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Applications of Powder Diffraction

Helen Brand

VICTORIA State Government

Australian Synchrotron

Advantages of synchrotron powder diffraction

High intensity

Small samples (powder or single crystal)

High speed (fast *in situ* processes, unstable compounds…)

High signal-to-noise → better data

→ weak features (impurities, satellite reflections, diffuse scattering)

High resolution → complex structures with big unit cells

→ fine peak splitting (phase transitions, decomposition)

→ peak shapes defined by sample properties (strain, particle size)

Tunable energy

Highlight elements of interest

Minimise absorption

High energy

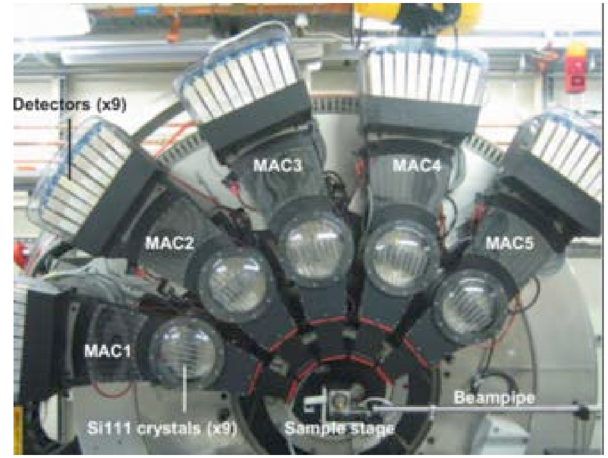
High Q → more accurate ADPs, potential for PDF analysis

Compressed patterns → can use restrictive sample environments (pressure, fields)

High penetration → minimise surface effects

Multi Analyser Crystal Detectors

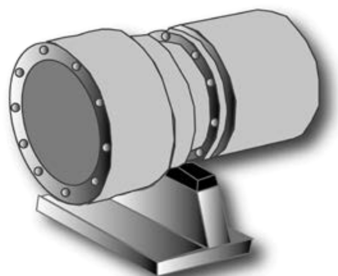
Extremely high resolution but slow



Strip detectors:

High resolution and fast but poor energy discrimination

e.g. Mythen



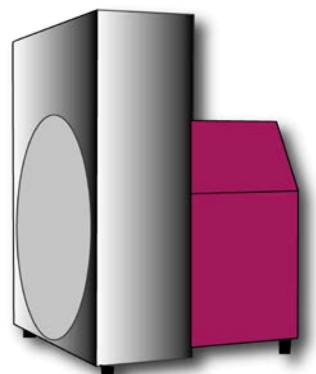
Area detectors:

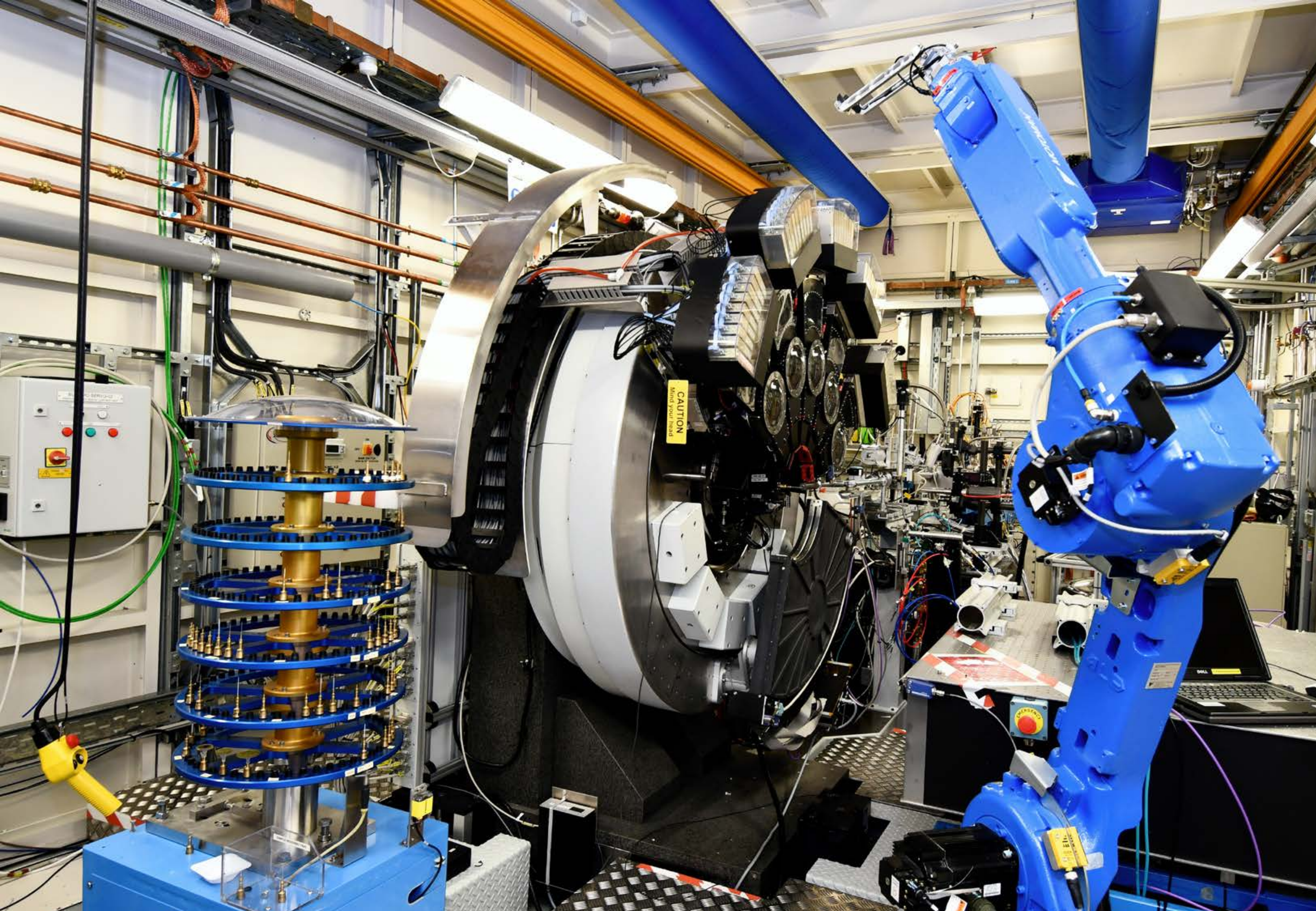
Lower resolution but provide texture information

e.g. Mar CCD

Mar 345 image plate

Eiger




CAUTION
Mind your head

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High Resolution

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2006: Jarosite minerals detected by the Mössbauer instrument on the *Opportunity* rover in Meridiani Planum.

Why is this significant?

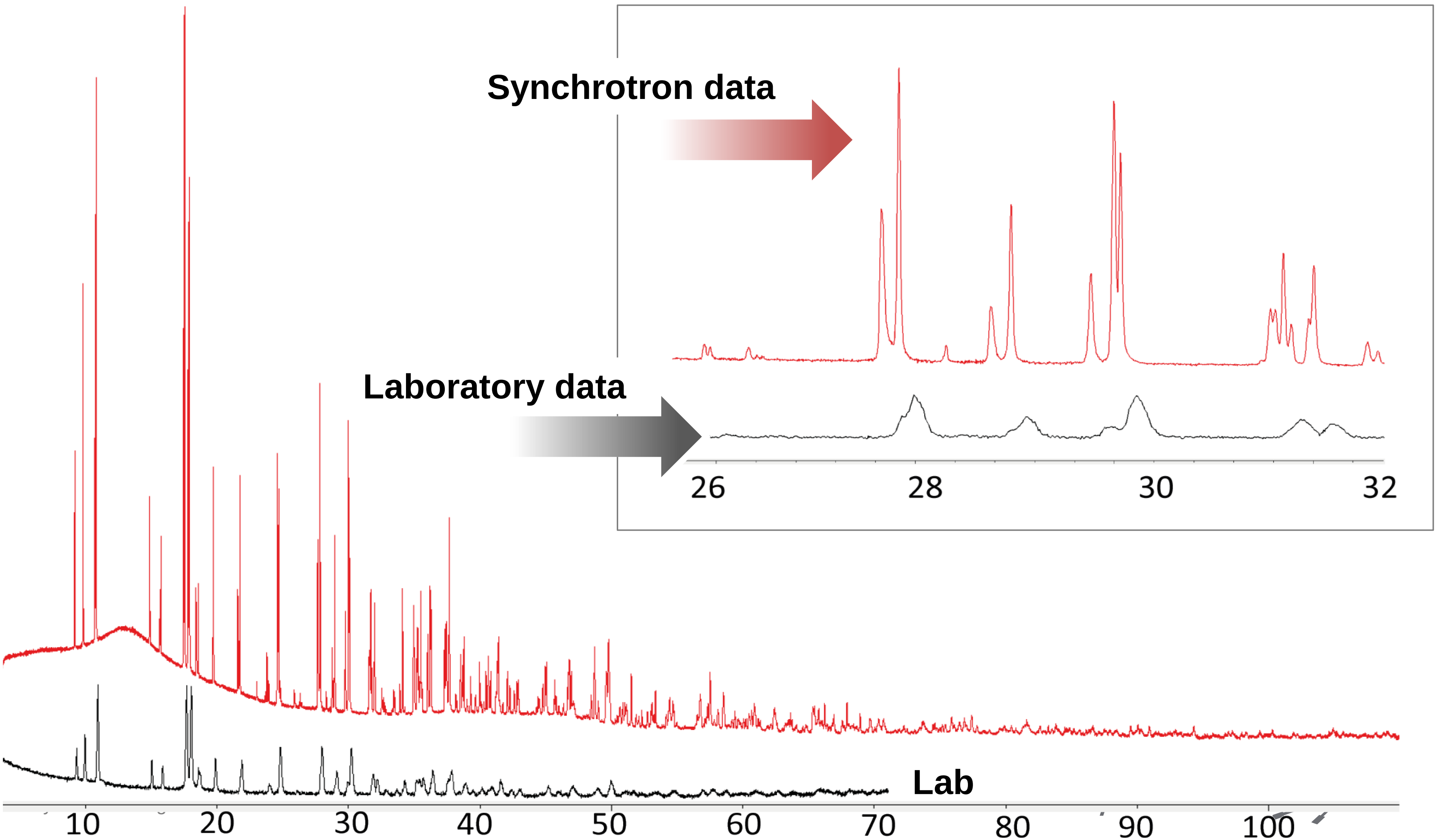
- Jarosite is the first hydrated mineral to be positively identified on the surface of Mars.
- Jarosites need a “wet” environment to form but an arid one to persist.
- Jarosite is crucial to understanding the role of water in the environmental evolution of Mars.

Bioheap leaching

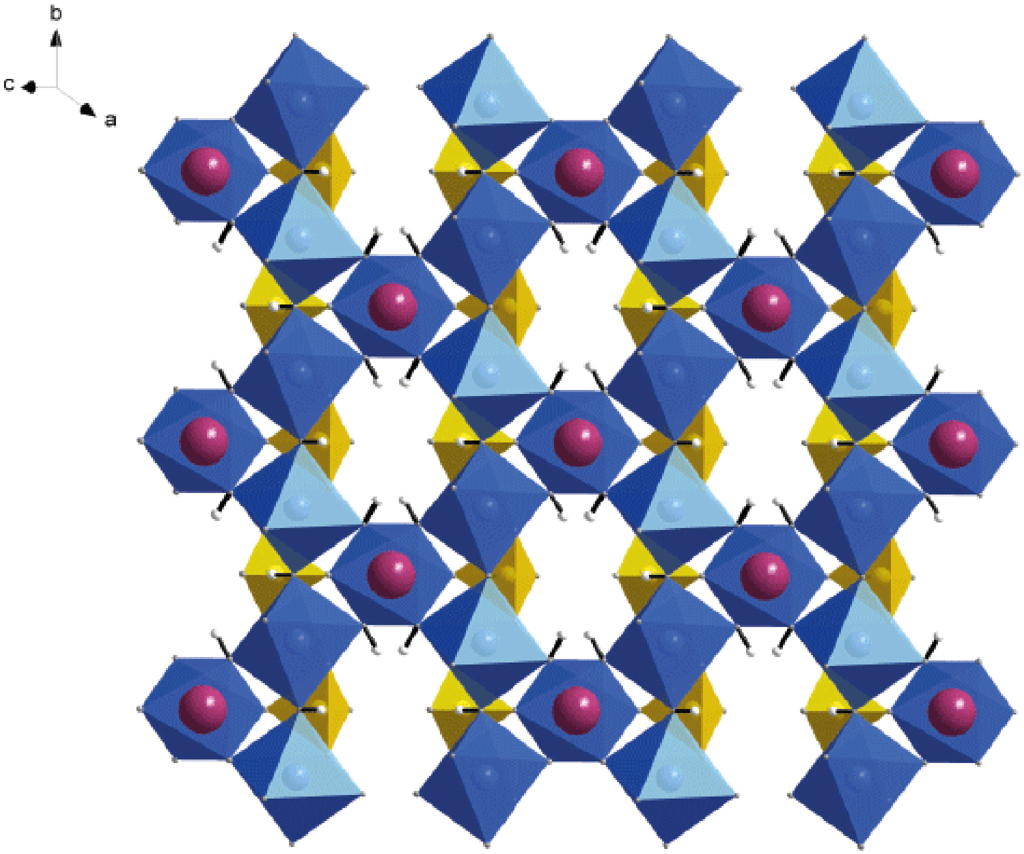
Jarosite forms a kinetic barrier to the desired reaction.

Zinc Smelting

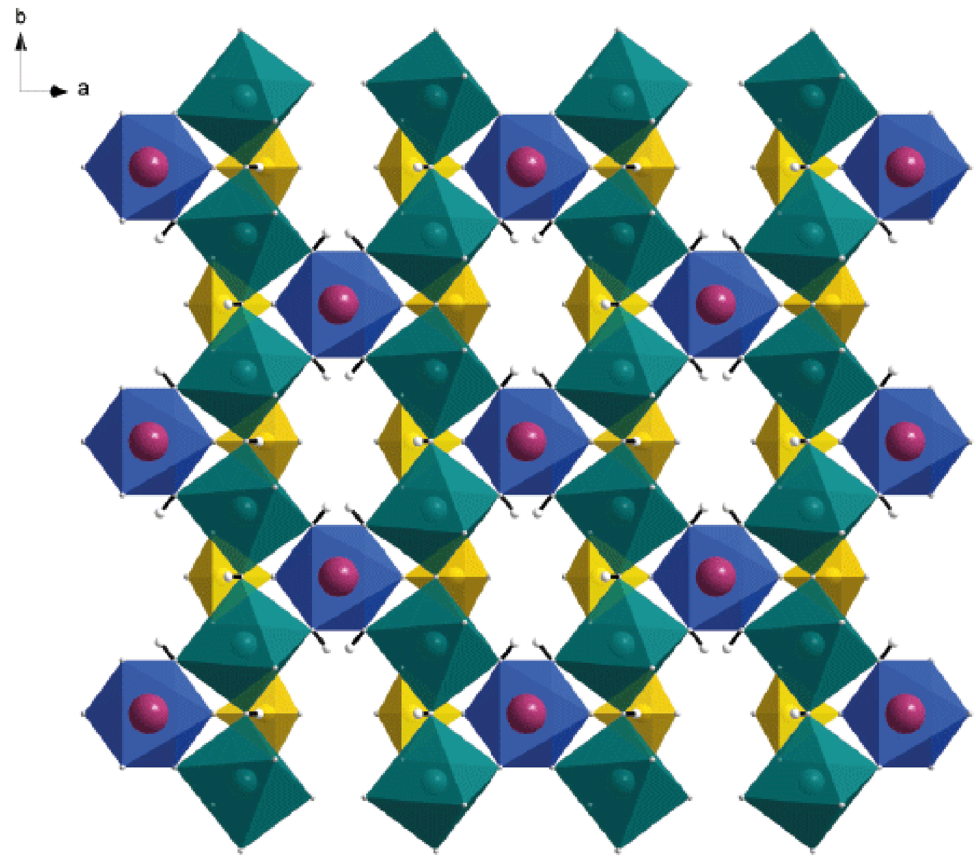
Jarosite formation is a way of removing Iron impurities from solution.


Synchrotron data
Laboratory data
26
28
30
32
Lab
10
20
30
40
50
60
70
80
90
100

A. Rhombohedral Jarosite

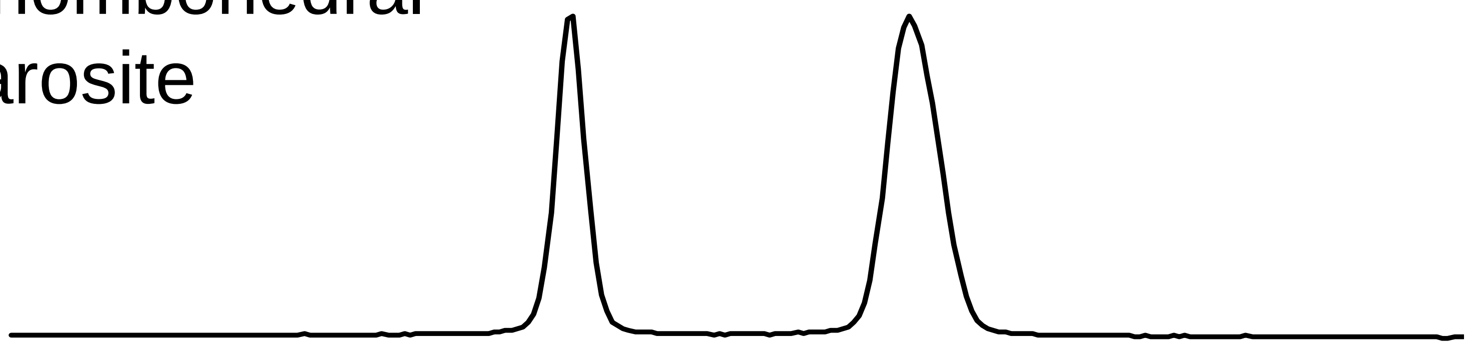


B. Monoclinic Jarosite

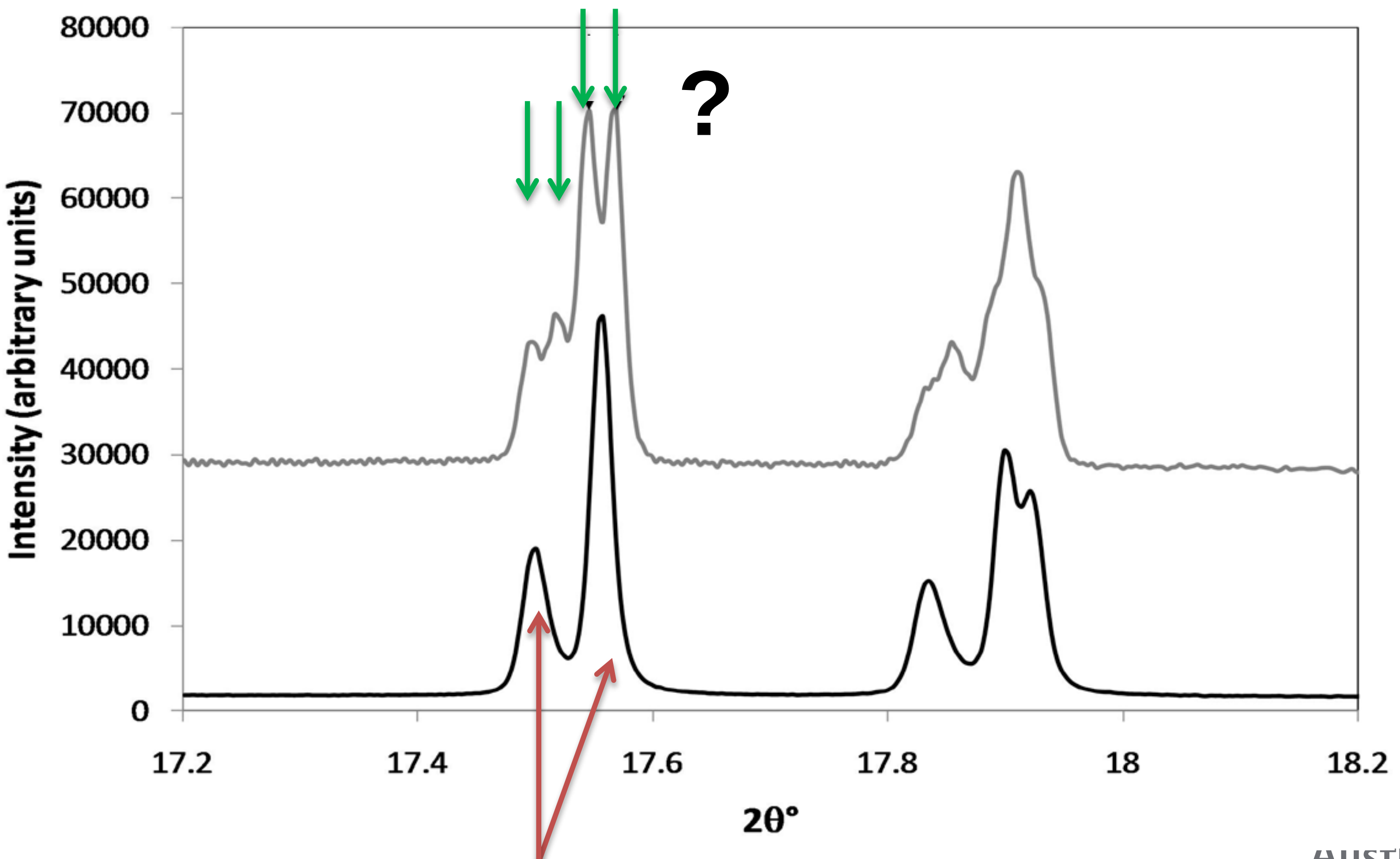


This is what we initially expected…

Rhombohedral
Jarosite



This is what we got…



Monoclinic Jarosite

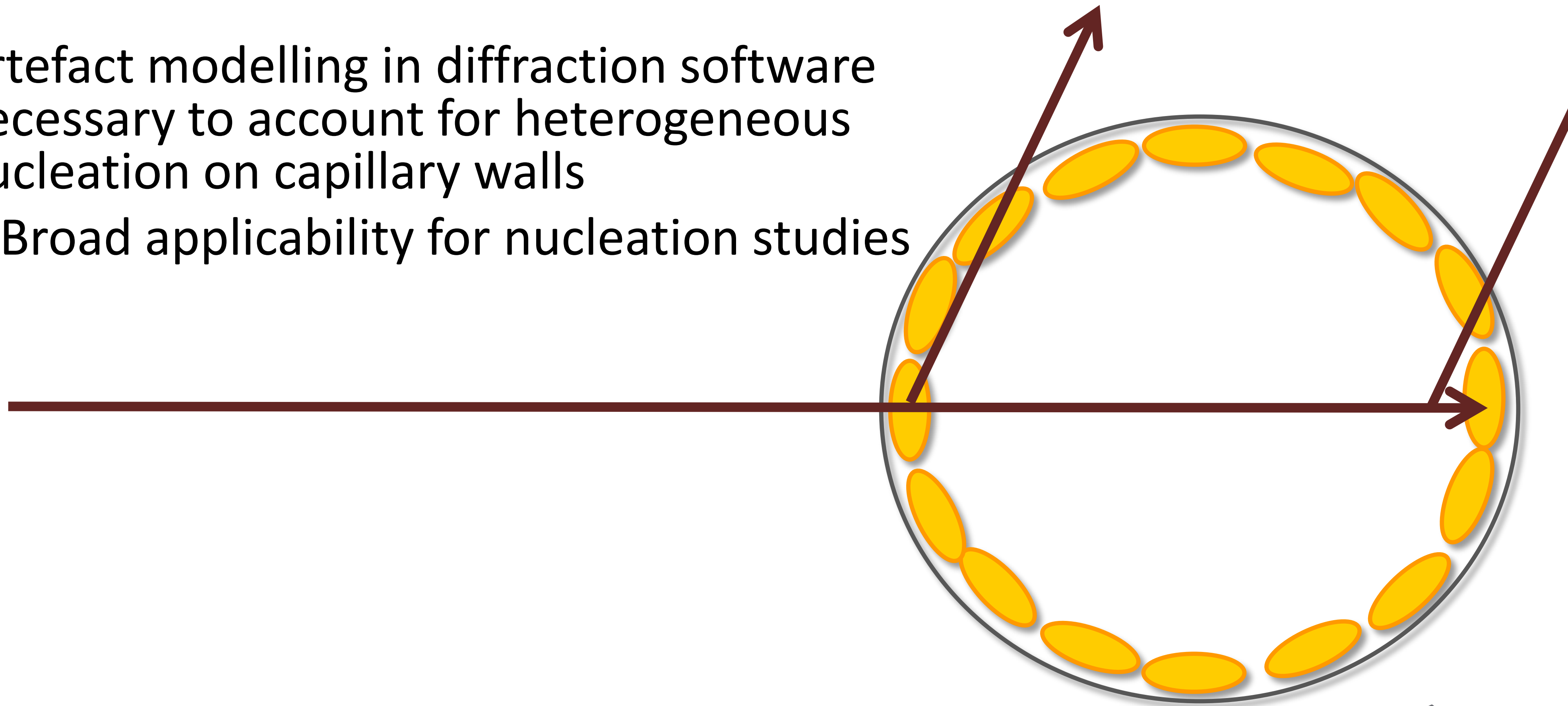
Too much resolution?

Caused by crystallisation on capillary walls

- Effectively two displaced samples

Artefact modelling in diffraction software necessary to account for heterogeneous nucleation on capillary walls

- Broad applicability for nucleation studies



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Energy Selection

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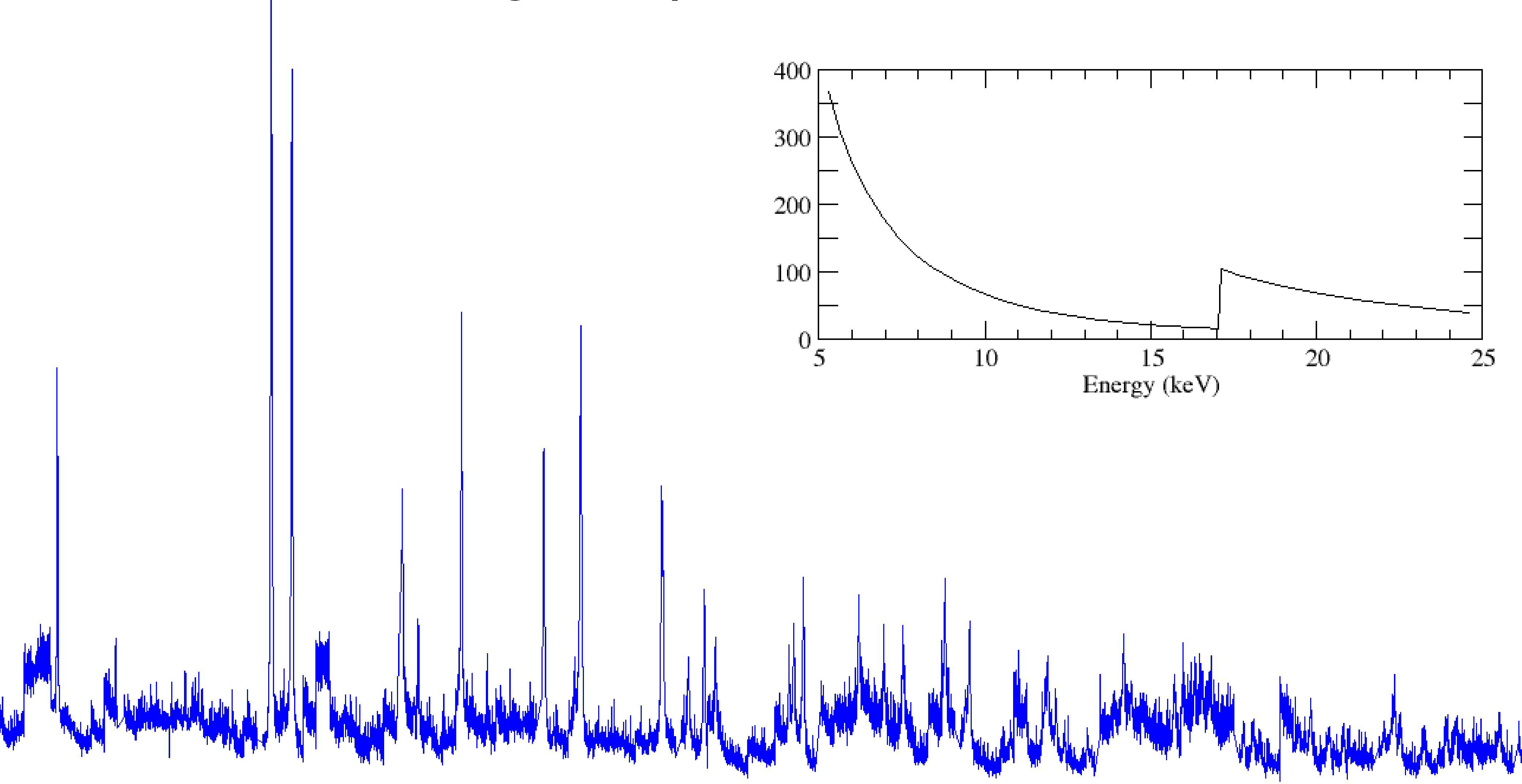
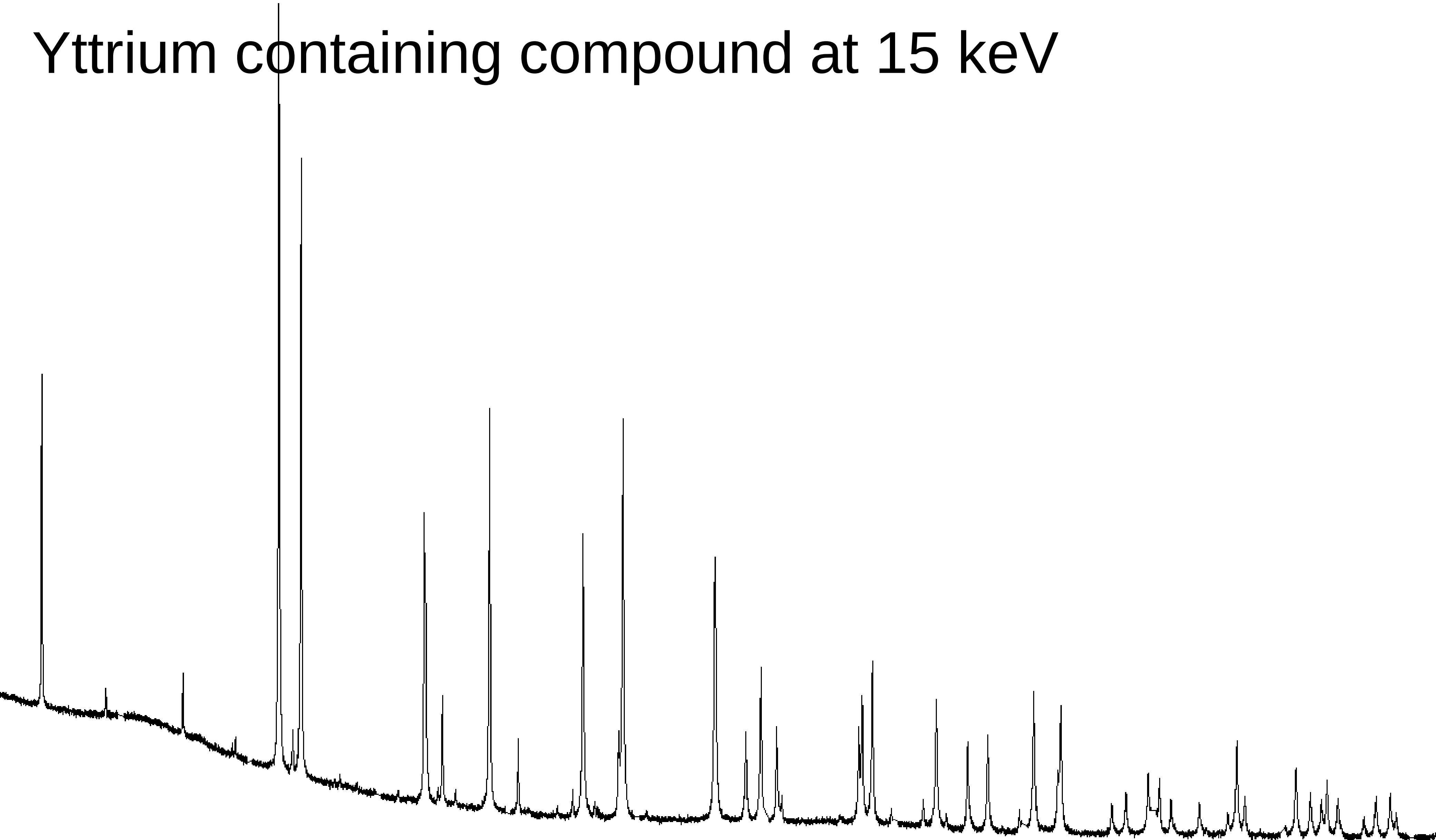
Yttrium containing compound at 18 keV



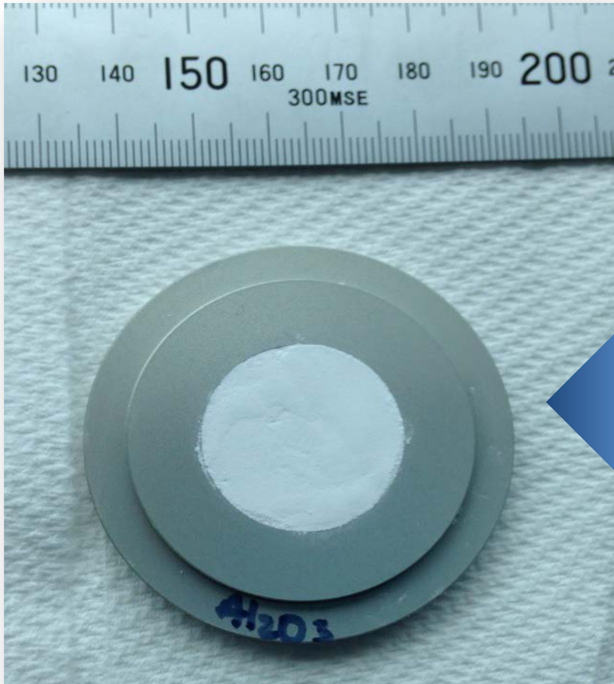
Yttrium containing compound at 15 keV



Signal to noise

(We like tiny samples)

Tiny samples



Lab Sample

- Large amount of material required
- Sample loading can produce texture effects

Synchrotron Sample

Tiny samples

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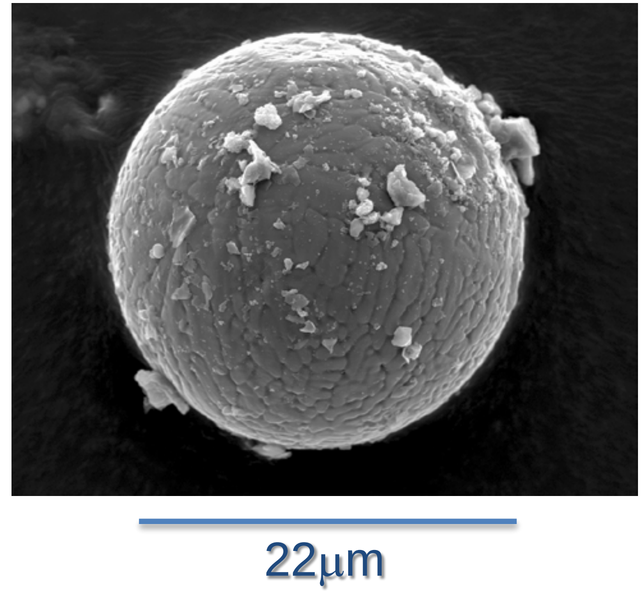
LETTER

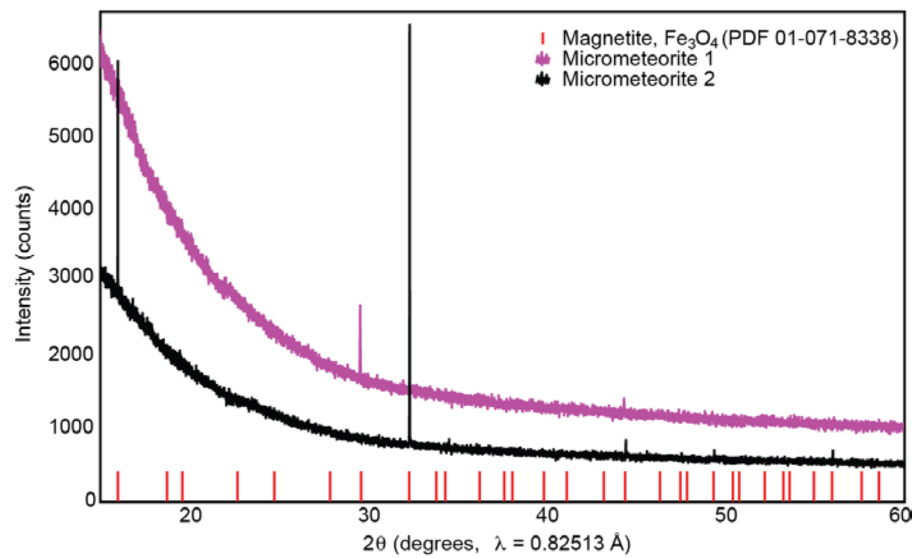
doi:10.1038/nature17678

Ancient micrometeorites suggestive of an oxygen-rich Archaean upper atmosphere

Andrew G. Tomkins[1], Lara Bowlt[1], Matthew Genge[2,3], Siobhan A. Wilson[1], Helen E. A. Brand[4] & Jeremy L. Wykes[1,4,5]

[redacted]





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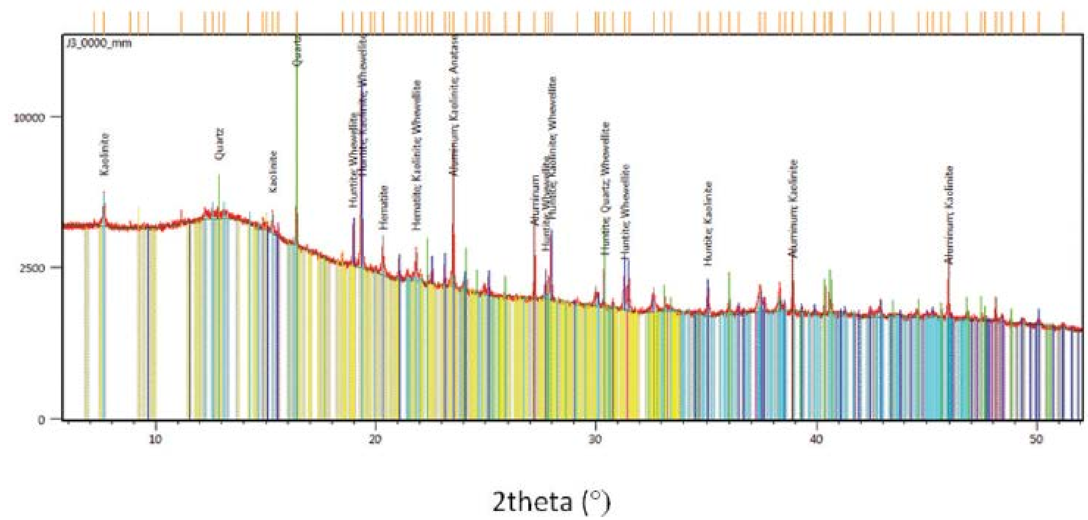
The first Australian Synchrotron powder diffraction analysis of pigment from a Wandjina motif in the Kimberley, Western Australia

Jillian Huntley[1], Helen Brand[2], Maxime Aubert[3] and Michael J. Morwood[3]



Infinite building blocks

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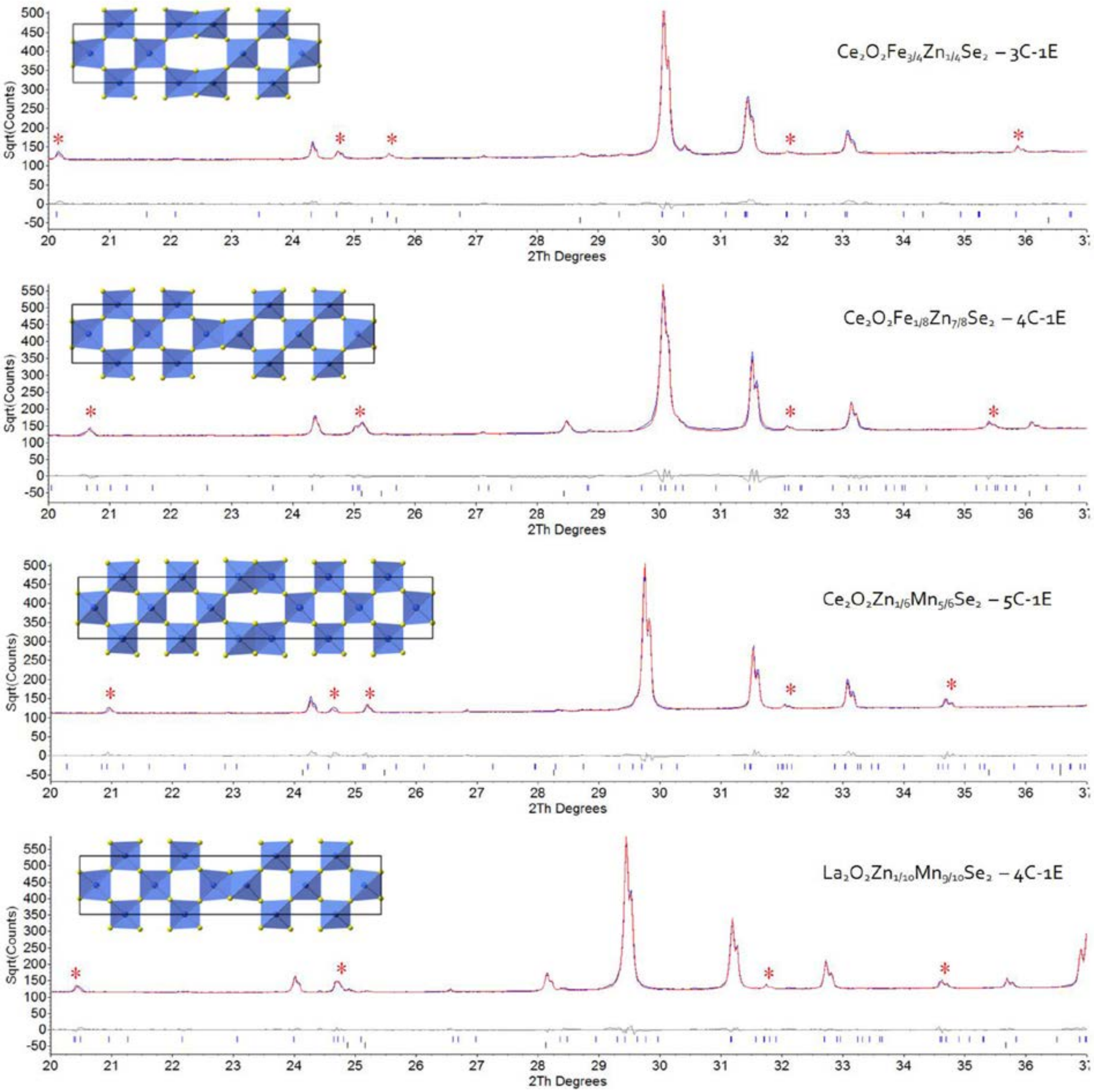
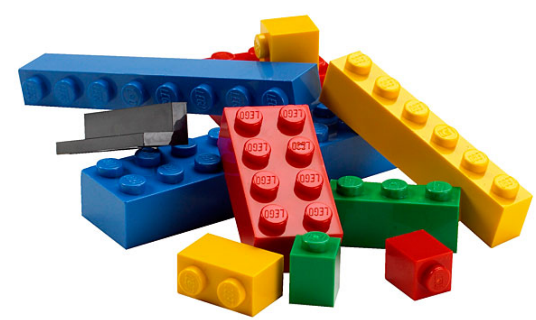


Designing thermoelectric Materials.

Small changes in chemistry can have big changes in physical properties.

These small structural changes can only be mapped with the highest signal to noise.



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Throughput

synchrotron.org.au

Victoria State Government

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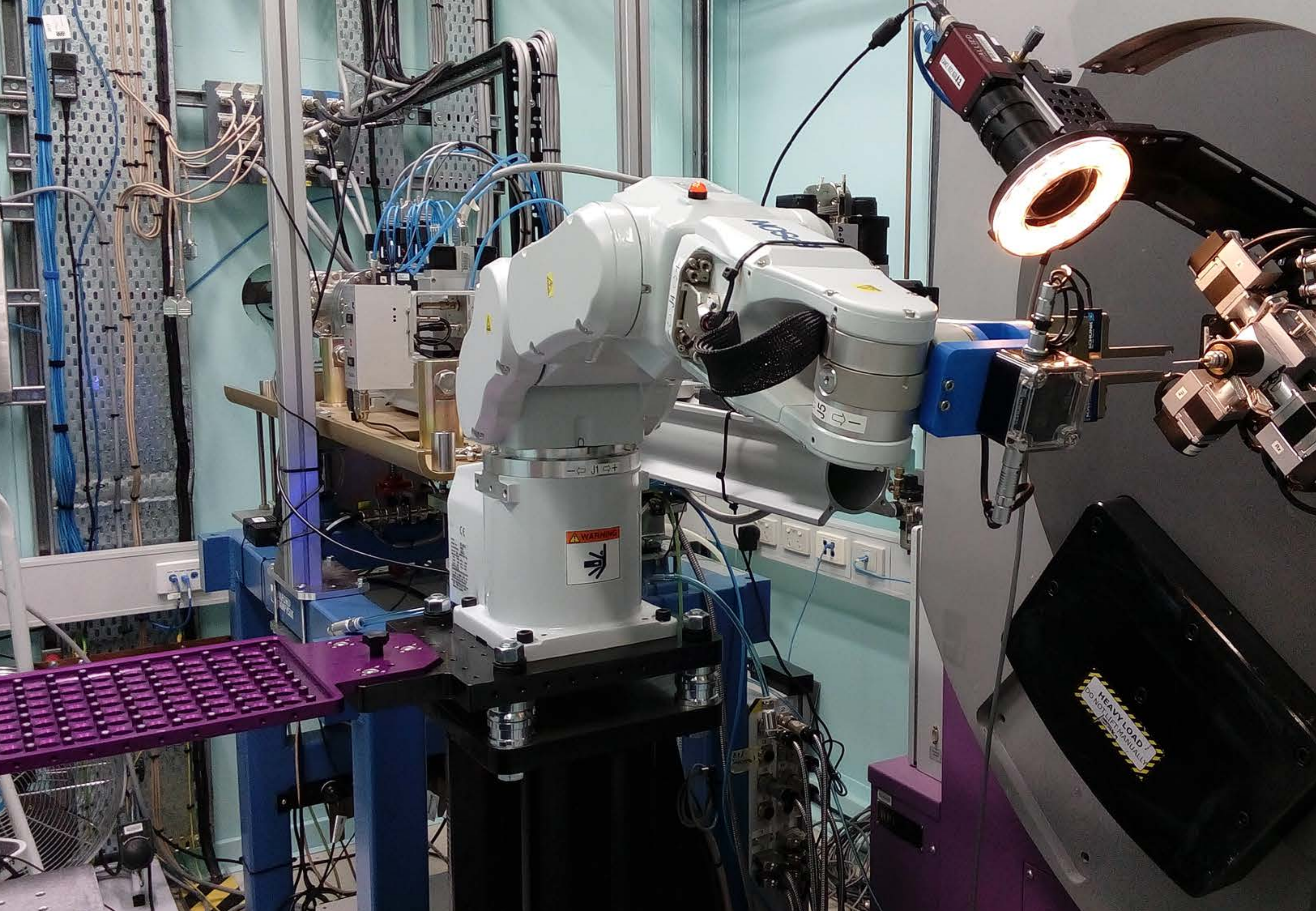
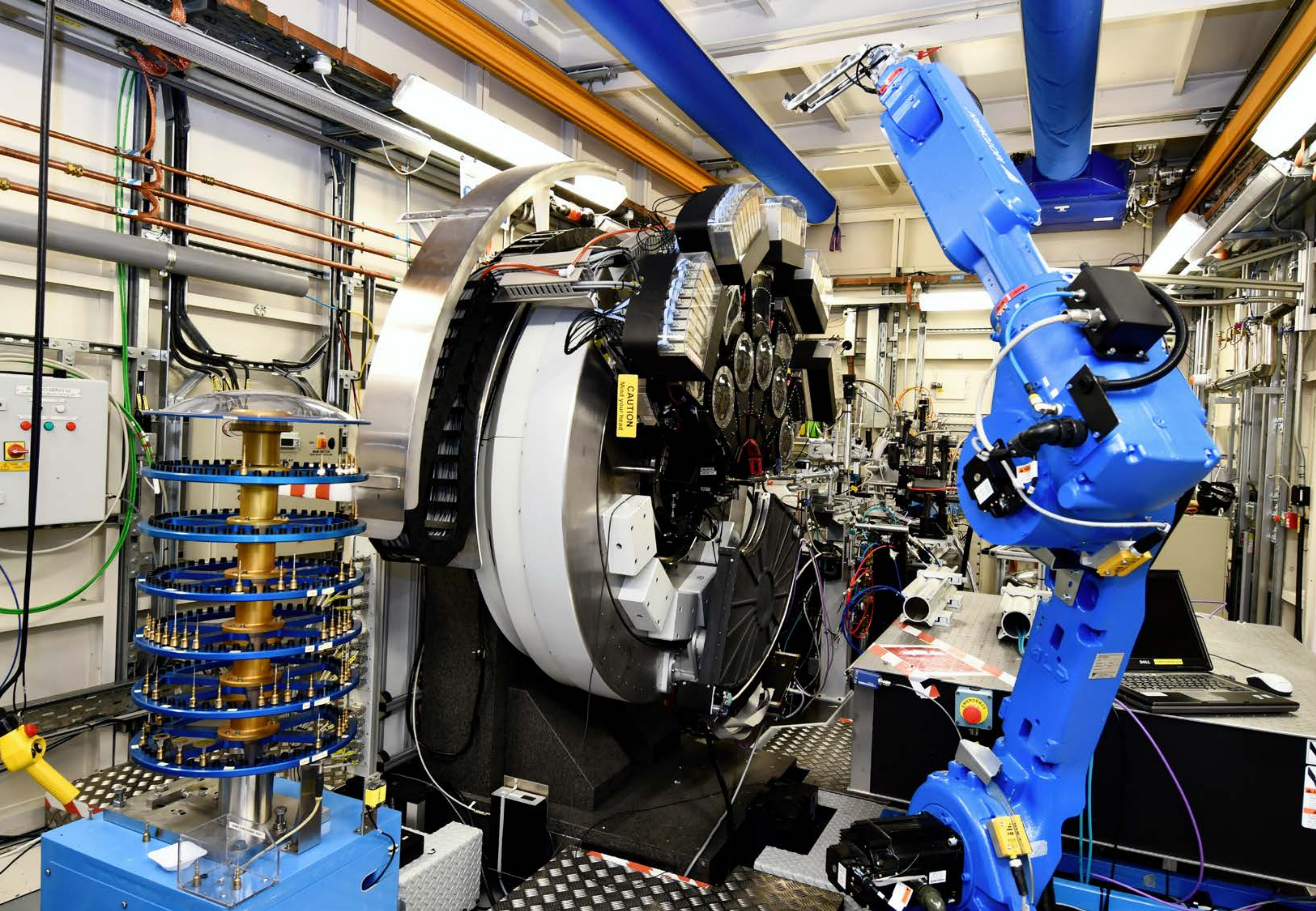
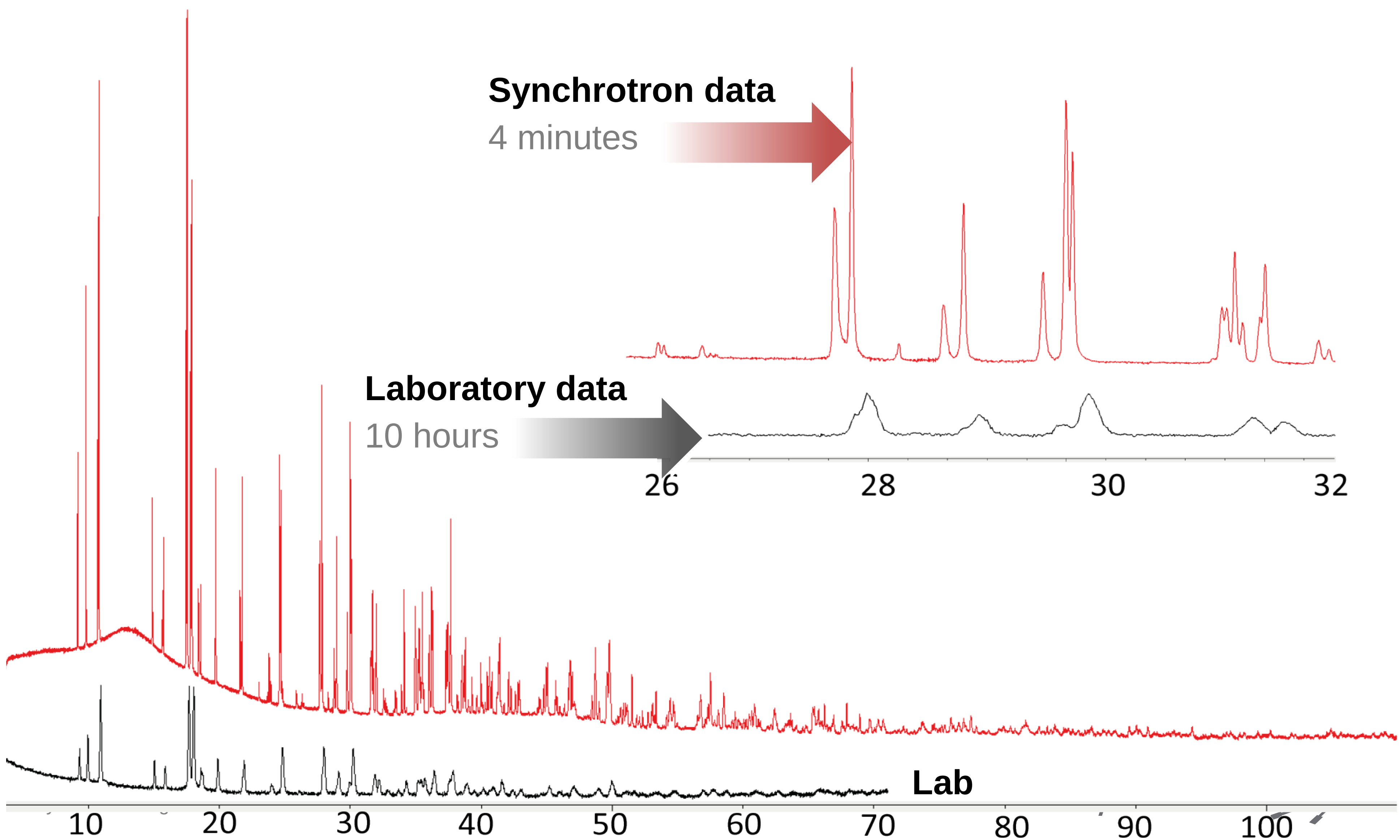

WARNING
J1
J5
HEAVY LOAD
DO NOT LIFT MANUALLY


CAUTION
Mind your head

Speed


Synchrotron data
4 minutes
Laboratory data
10 hours
26
28
30
32
Lab
10
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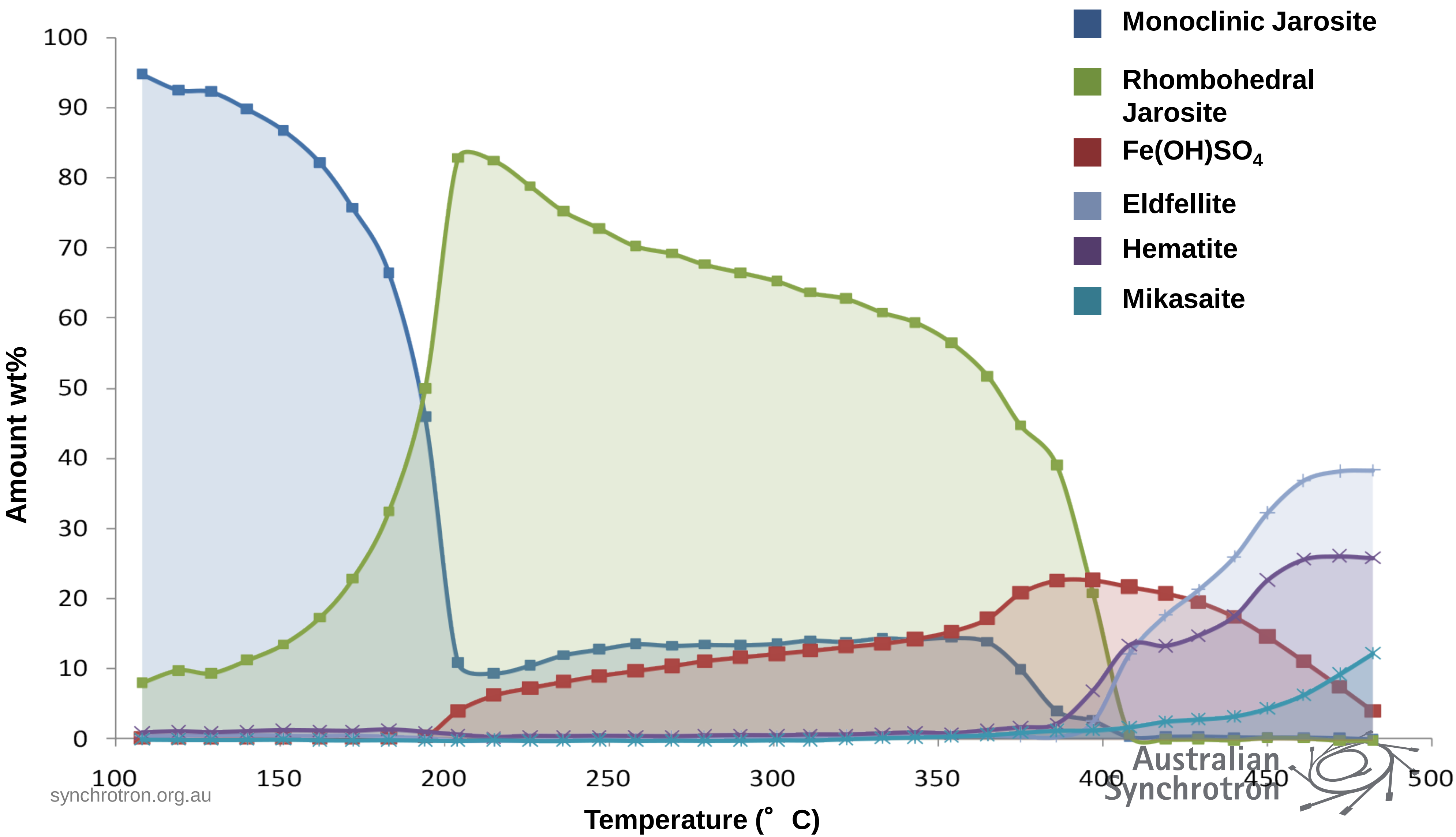
90
100

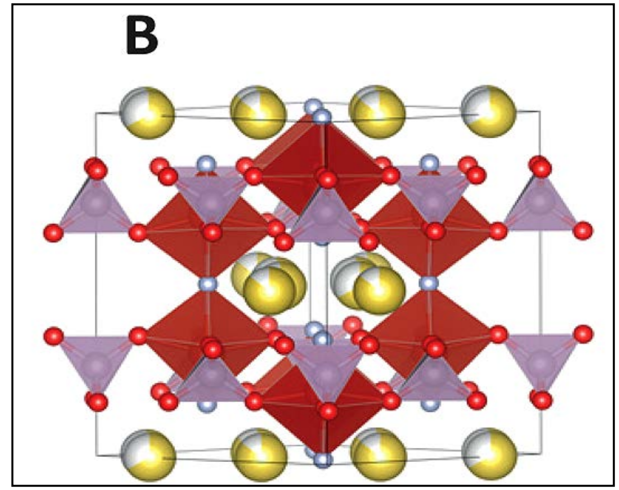
In situ studies: phase evolution



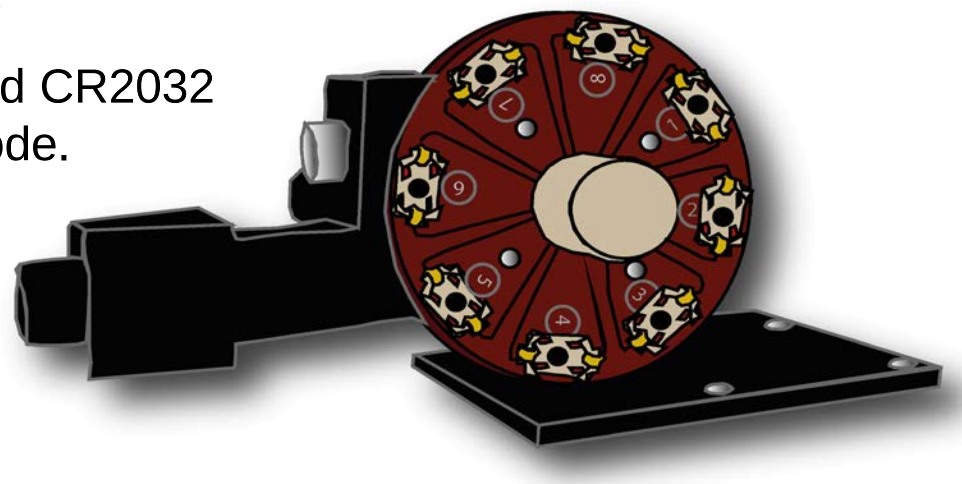
Sodium Distribution and Reaction Mechanisms of a $Na_3V_2O_2(PO_4)_2F$ Electrode during Use in a Sodium-Ion Battery

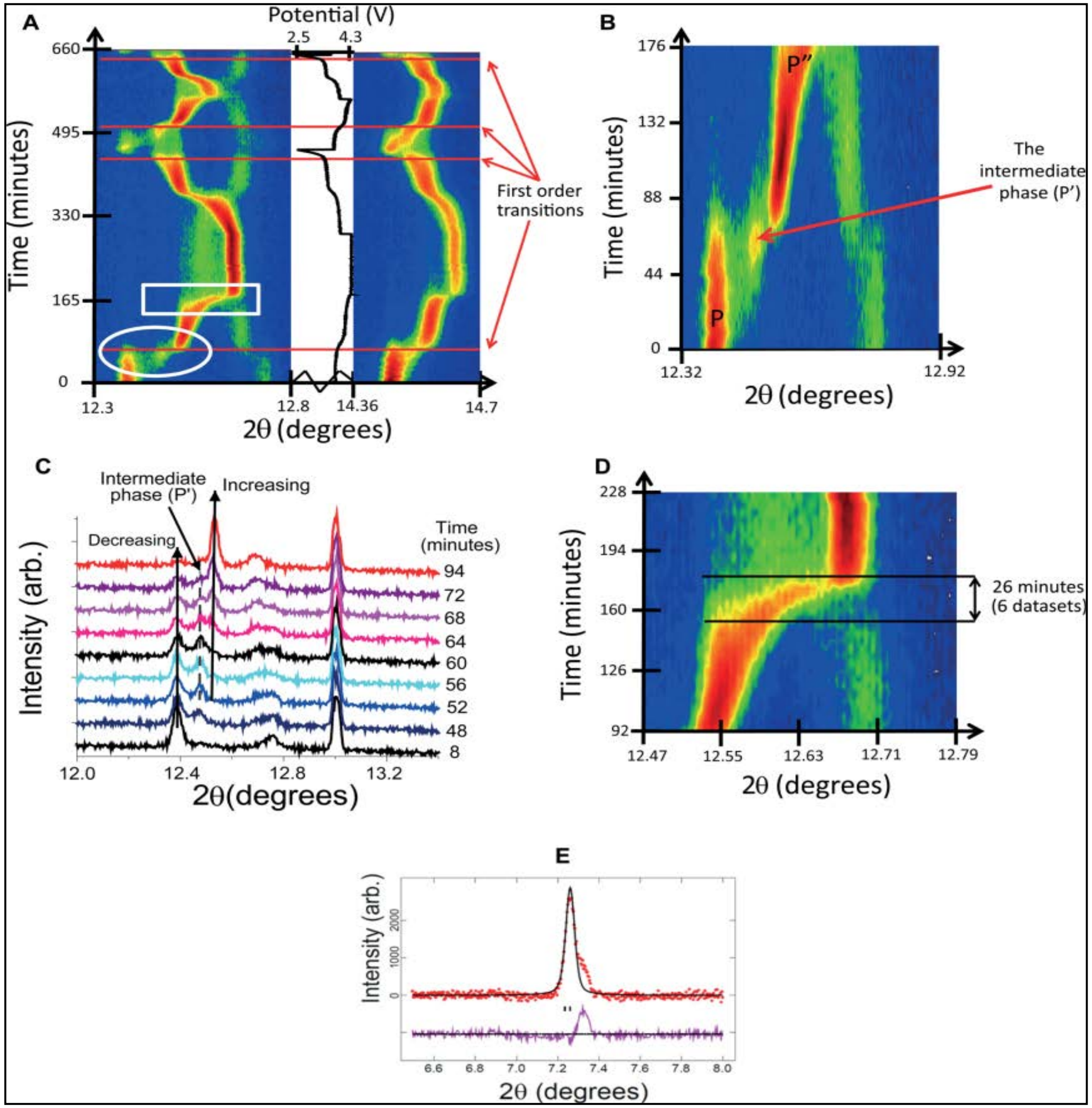
N. Sharma, P. Serras, V. Palomares, H. E. A. Brand, J. Alonso, P. Kubiak, M.L. Fdez-Gubieda and T. Rojo

Published: ***Chem. Mater.* 2014, 26, 3391-3402**



- Na-ion batteries offer a more economical alternative to Li-ion batteries because Na is globally more abundant than Li, but…
- New electrode materials to improve the energy density and reversibility of Na insertion/extraction processes
- *In situ* charging and discharging using a modified CR2032 cell to observe changes in structure at the cathode.





- Key features include an initial region in the charging profile where at least three isostructural phases are formed with varying amounts of Na in each phase
- These transform via two two-phase reaction mechanisms both on charging and discharging.
- There are significant differences in behaviour during charging and discharging
- Work continues…

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Complex sample environments

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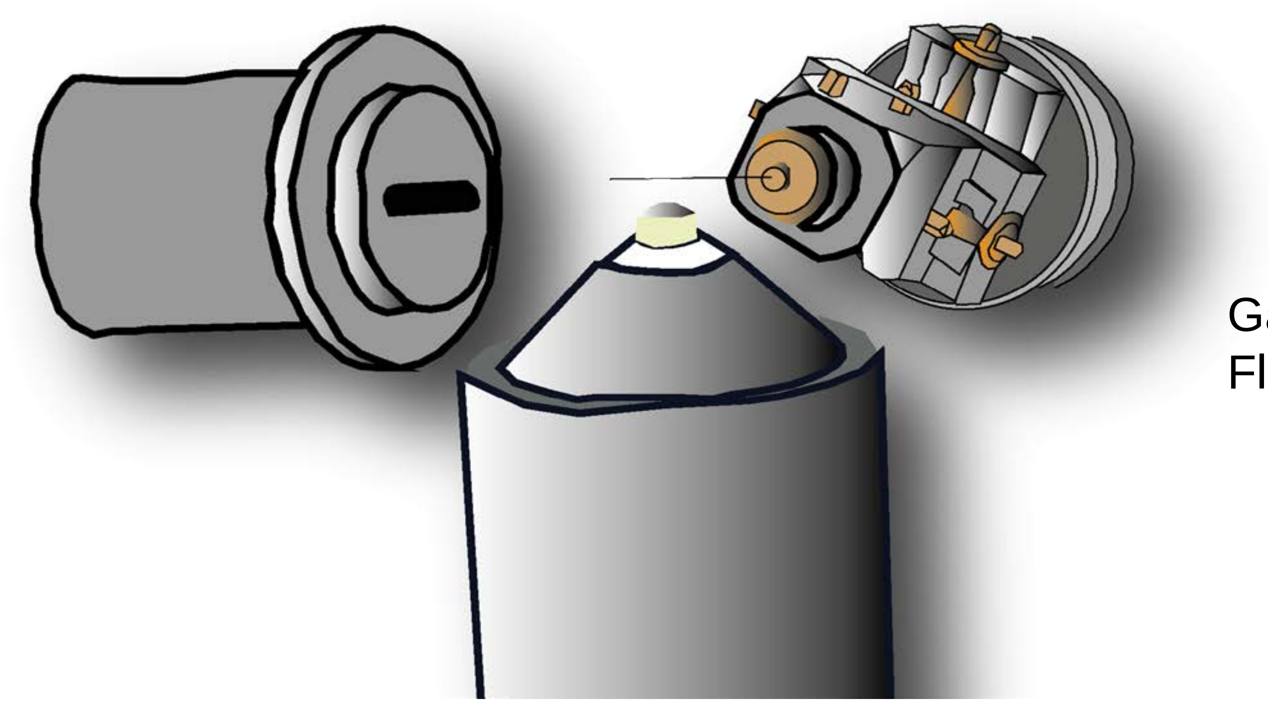
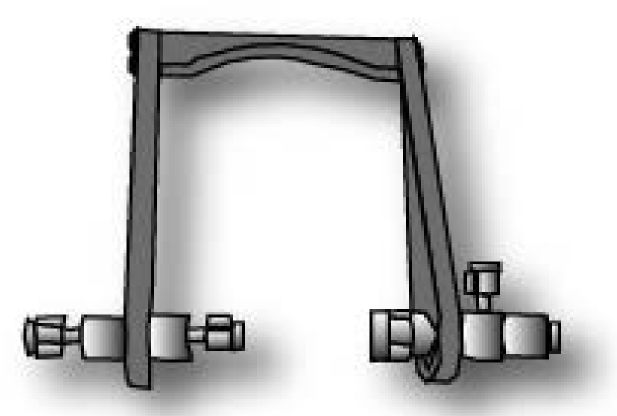
Capillary sample environments

High Temperature (RT – 1500° C)

Low Temperature (80 – 480 K)



Gas environments
Flowing or static – 20 bar*



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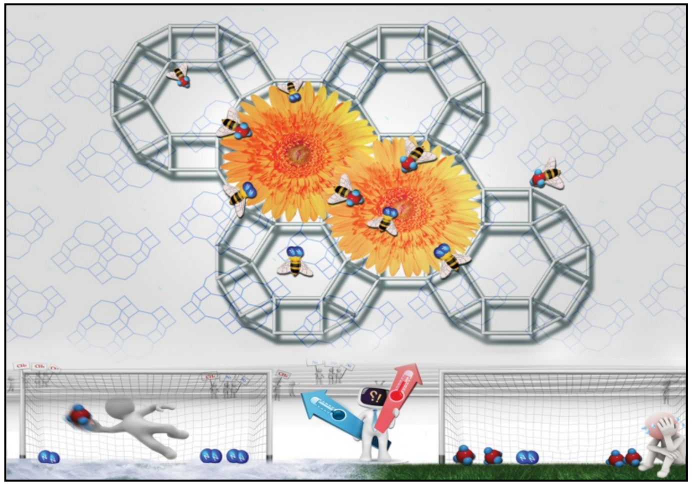
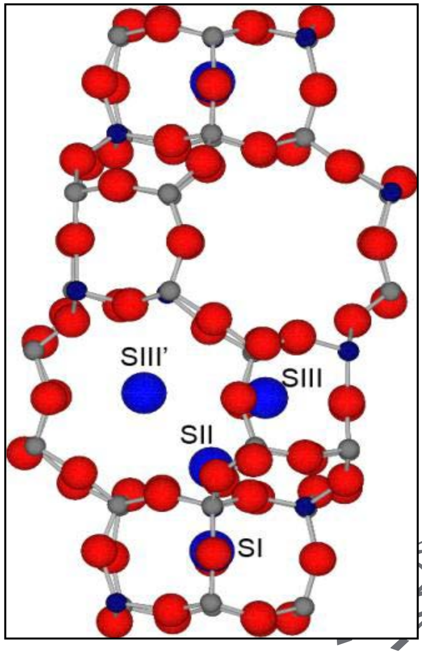
Temperature controlled invertible selectivity for adsorption of N_2 and CH_4 by molecular trapdoor chabazites

J. Shang, G. Li, Q. Gu, R. Singh, P. Xiao, J. Z. Liu and P. A. Webley

Published: ***Chem. Commun.*, 2014, 50, 4544**

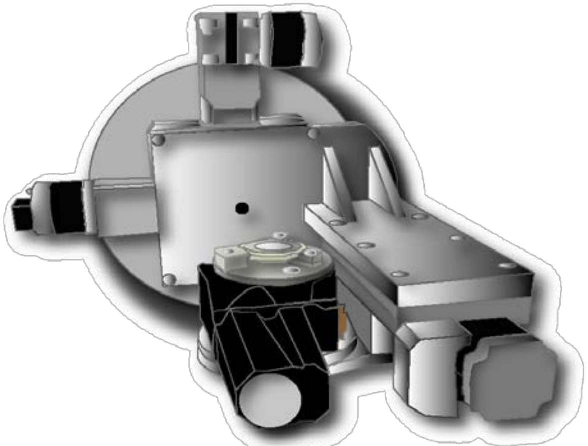


- N_2 in CH_4 gas streams presents a problem for the methane economy
- A molecular trap door gas separation mechanism in the chabazite zeolite has been identified.
- Chabazite consists of an 8-member ring with additional ‘door keeping’ cations (K^+) that block the path for gas molecules and prevent them entering the ring
- Thermal vibration can cause deviation of the ‘door keeping’ cation to allow the gas molecule to pass into the ring

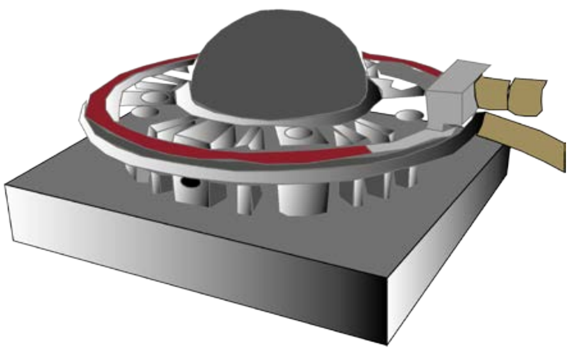


Other sample environments

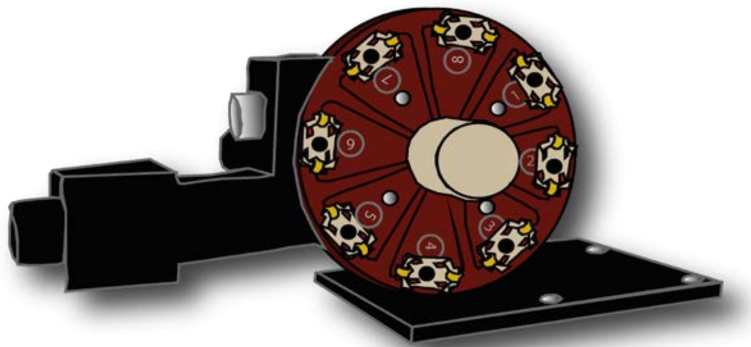
Flat plate spinner



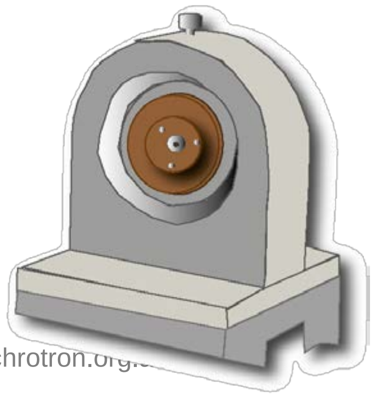
High Temperature
(RT – 1500 ° C)



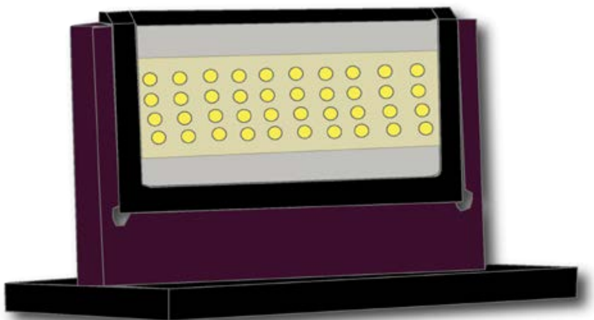
Battery Cycling



High Pressure (0 – 30 Gpa)



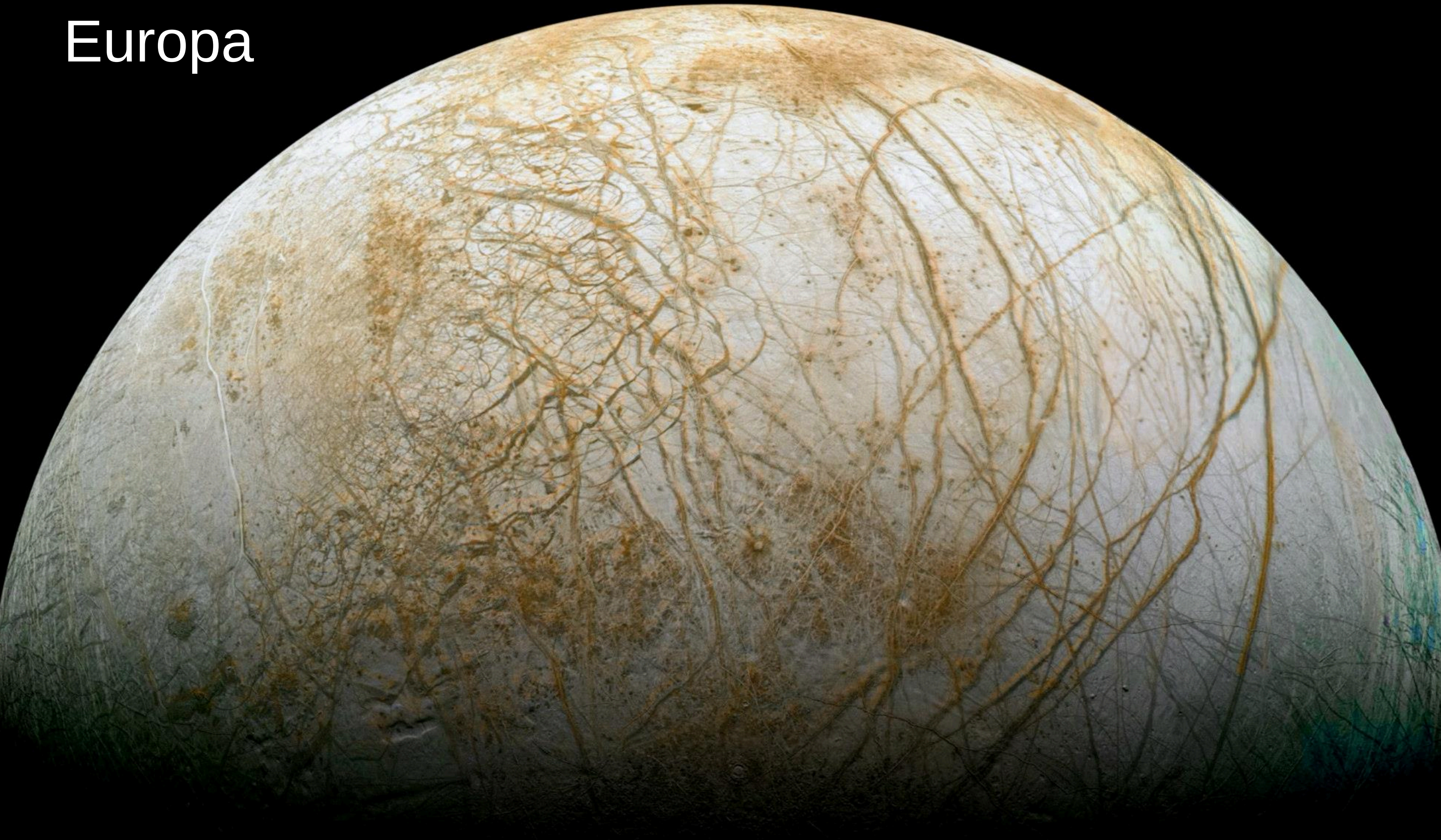
High throughput

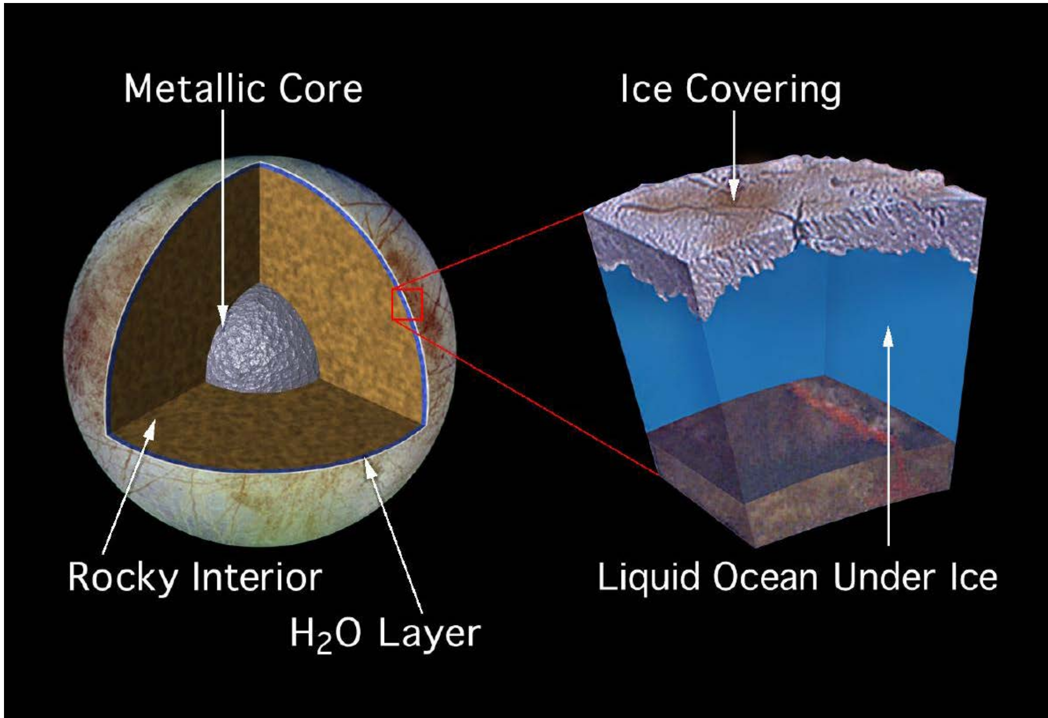


User defined sample environments

Complementary techniques

Europa



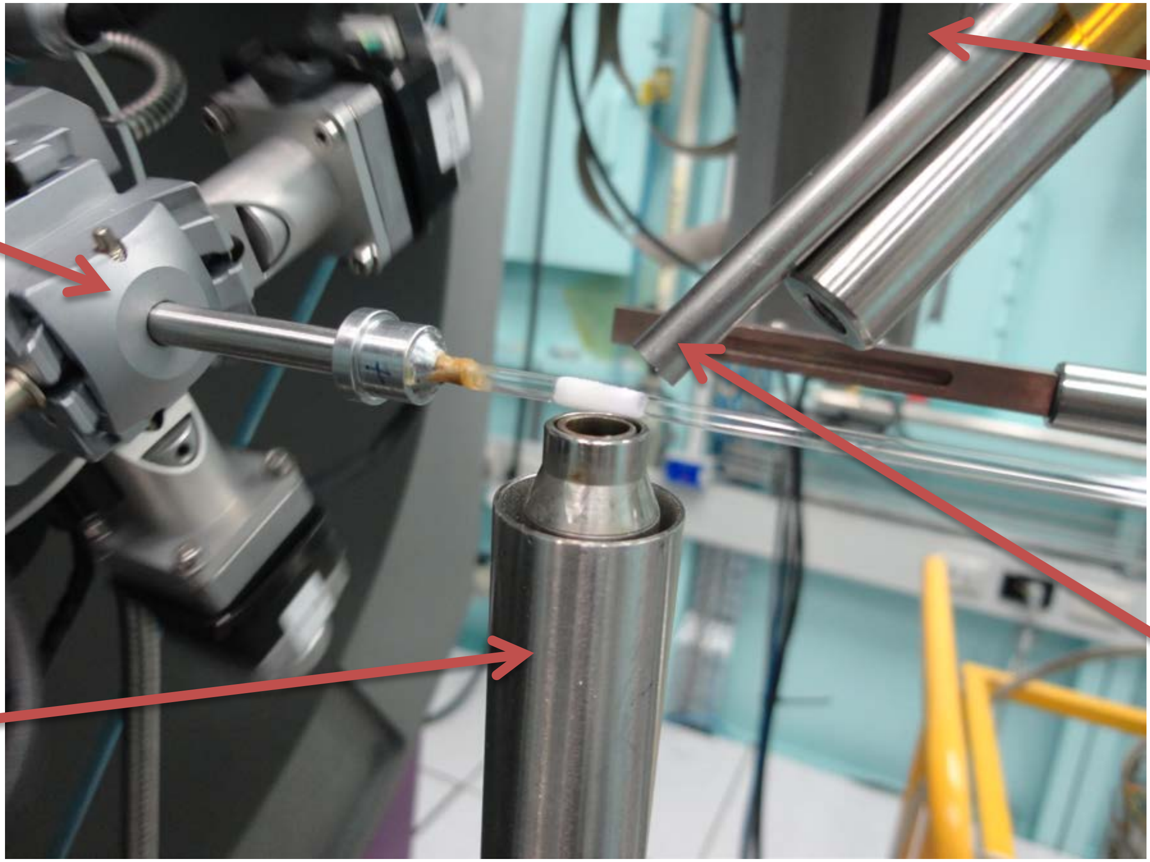

Metallic Core
Ice Covering
Rocky Interior
H_2O Layer
Liquid Ocean Under Ice


Jet Propulsion Laboratory
California Institute of Technology
NASA
Jupiter
www.jpl.nasa.gov
Image Credit:
NASA/JPL/University of Arizona

Simultaneous synchrotron X-ray powder diffraction and Near IR characterisation

Sample spinner

Mythen Detector



Near-IR probe

Cryostream

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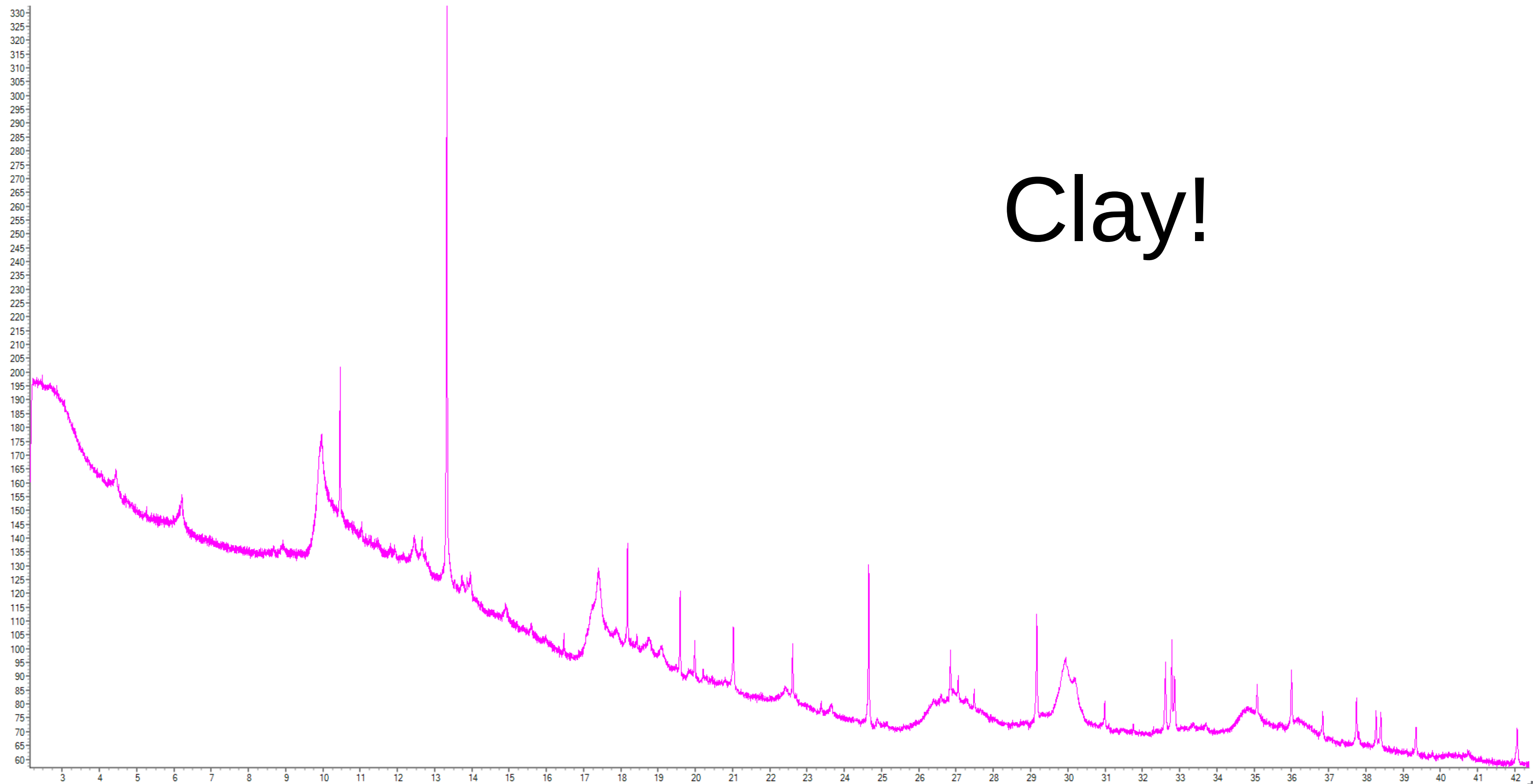
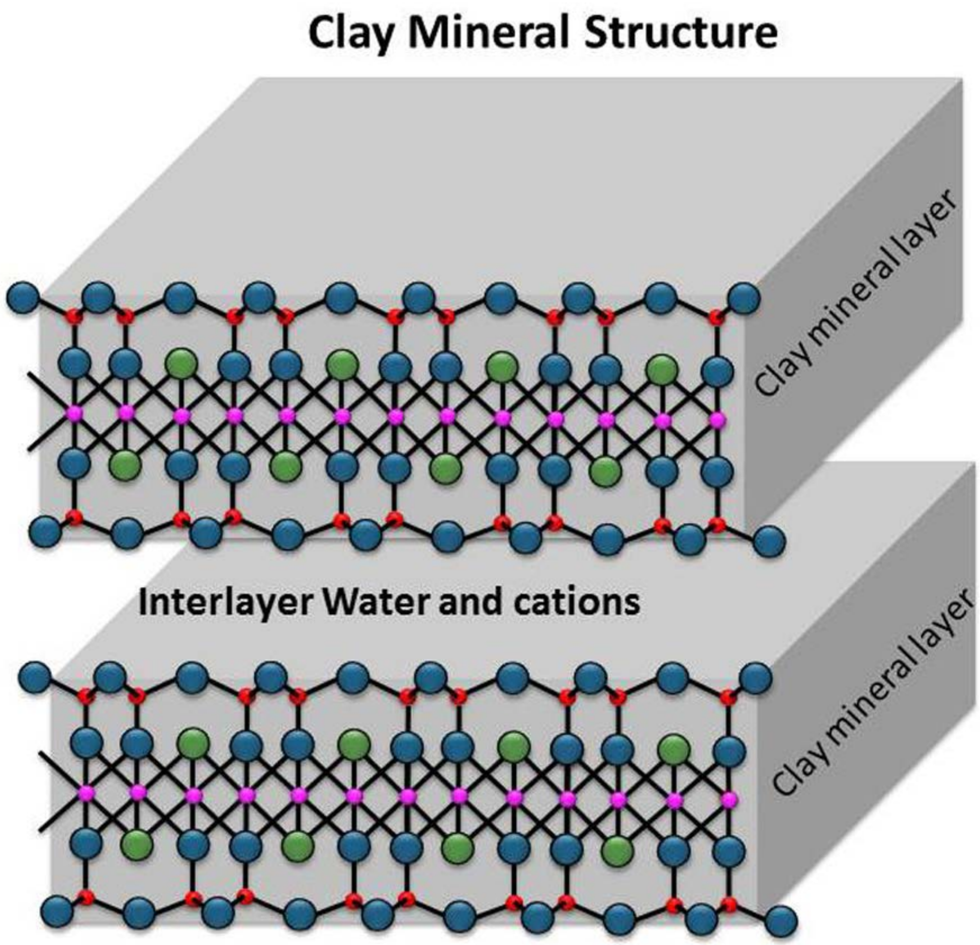
When is a synchrotron not necessarily the answer?

When can you get comparable results from a lab machine?

Poorly crystalline material



Clay!

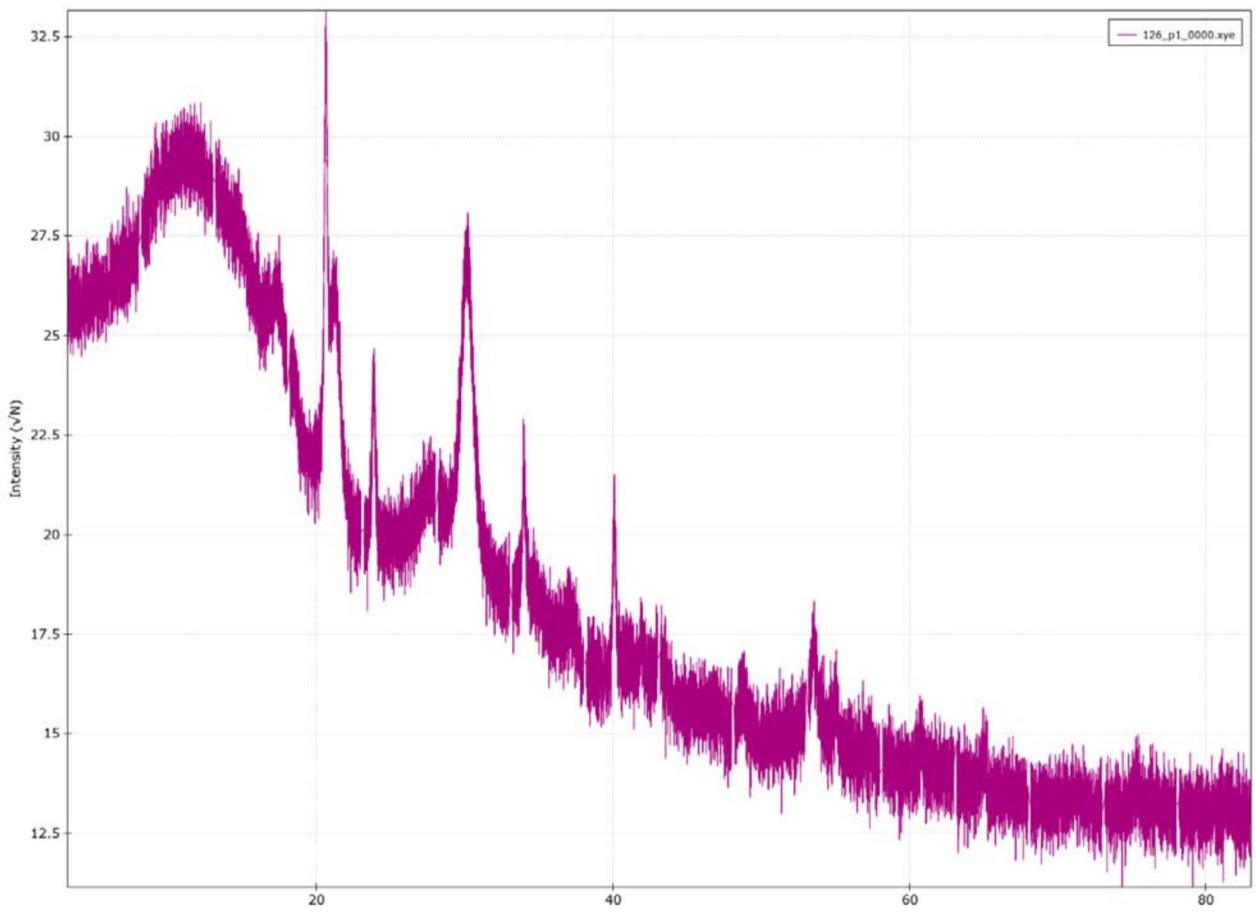


Clay is layered. The layers can be repeated or multiply stacked.

There can be cations and water in between the layers, or in between some layers and not others.

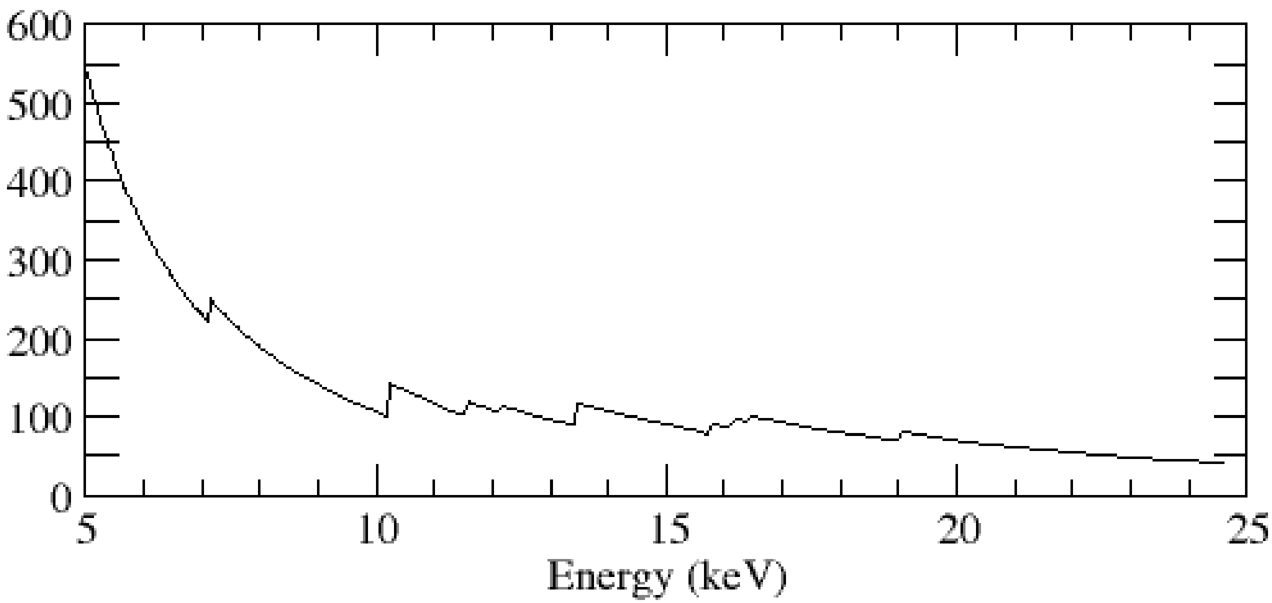
This causes the distances between similar planes of atoms to vary throughout the structure.

Nanomaterials



As the particles get smaller you start to see effects from the particle size not the layers of atoms.

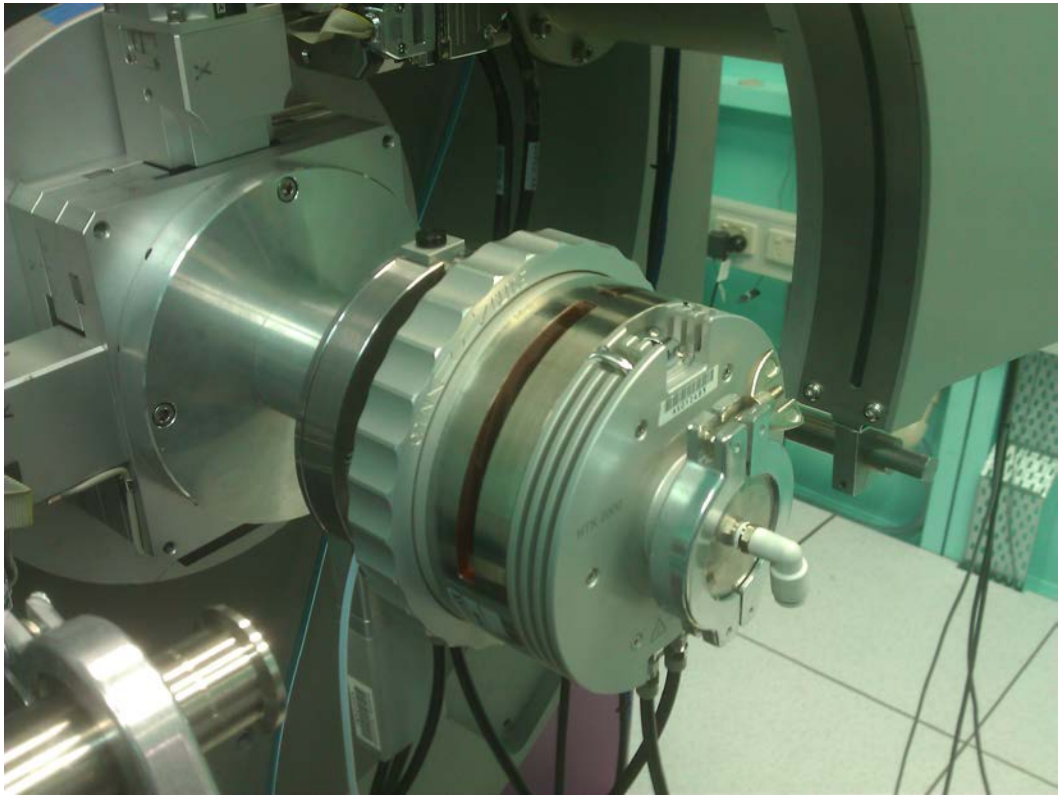
Complex high-Z element mixes

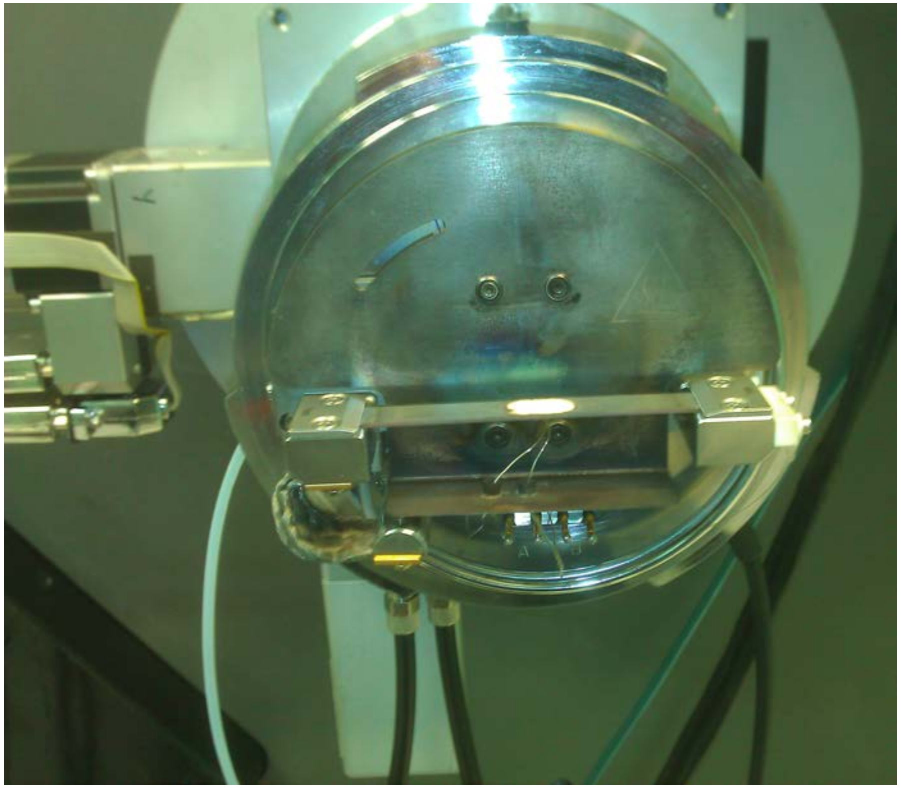


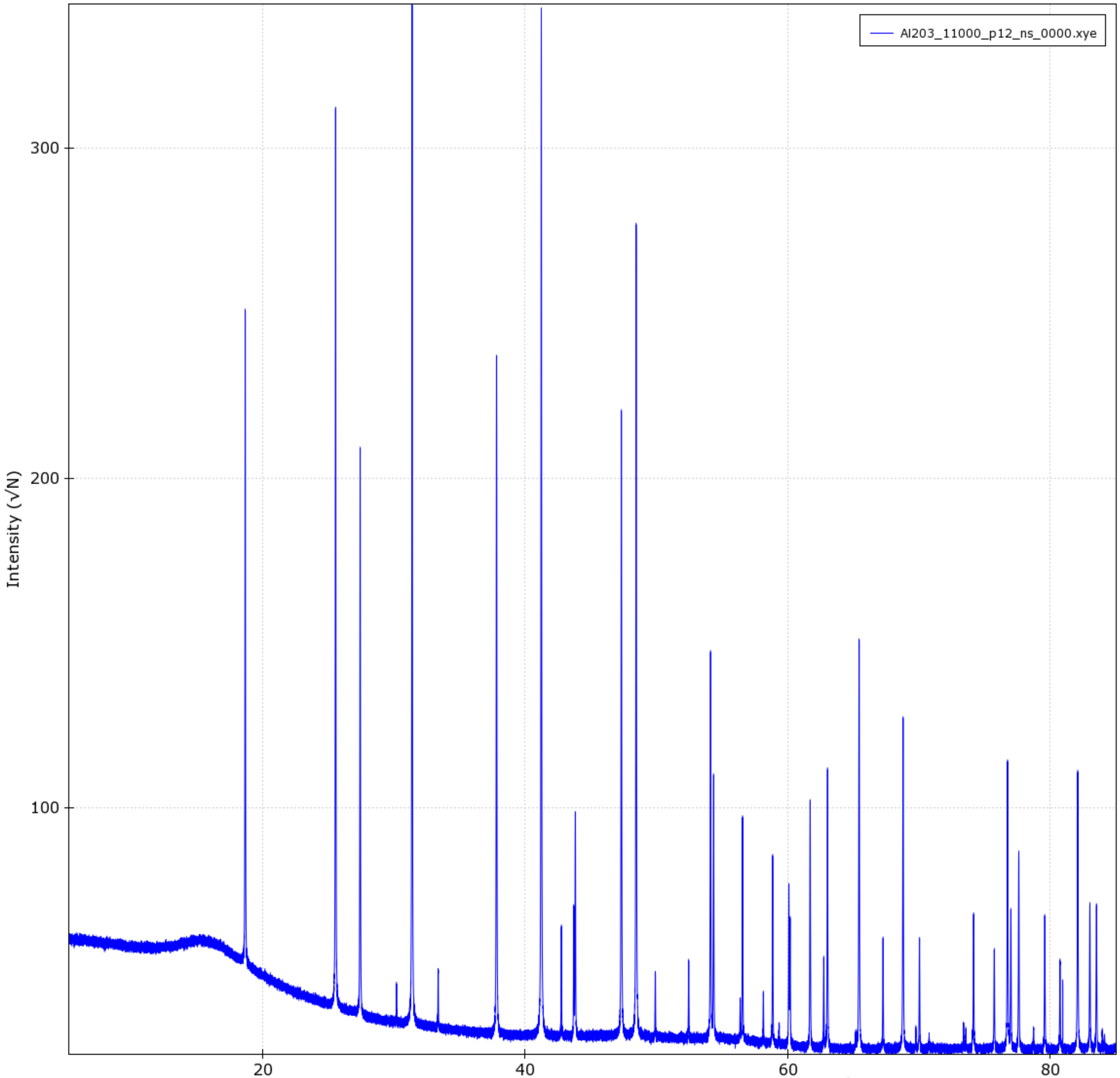
Sample containing:

Fe, W, Nb, Sr, Bi

Non – ideal geometry



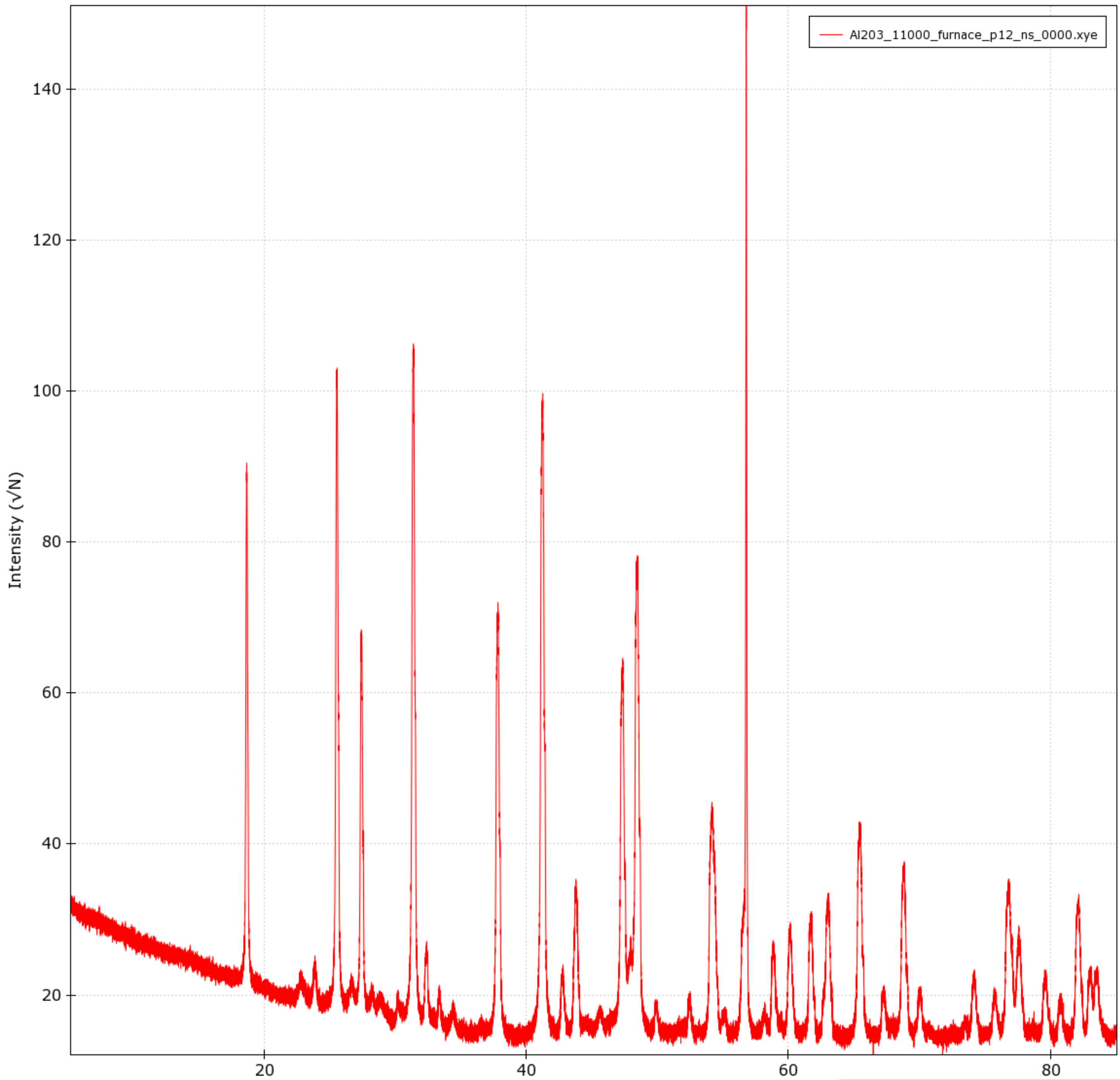




Al2O3 in a capillary

Nice, sharp peaks, sensible intensities

Good powder averaging



Broadened peak shapes

Different intensities

Poor powder averaging

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Talk to your beamline scientist!

(if you are the beamline scientist, know your instrument!)

Questions?