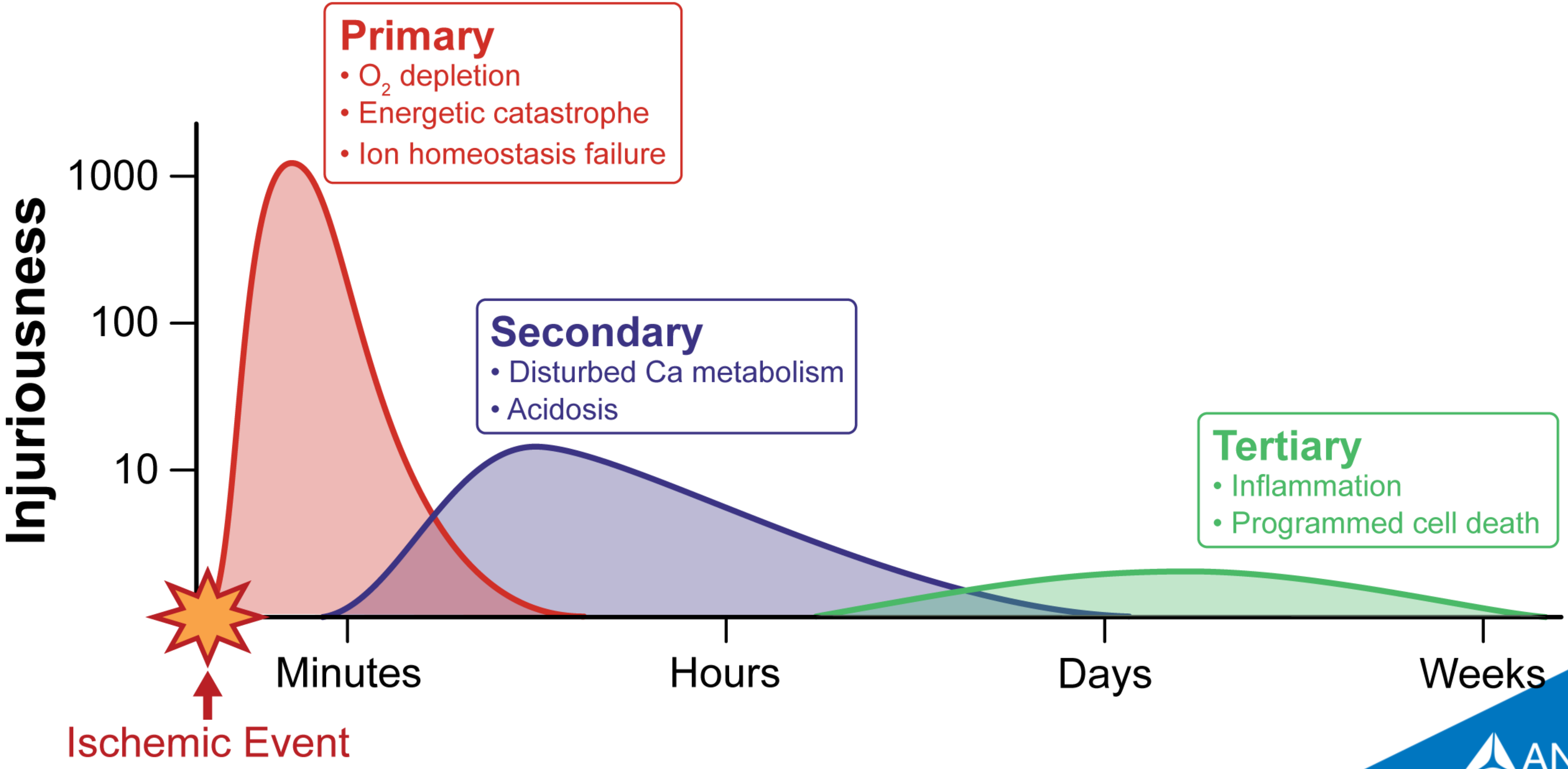
1 in 4 deaths in Australia

4. Ischemia | Burden of Disease in Australia

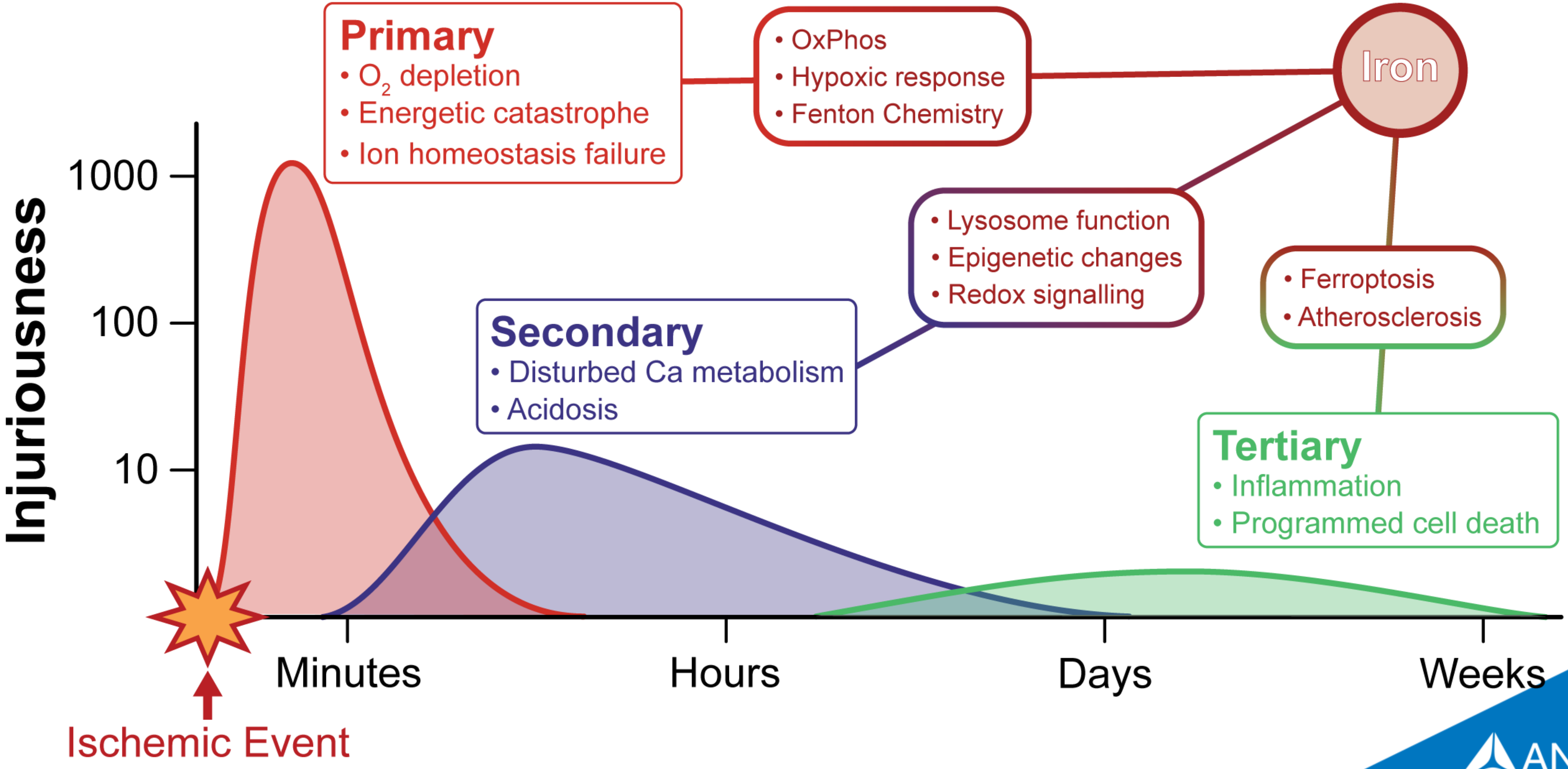


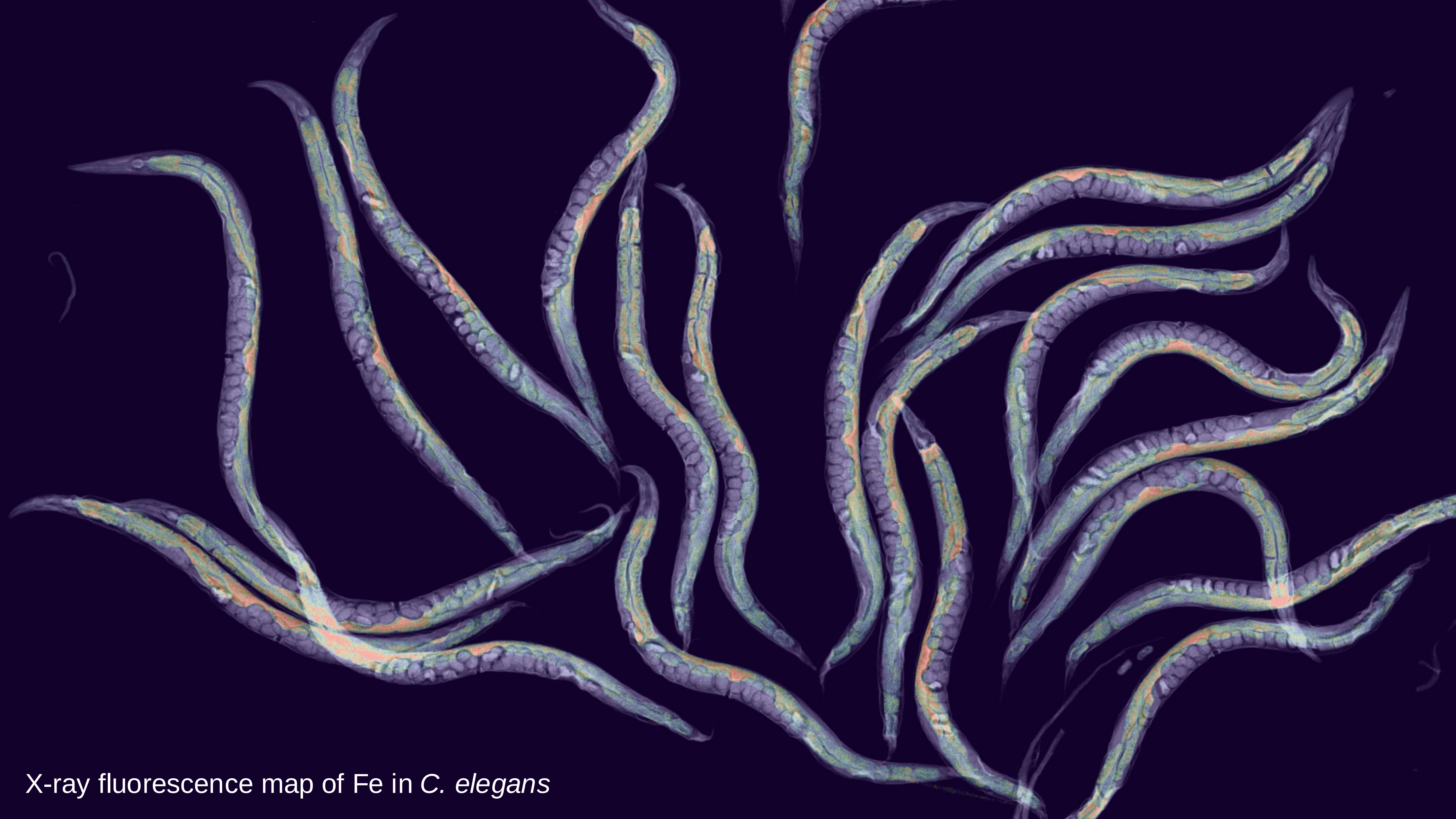


4. Ischemia | A Complex Cascade of Disease



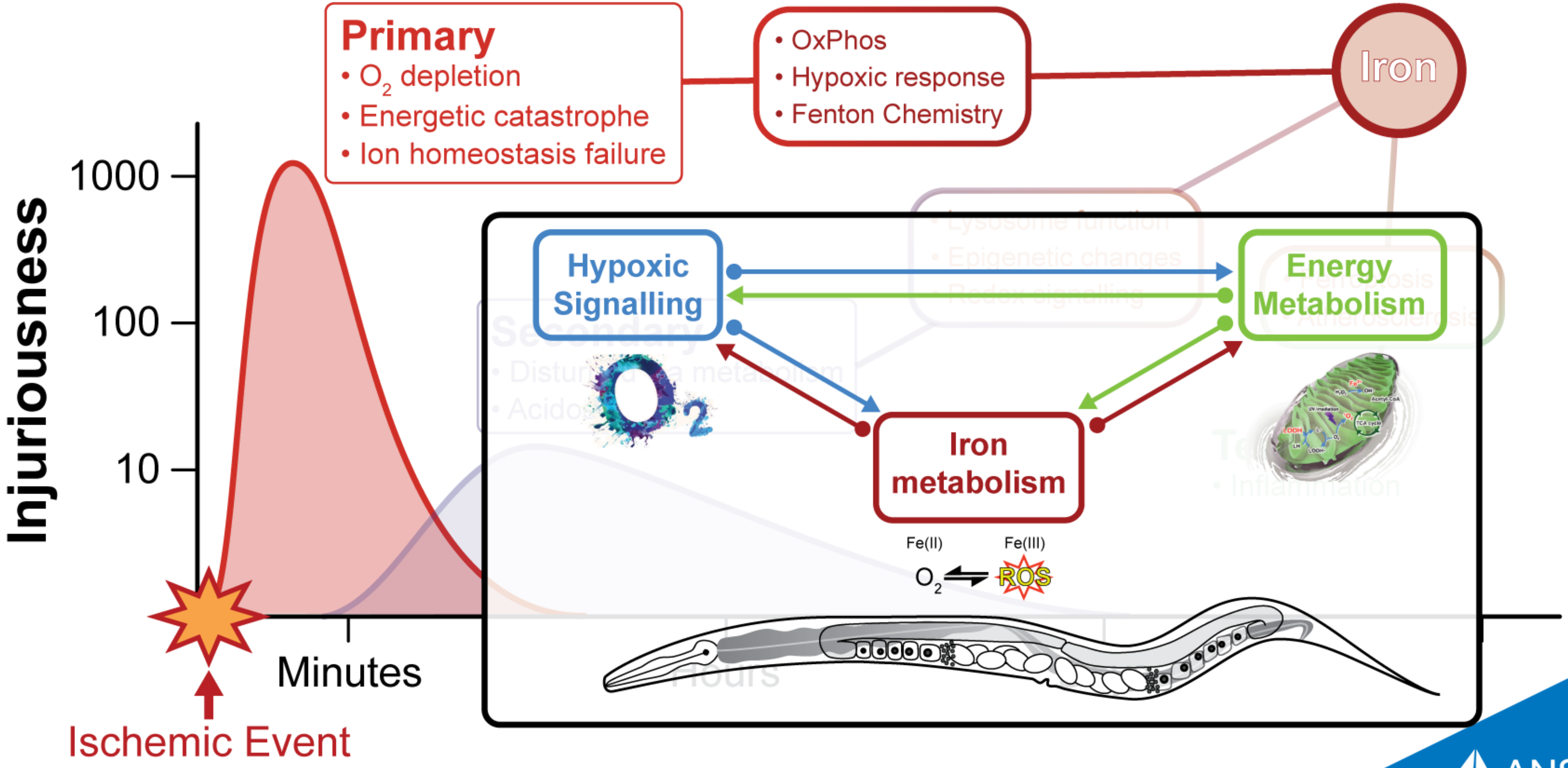
4. Ischemia | A Complex Cascade of Disease



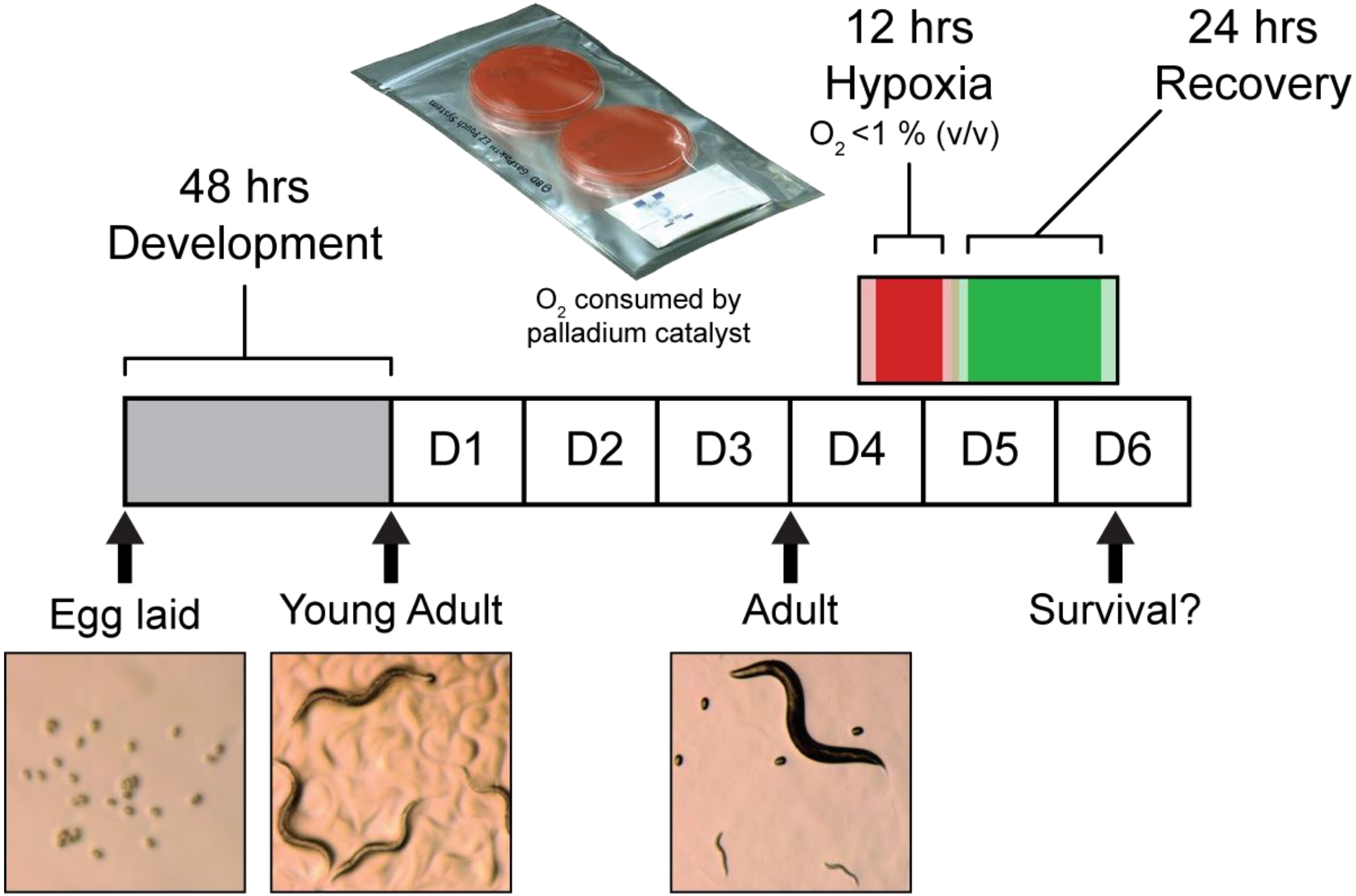


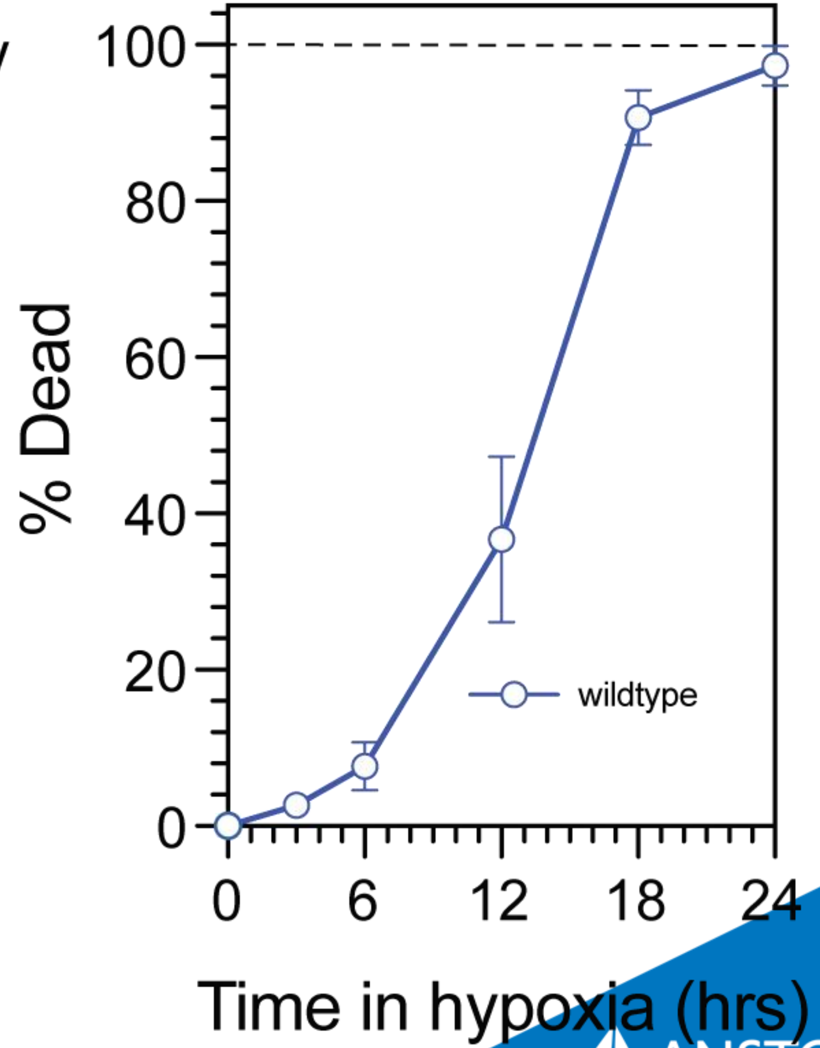
X-ray fluorescence map of Fe in *C. elegans*

4. Modelling in Ischemia | Utility of *C. elegans*



4. Modelling in Ischemia | Impact of hypoxia on *C. elegans*

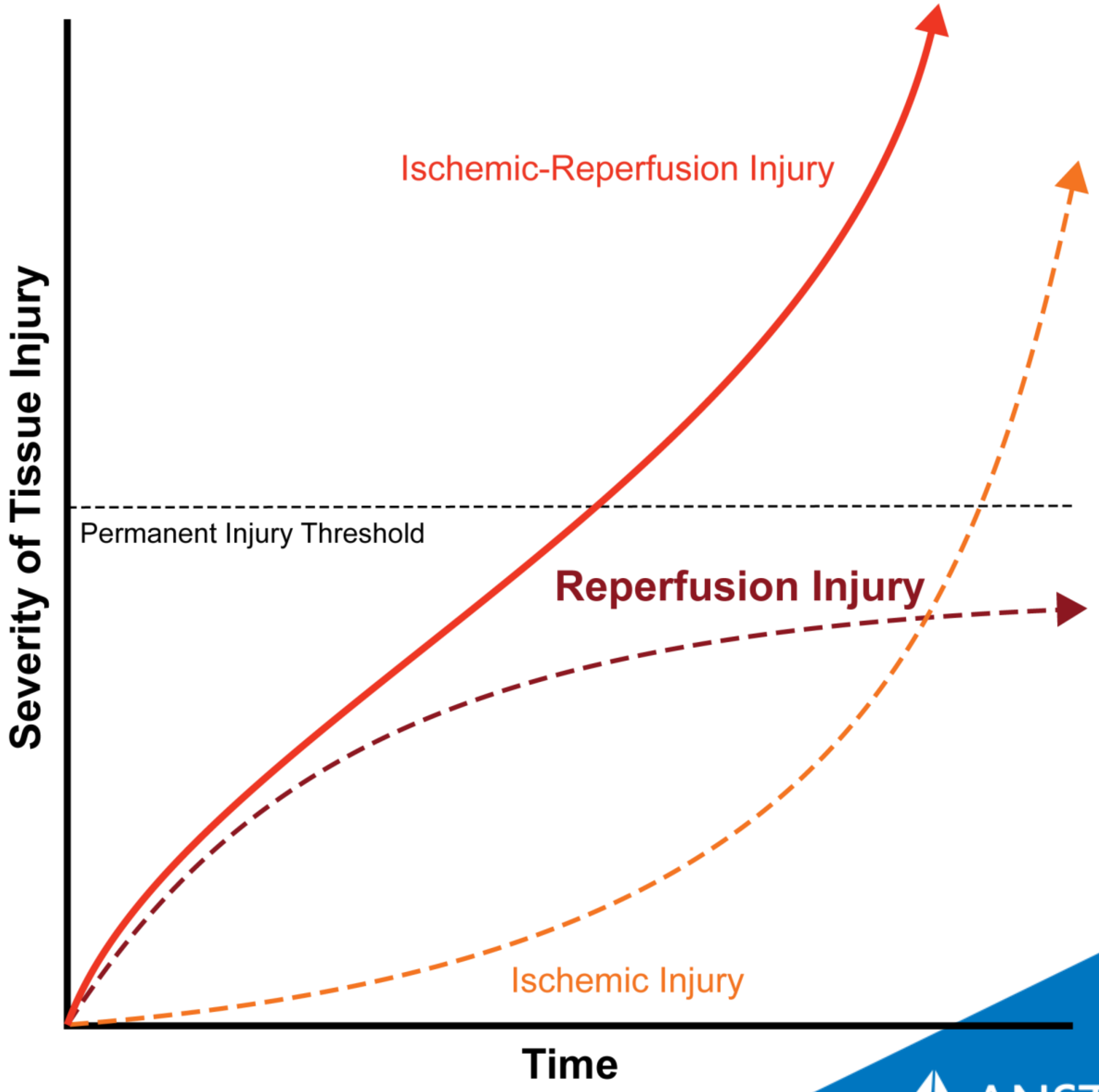




4. Modelling in Ischemia | Hypoxia isn't the whole story…

Reperfusion Injury

- Tissue damage caused when blood supply returns to tissue after a period of ischemia or hypoxia.
- The absence of oxygen and nutrients from blood during the ischemic period creates a condition in which the restoration of circulation results in **inflammation** and **oxidative stress** rather than (or along with) restoration of normal function.



4. Studying Bioiron using X-rays | Cryogenic μXAS

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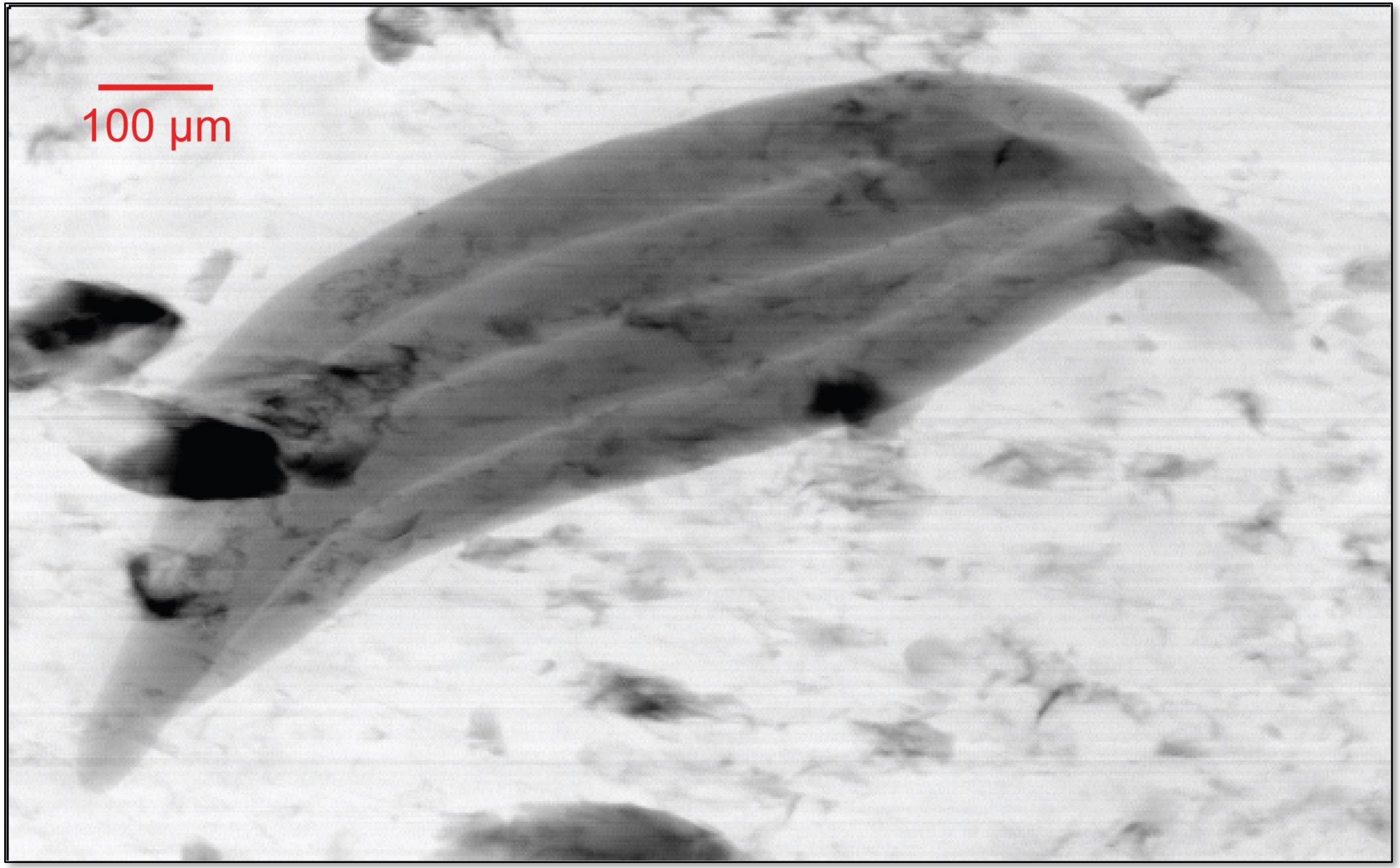
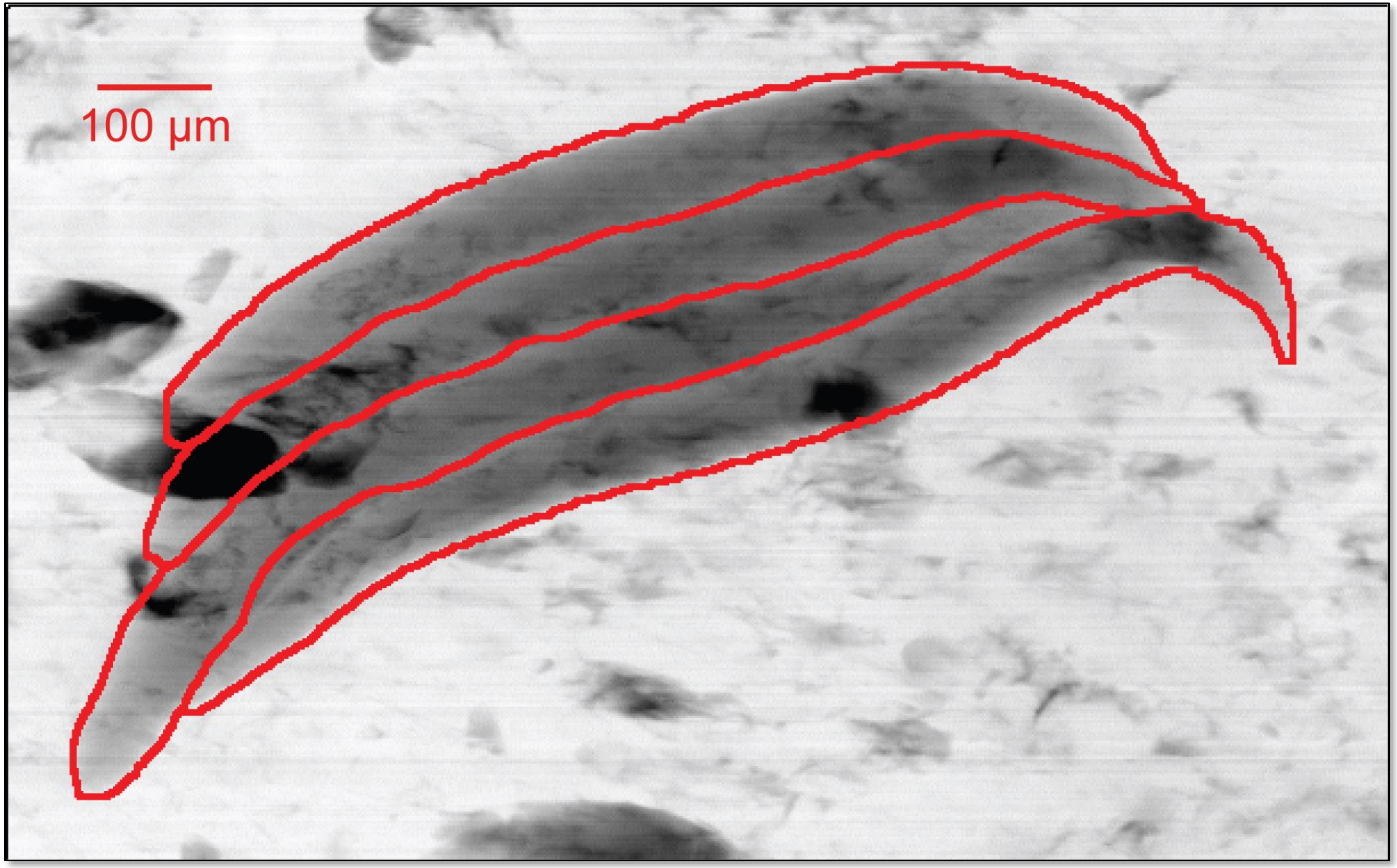


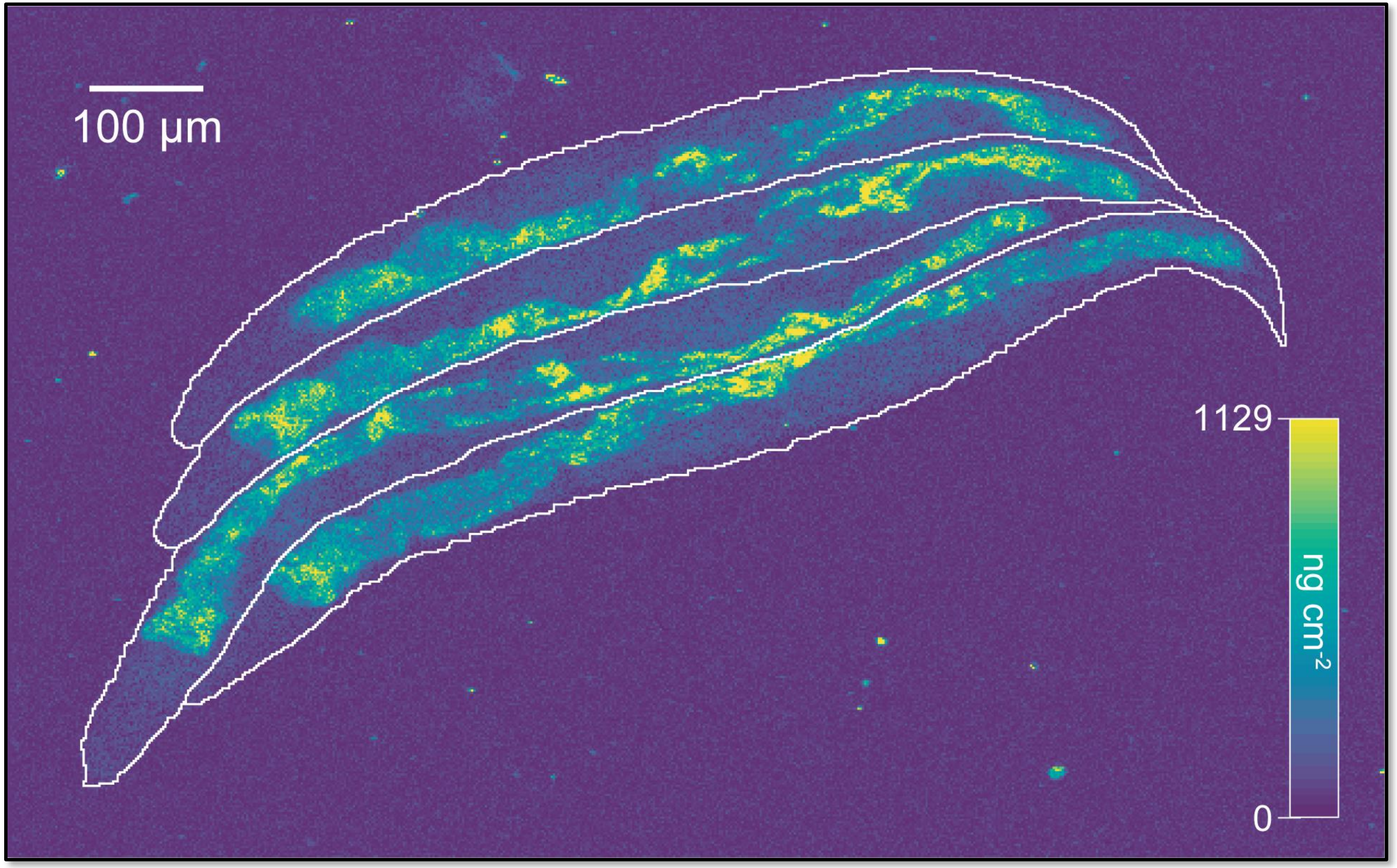
Scanning transmission map of x4 *C. elegans*. Frozen in place, on a pad of agar.

4. Studying Bioiron using X-rays | Cryogenic μXAS



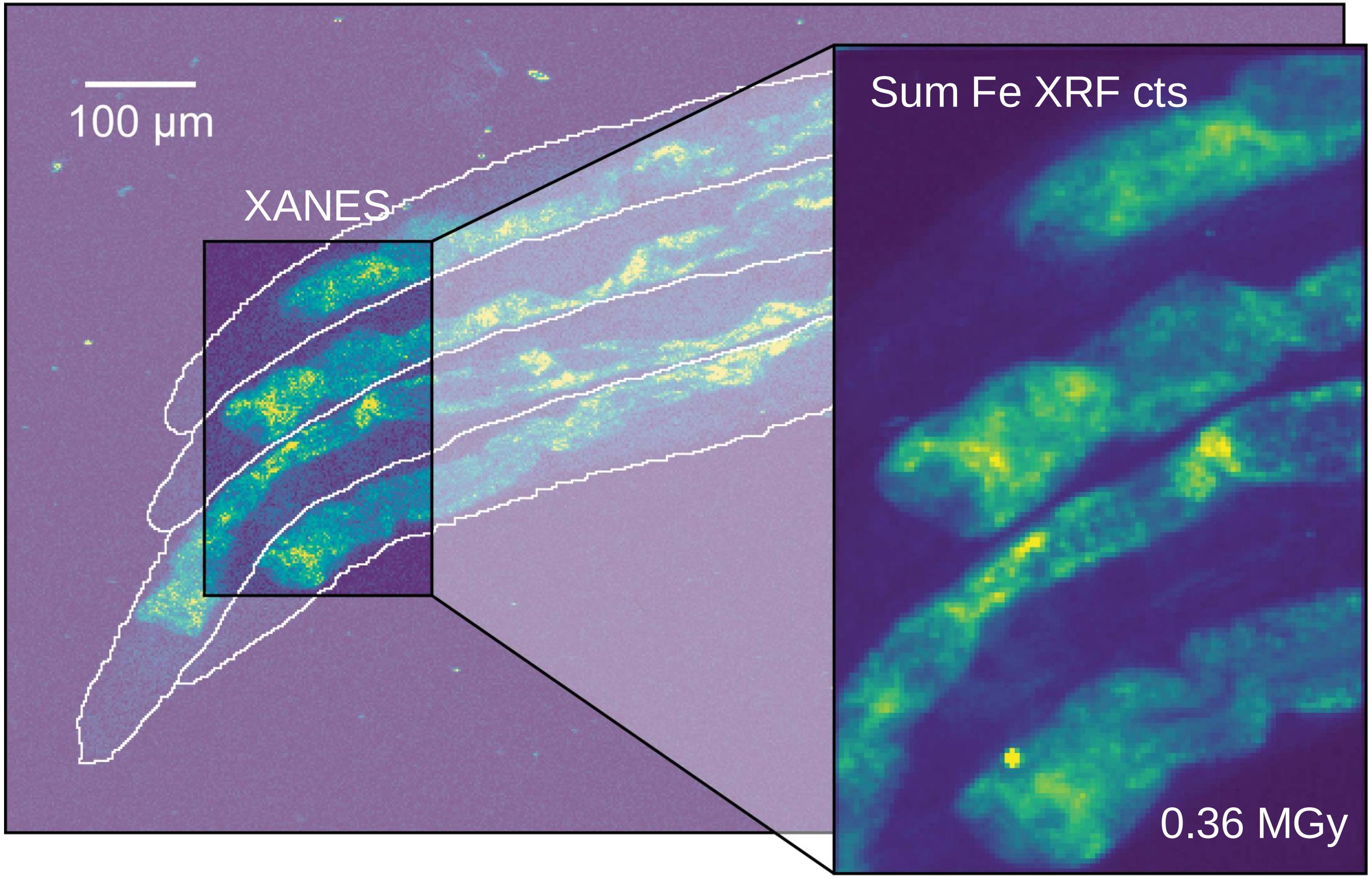
Scanning transmission map of x4 *C. elegans*. Frozen in place, on a pad of agar.

4. Studying Bioiron using X-rays | Cryogenic µXAS



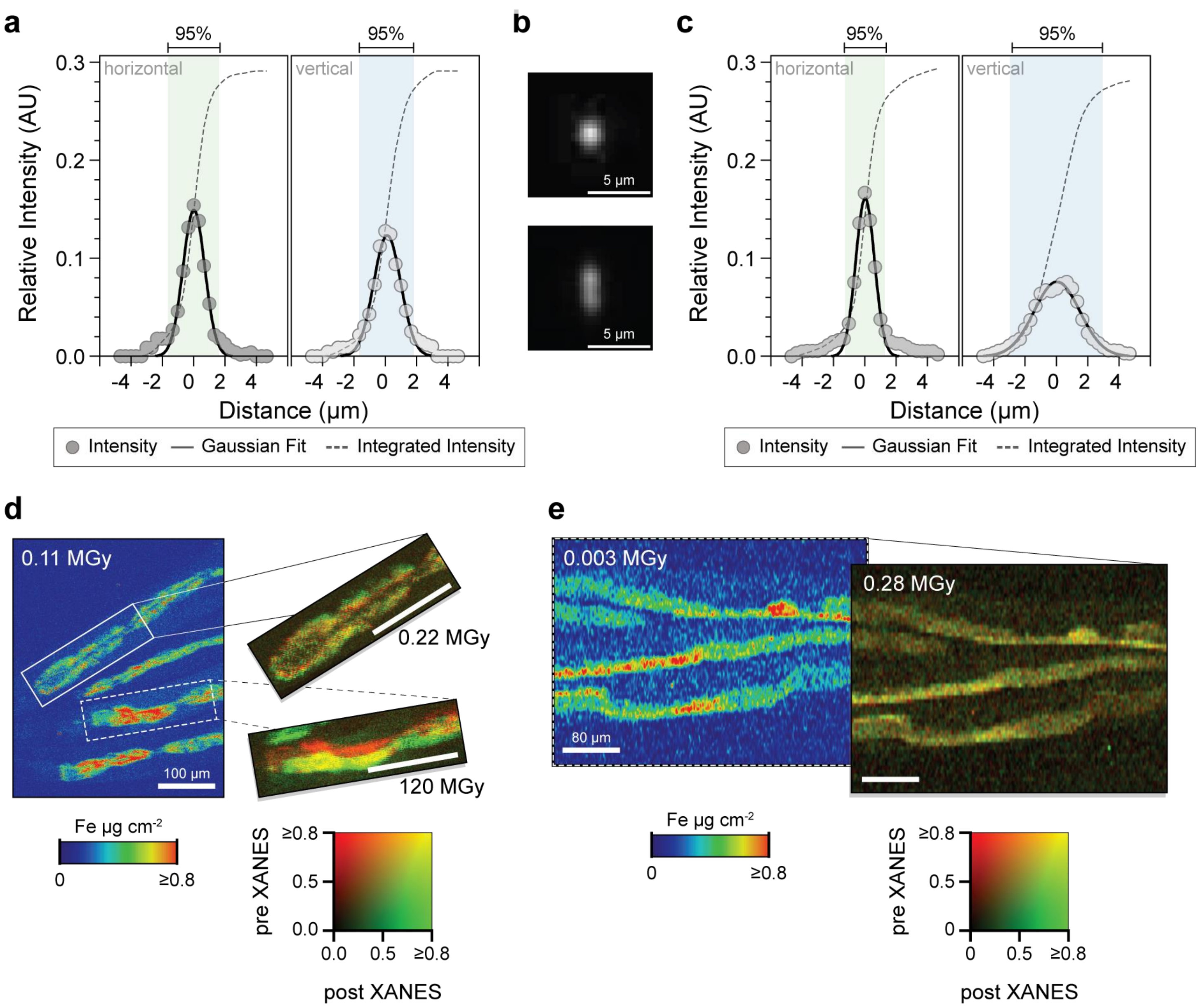
Scanning Fe XRF map of x4 *C. elegans*. Frozen in place, on a pad of agar.

4. Studying Bioiron using X-rays | Cryogenic µXAS

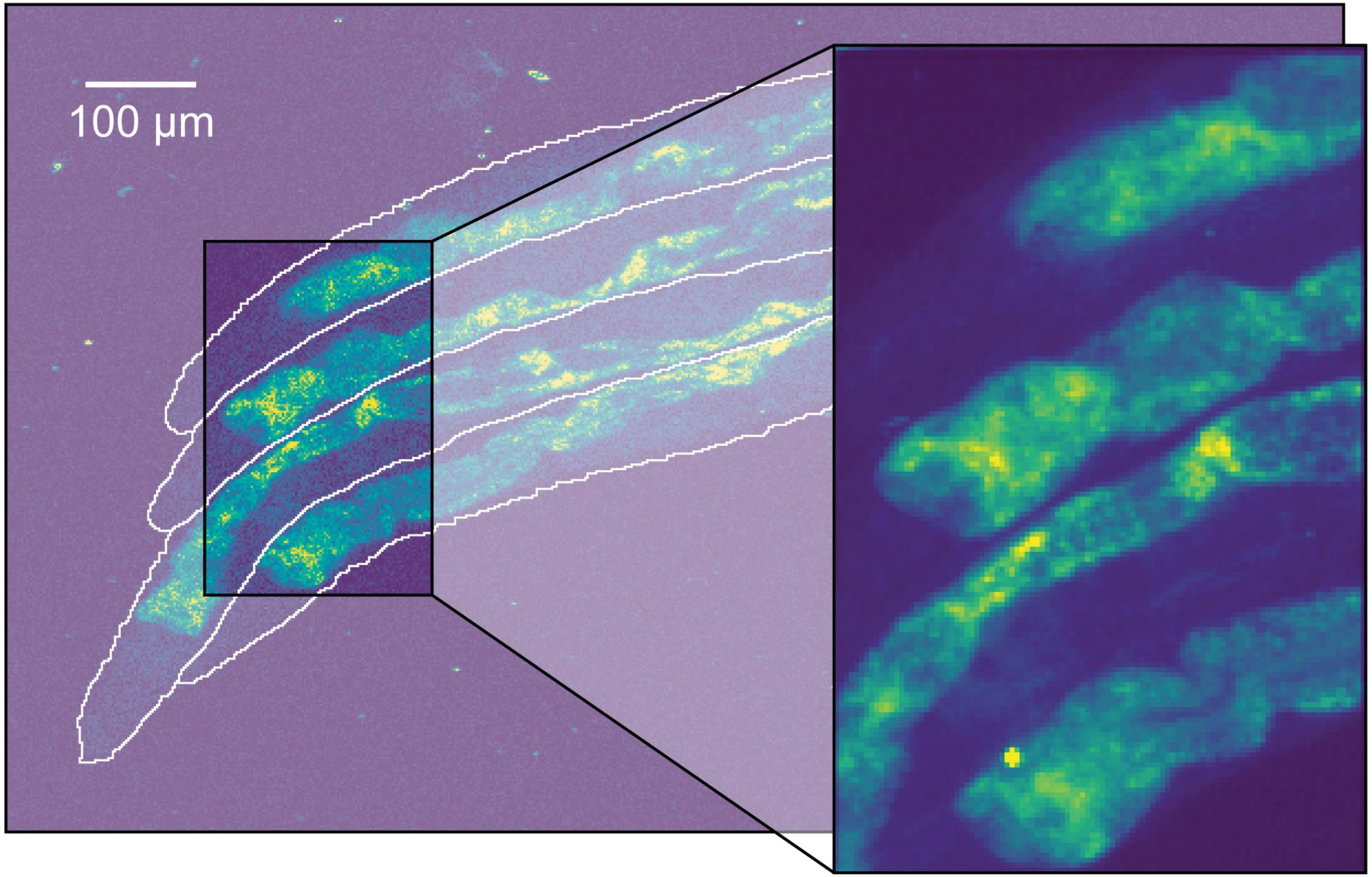


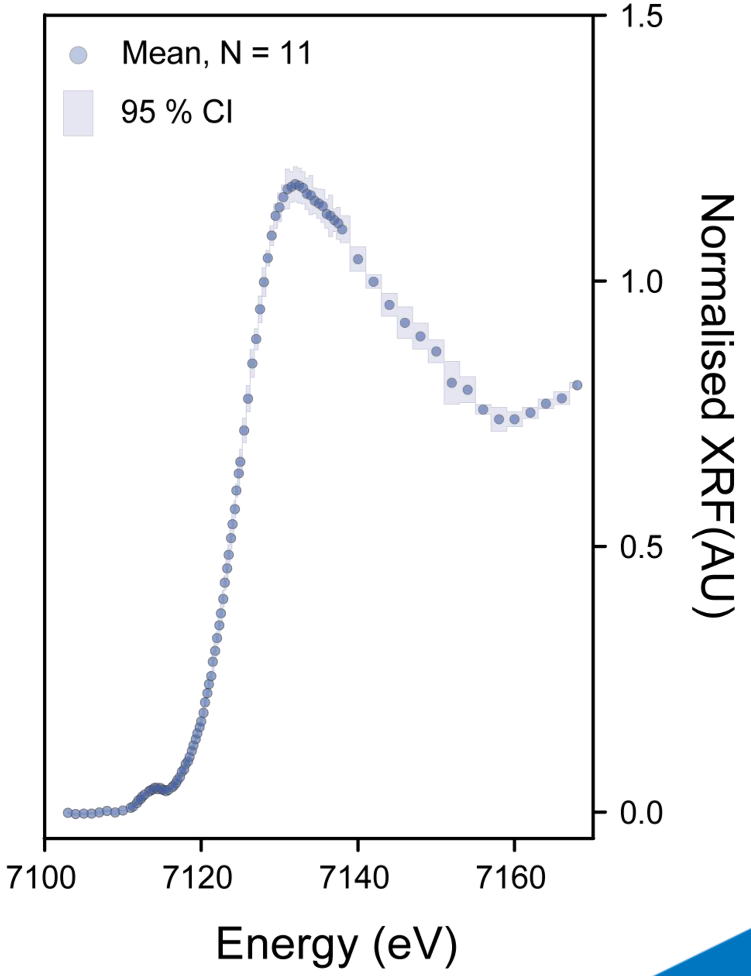
Scanning Fe XRF map of x4 *C. elegans*, x120 incident energies

4. Studying Bioiron using X-rays | Cryogenic µXAS

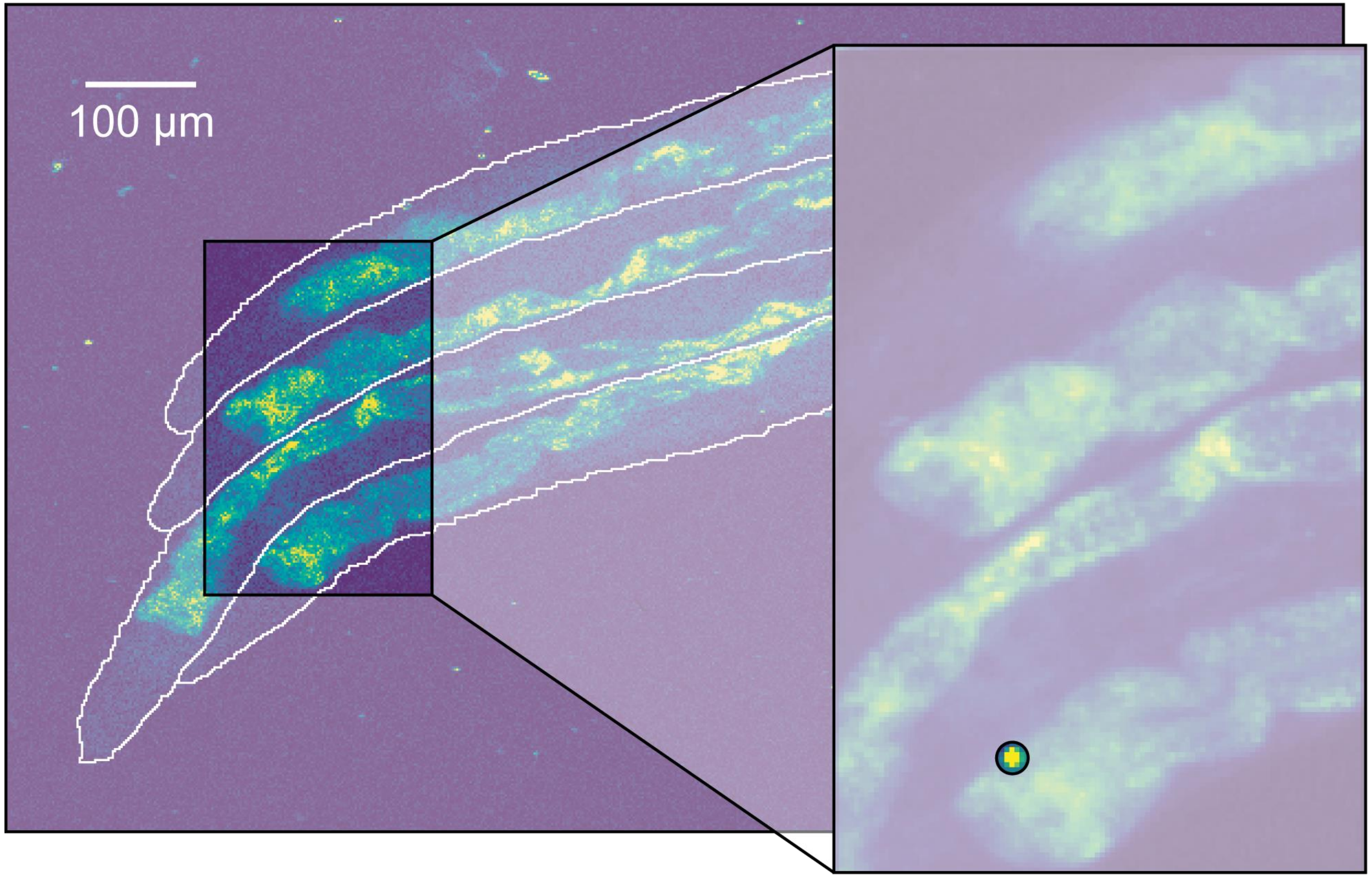


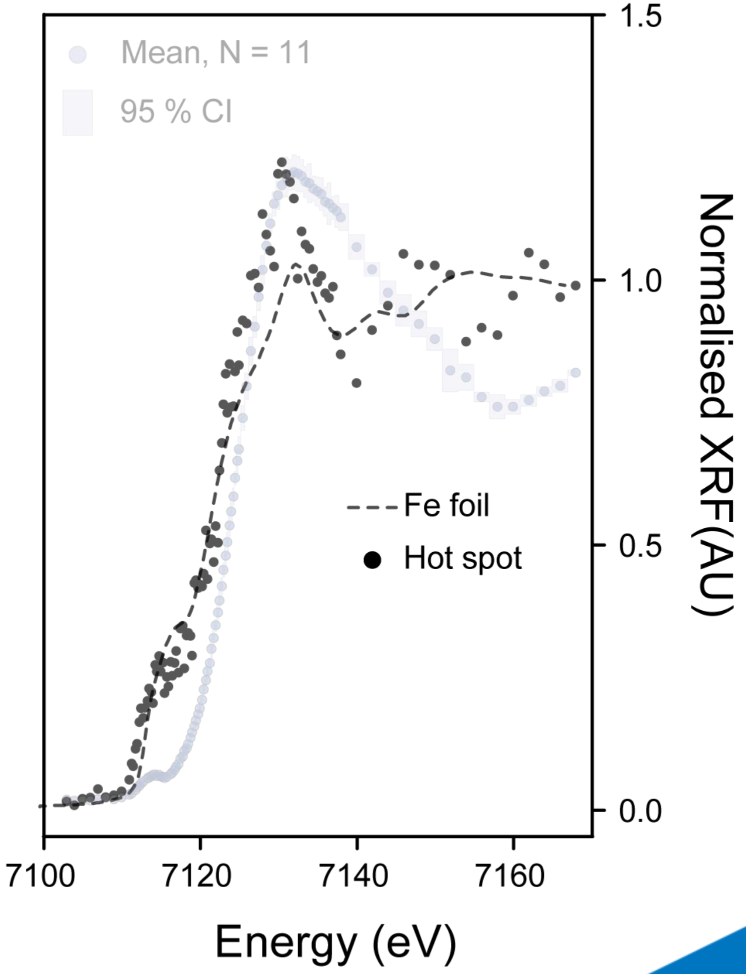
4. Studying Bioiron using X-rays | Cryogenic μXAS



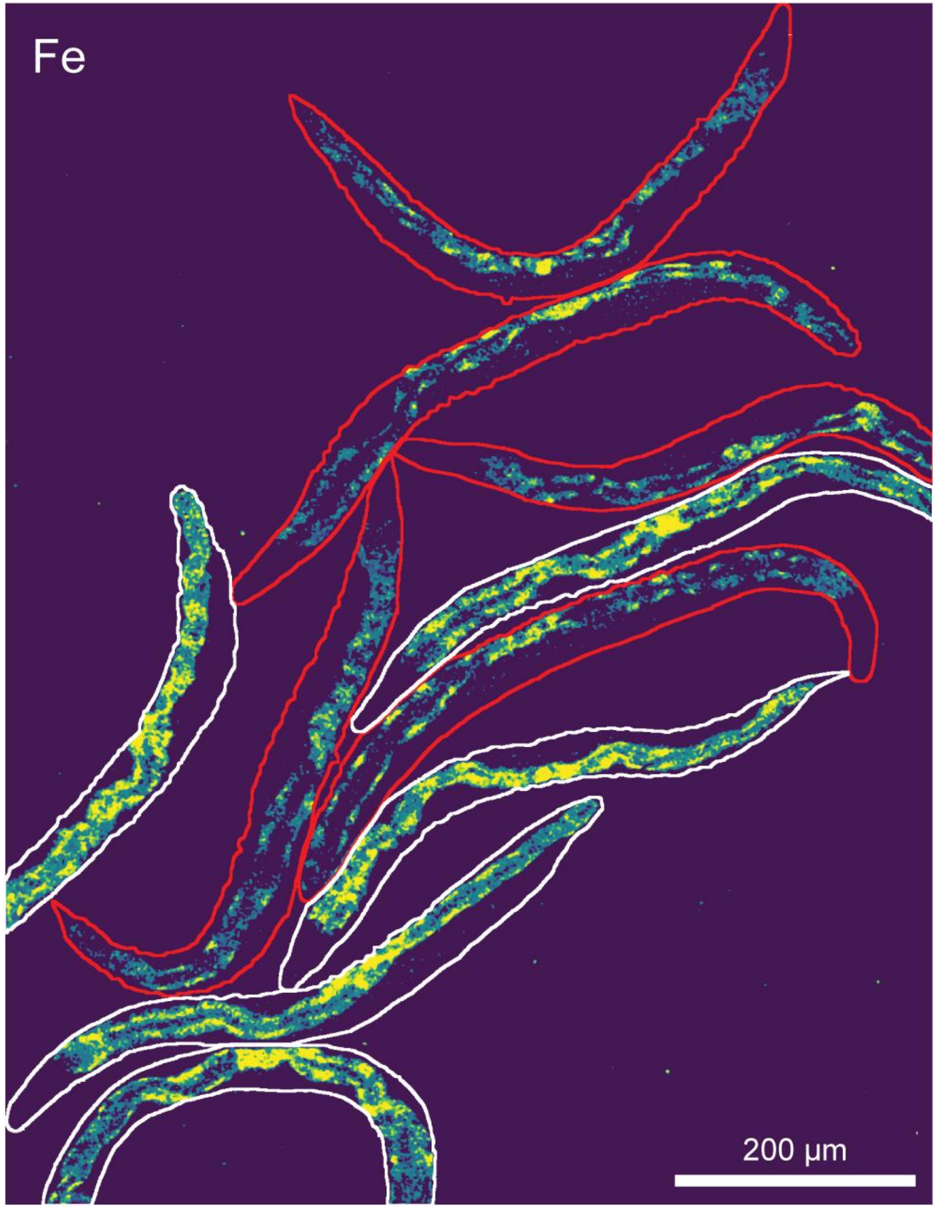


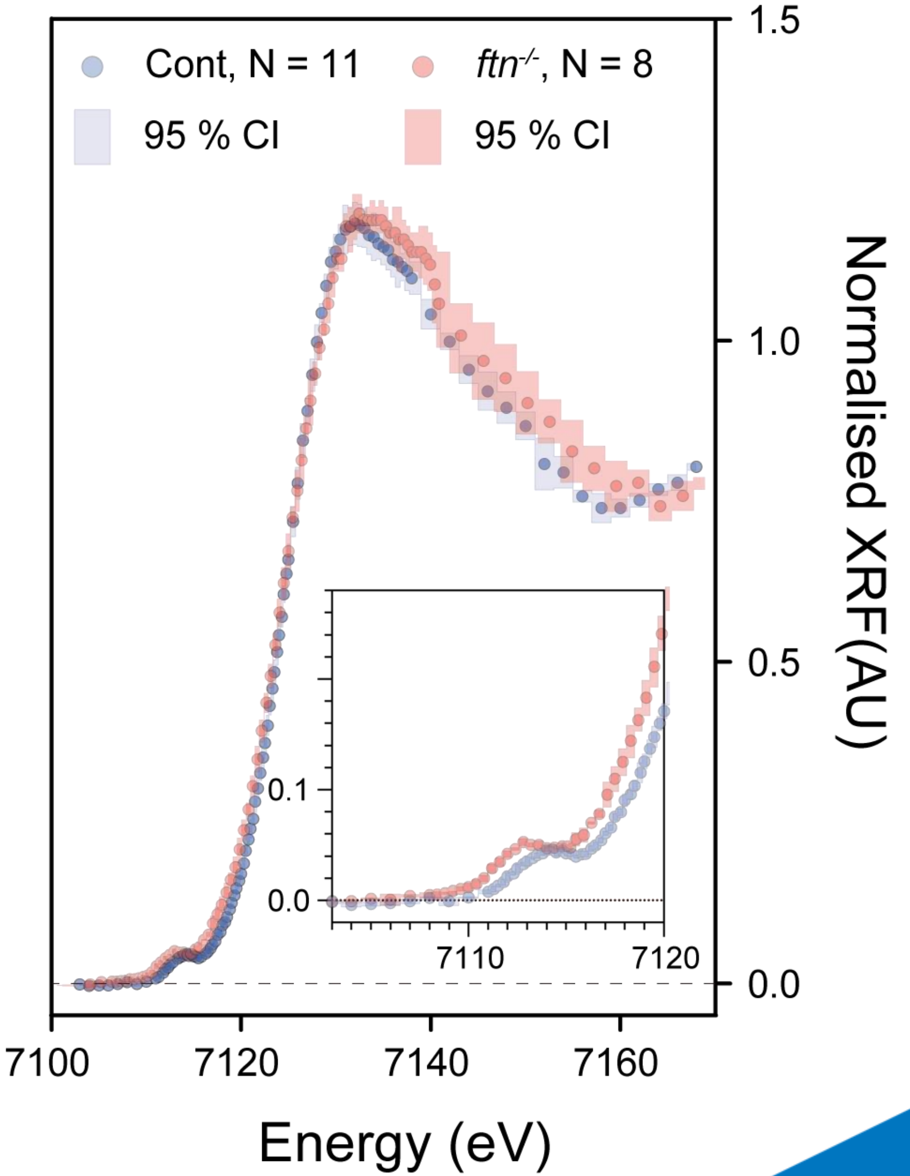
4. Studying Bioiron using X-rays | Iron is Everywhere...





4. Studying Bioiron using X-rays | Changes in Fe^{2+}/Fe^{3+}





4. Studying Bioiron using X-rays | Changes in Fe^{2+}/Fe^{3+}

Loss of *ftn-1* and *ftn-2*;

- Decreased iron load
- Increases the amount of;
  - i. Labile iron
  - ii. Ferrous iron
- Sets up the animal for reperfusion injury

Loss of *pink-1*;

- Has marked impact on iron metabolism but less clear what's happening…