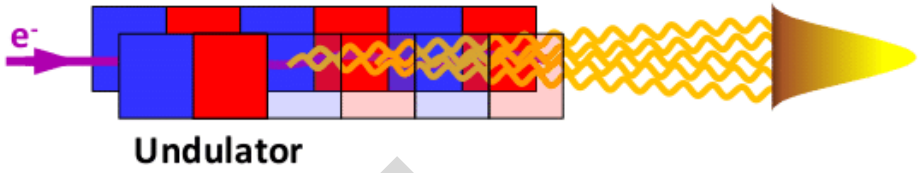
PDF measurements at synchrotron X-ray facilities

Daniel Irving, Beamline Scientist I15-1, Diamond Light Source

PolyU Synchrotron Summer School

19th June 2024

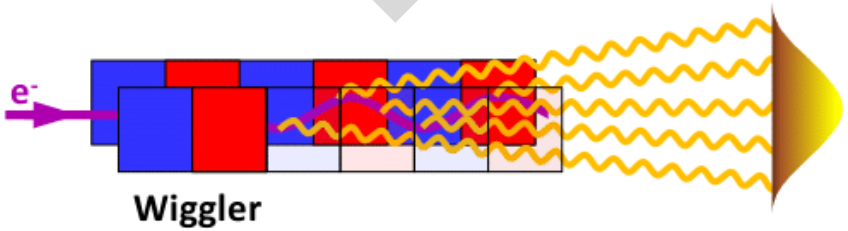
PDF Beamline **Sources**

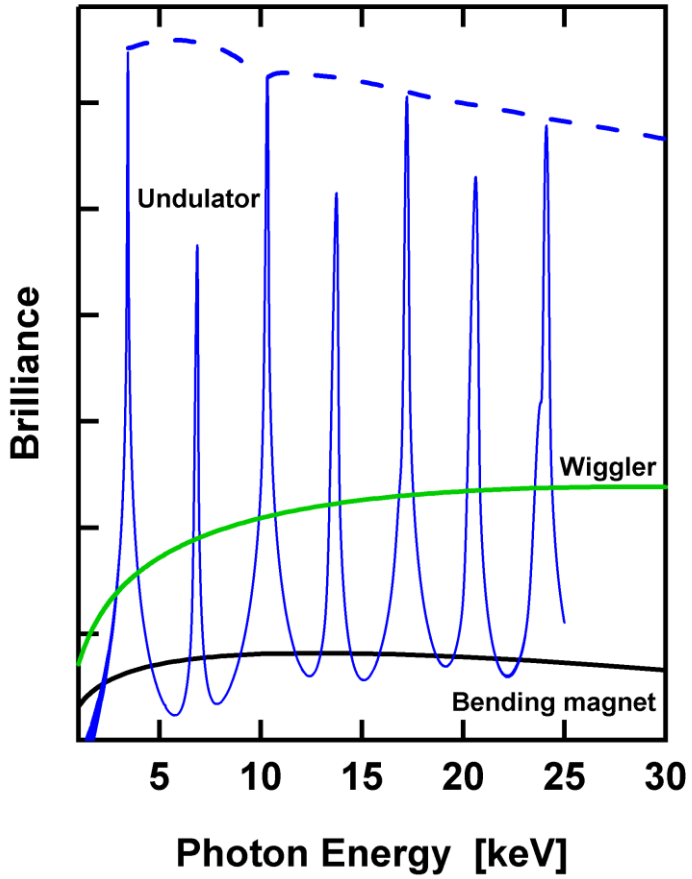


High-energy storage rings

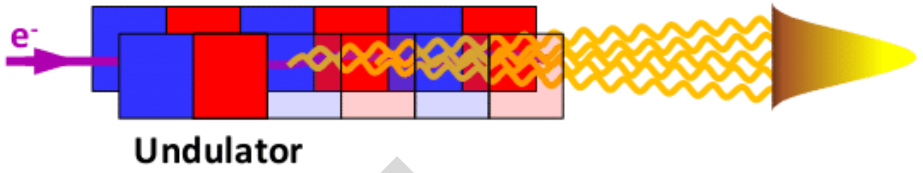
High energy X-rays
(40-120 keV)

Medium-energy storage rings





PDF Beamline **Sources**

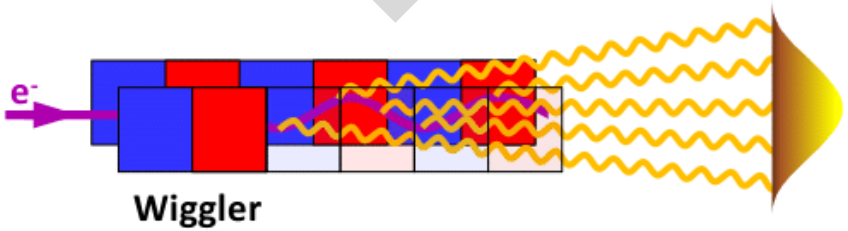


High-energy storage rings

11-ID-B, **APS** (7 GeV), USA
ID11, ID15A & ID22, **ESRF** (6 GeV), France
P02.1 & P07, **PETRA-III** (6 GeV), Germany
EM (planned), **HEPS** (6 GeV), China

High energy X-rays
(40-120 keV)

Medium-energy storage rings

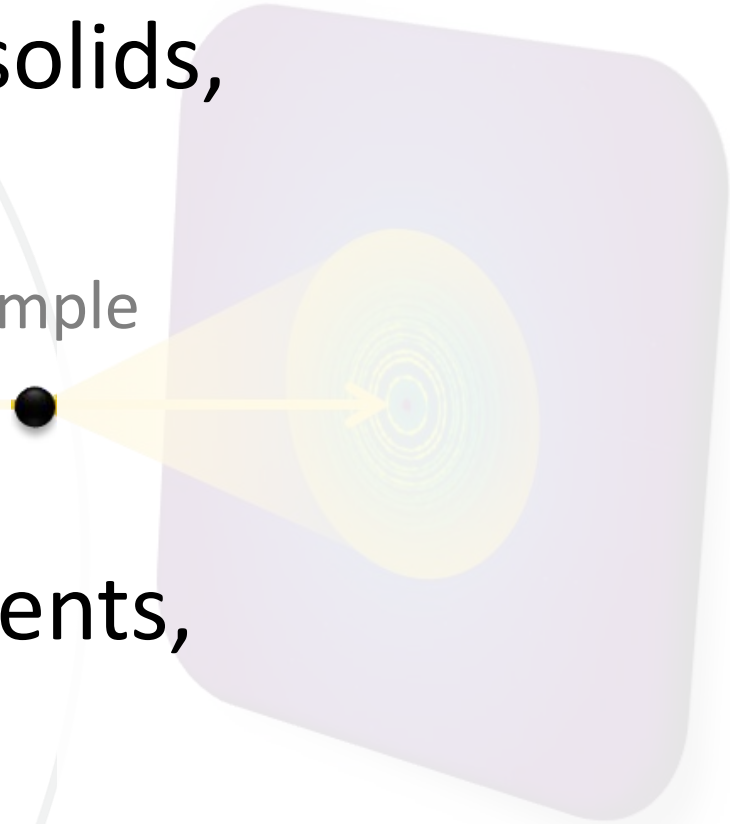


I15-1, **DLS** (3 GeV), UK
28-ID-1, **NSLS-II** (3 GeV), USA
BXDS-WHE, **CLS** (2.9 GeV), Canada
BL13W , **SSRF** (3.5 GeV), China

diamond

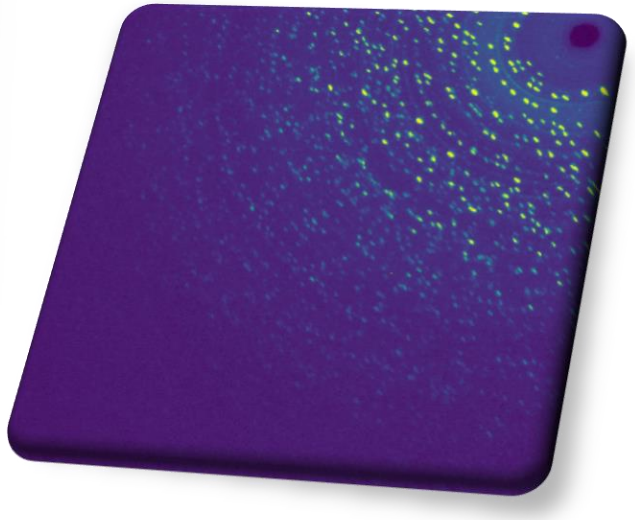
PDF Beamline **Samples**

powders, liquids, solids, gels, films…



sample environments, devices…

Spinning helps for crystalline powders



PDF Beamline **Detectors**

Indirect detection

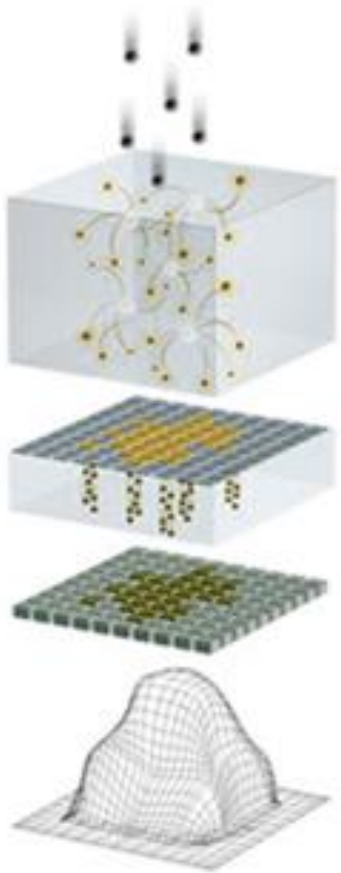
X-rays

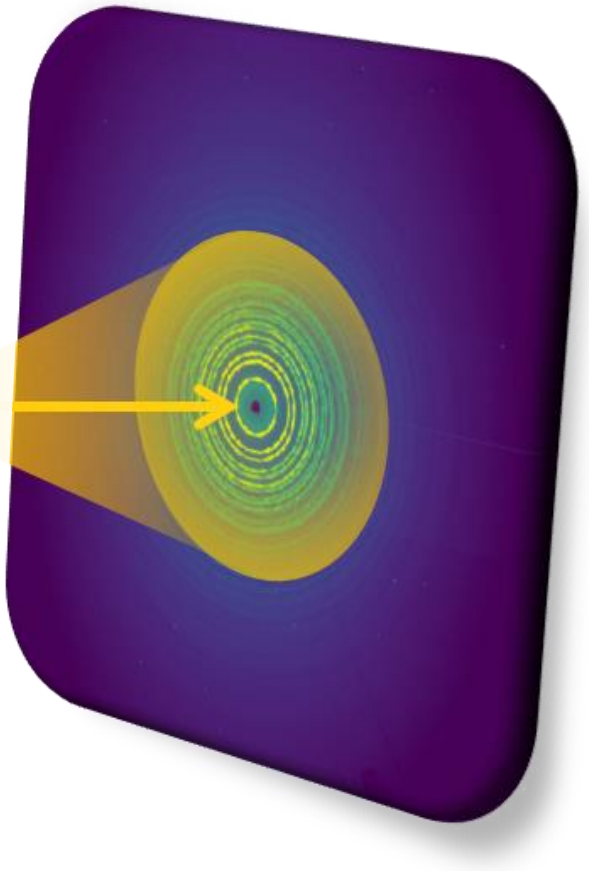
Scintillator
$\gamma_{X\text{-ray}} \rightarrow \gamma_{Visible}$

Photodiode
$\gamma_{Visible} \rightarrow e^-$

Electronics

Image





Direct detection



X-rays

Sensor
$\gamma_{X\text{-ray}} \rightarrow e^-$

Electronics

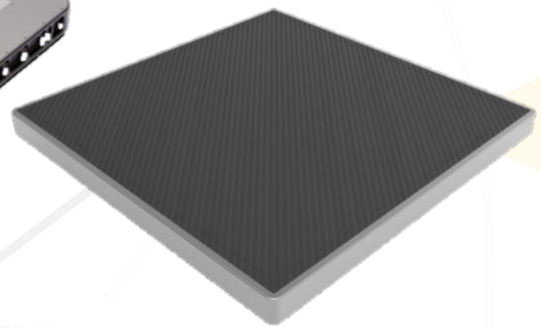
Image

PDF Beamline **Detectors**

Indirect detection
a-Si TFT with **CsI** scintillators

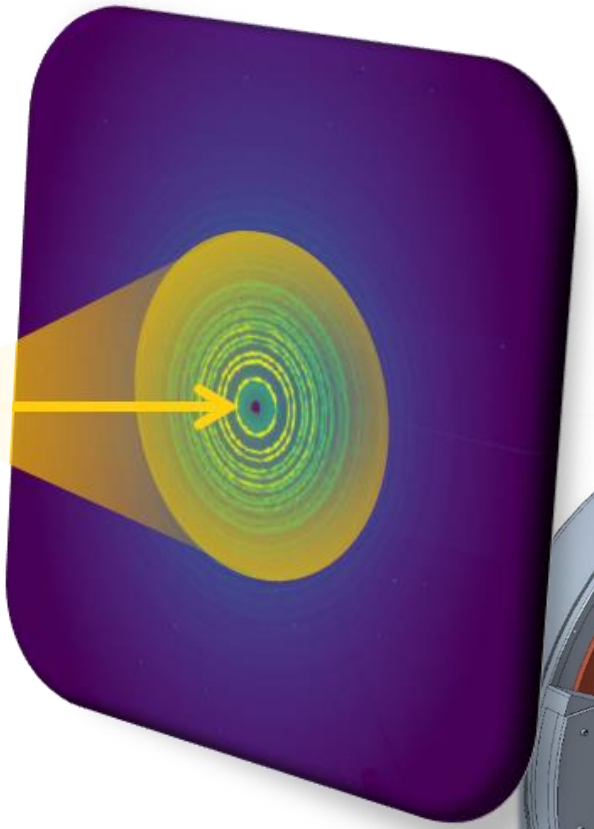
Perkin Elmer / Varex





Thales

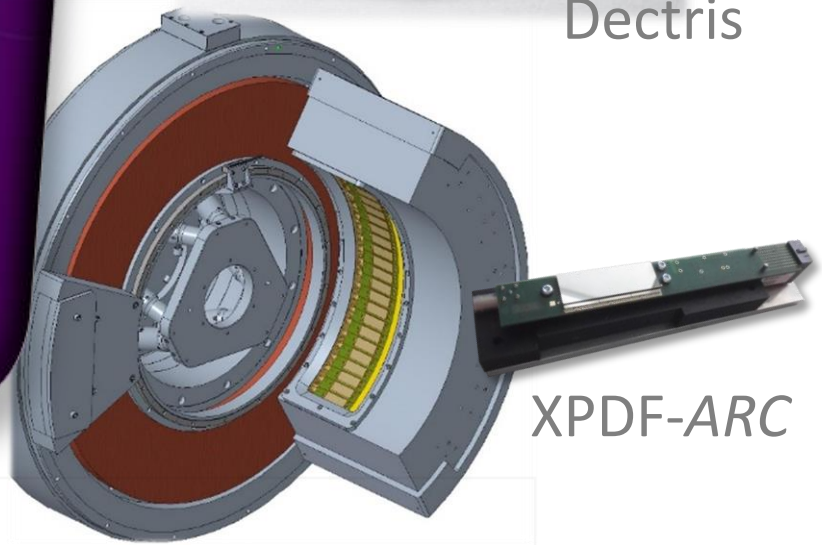




Direct detection
CdTe sensors



Dectris



XPDF-*ARC*

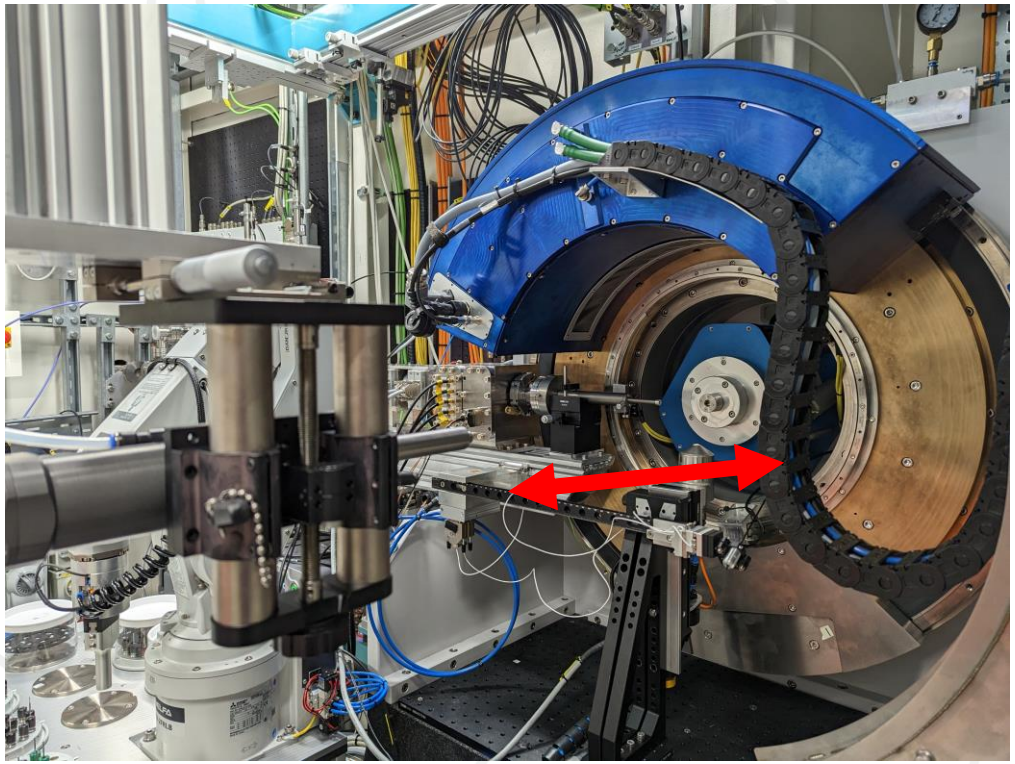
diamond

Experimental setups

I15-1, Diamond Light Source

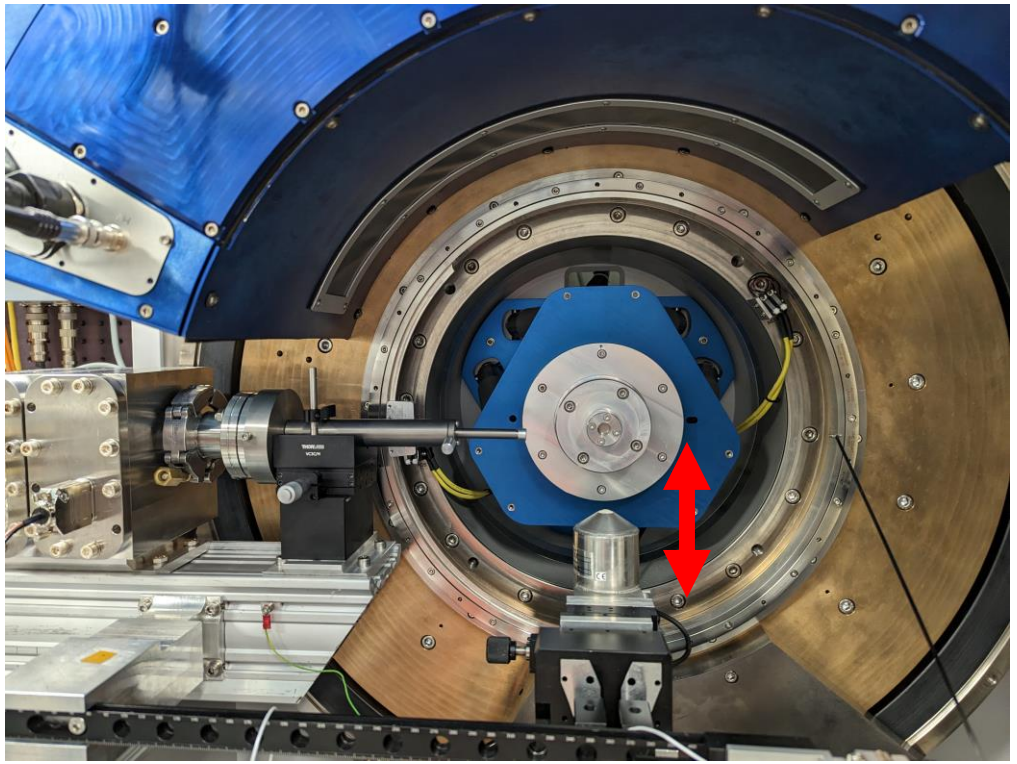
(Other beamlines may vary)

Standard Collections – Temperature Devices



Cobra – 80K – 450K

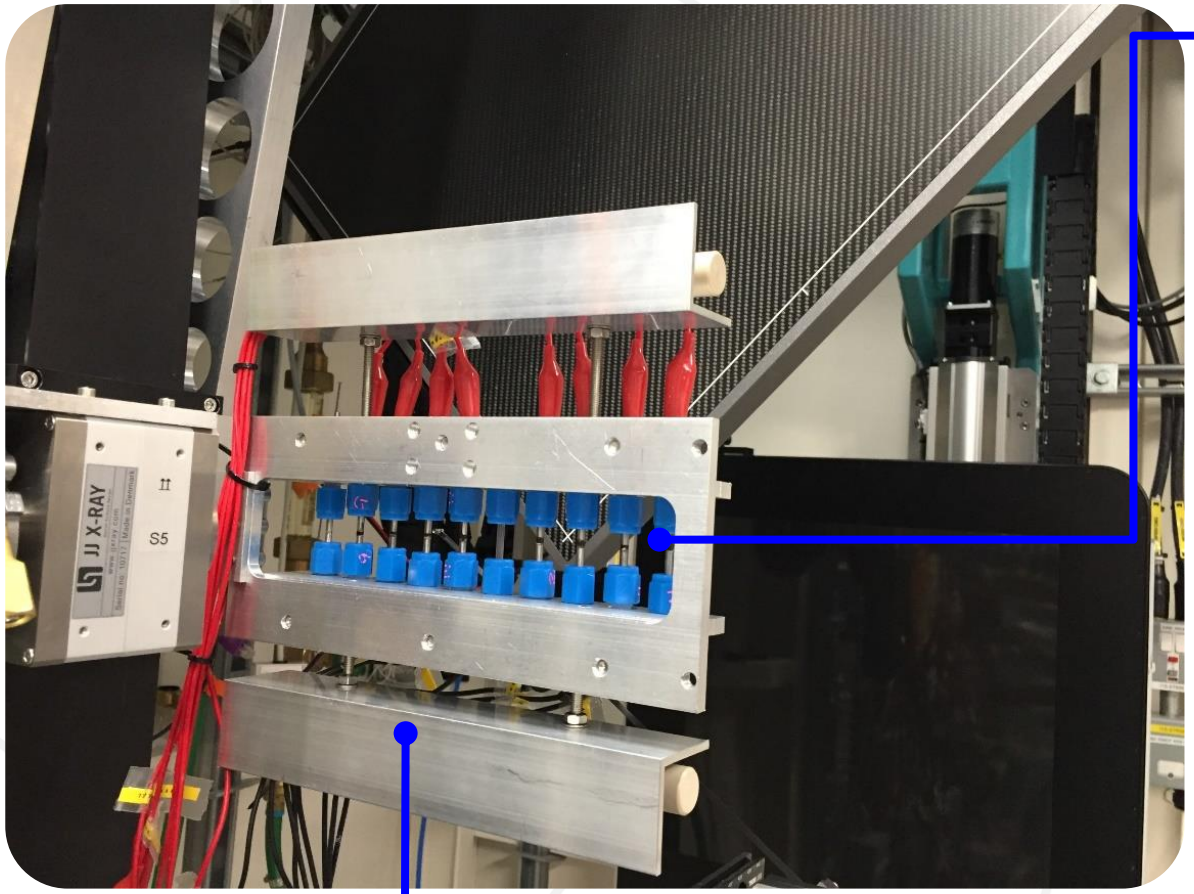
- Dry nitrogen supply
- Moves in/out for sample changing & removing temperature device



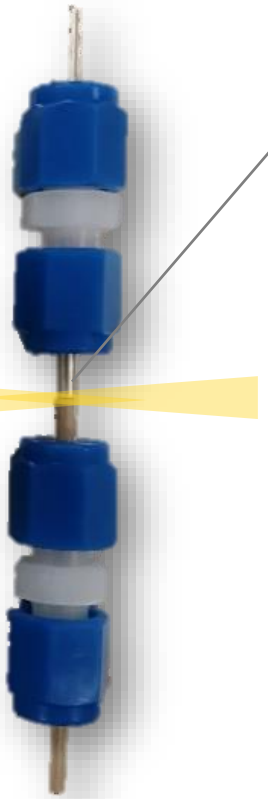
Hot Air Blower – 400K – 1000K

- Moves in/out for sample changing & removing temperature device

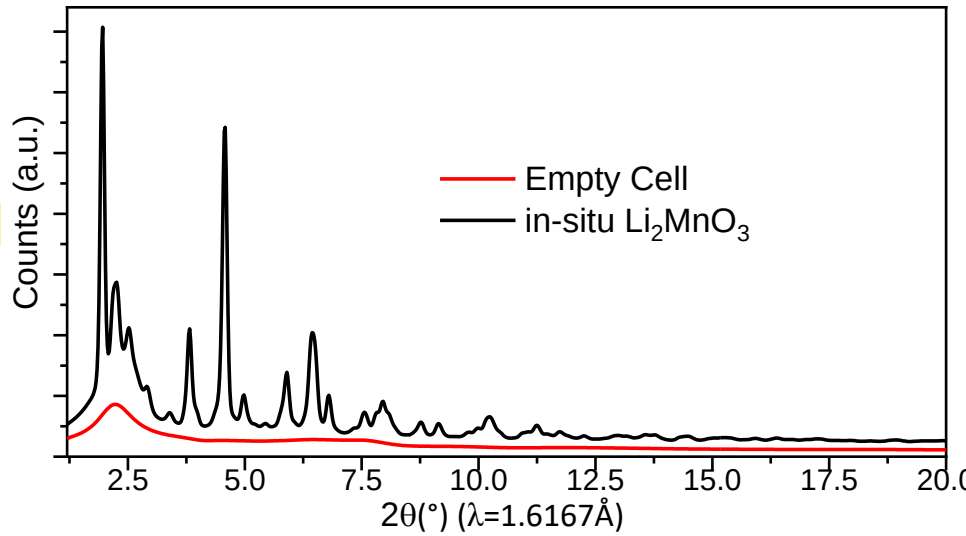
I15-1 “DRIX” eChem Cell



Modified Swagelok cell



Containment tube: think walled quartz glass



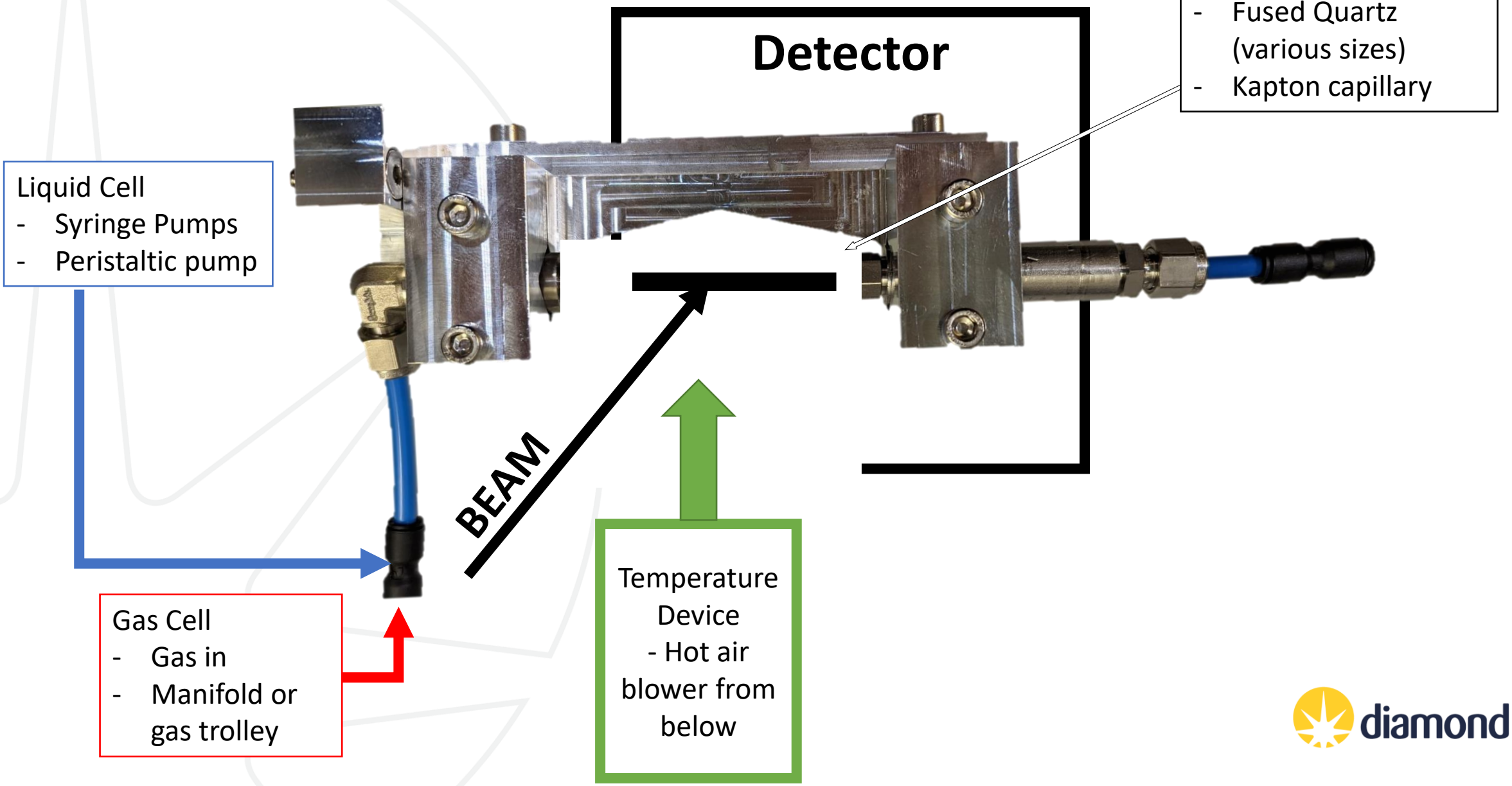
Cell cycling via Ivium-Stat



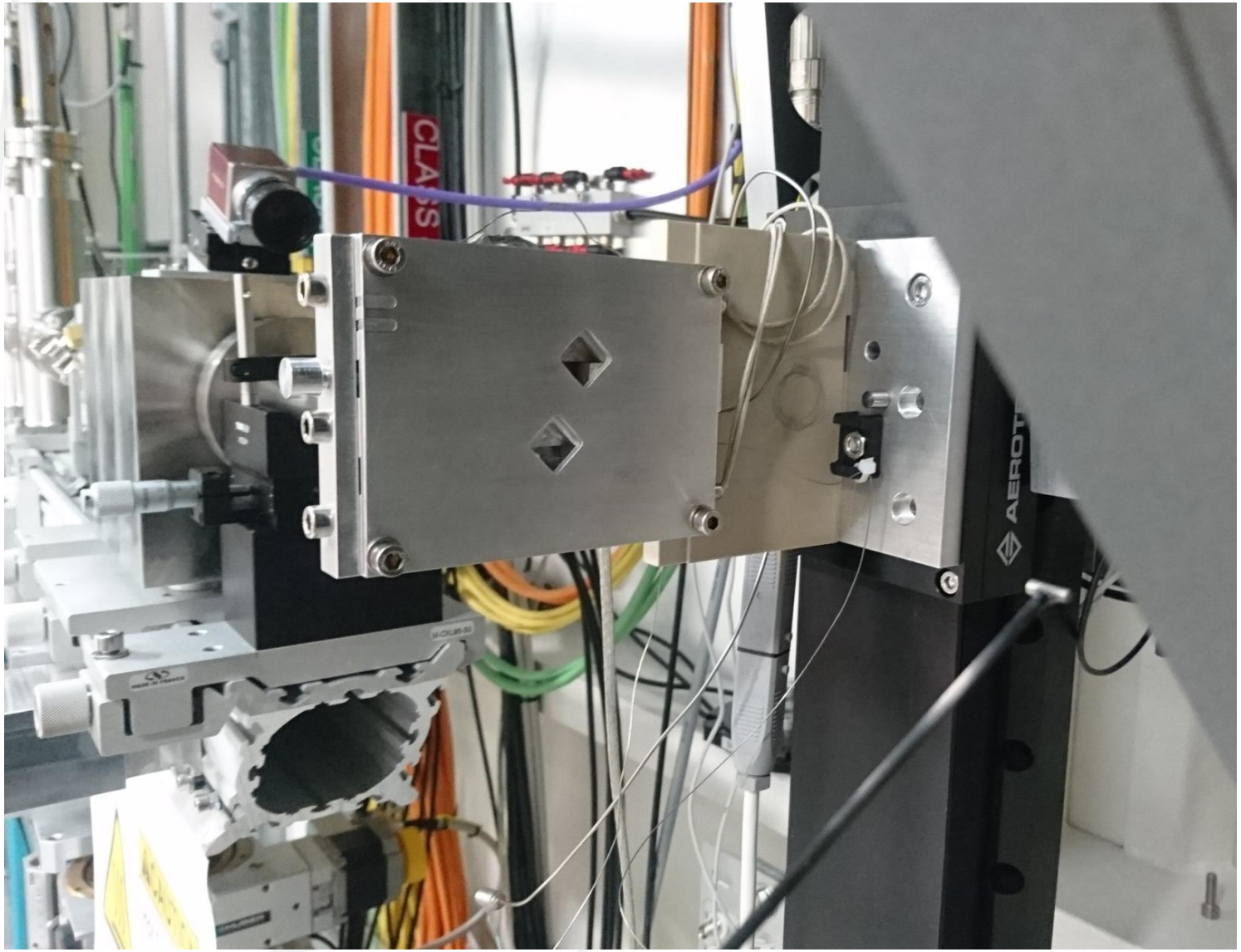
- Currently cycle 6 cells with current end station upgrades
- Heated 1-cell version also available

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Gas & Liquid Flow Cells



Hydrothermal Cell



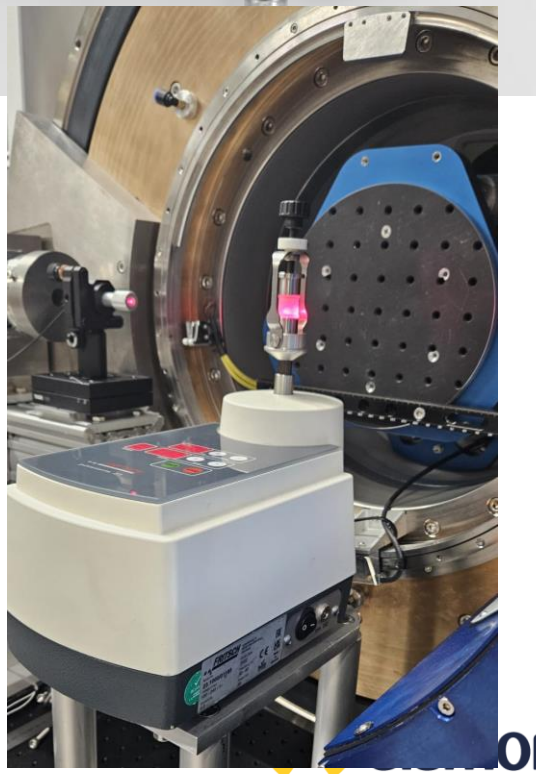
- In-situ synthesis under pressure and/or temperature
- Multi-chamber for switching between samples
- More improvements coming in the form of flow chemistry

Other Environments

- Heated battery cell
- Heated flow cells
- Linkam furnaces
- Ball mill
- Levitator
- Container-less cell (dropped flow)
- Jet flow cell
- AND user-built environments
  - This needs to be discussed with beamline scientists prior to proposal submission
  - BUT we're always happy to try and accommodate any user equipment



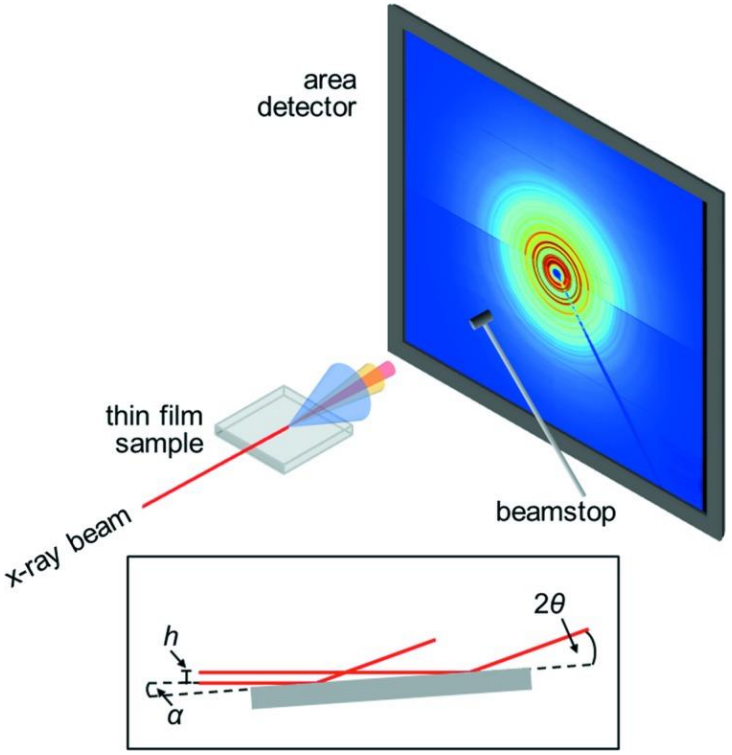




Data Processing & Advanced Experimental Discussions

Advanced PDF/Total Scattering Experiments

- Standard PDF
- In-situ/in-operando PDF
- Single crystal diffuse scattering
  - 3D-ΔPDF
- Grazing incidence PDF
- PDF tomography



If you can do it with PXRD, you can ***probably*** do it with total scattering and PDF!
(but **always** check with the beamline you're planning to use…)

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Collecting the data is the easy part…

Now you have to process and analyse it!

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Data Workflow

Integration from 2D to 1D (if using 2D detector)

- **Need to correct for:** flat field, dark field, detector masks, dead/hot pixels
- **Software includes:** DAWN, FIT2D, native software to diffractometer etc.
- Can just analyse the RAW diffraction data to analyse average structure (you get this data for free!)

From RAW scattering data to PDF

- **Need to correct for:** non-sample related scattering (container), Compton, polarisation, fluorescence, multiple scattering etc.
- **Need to know**: X-ray wavelength/energy, type of container (composition and diameter), sample information (composition, density)
- **Software includes**: GudrunX, PDFgetX2/3, Vaxadium (I15-1 soon to be automated software!), GSAS-II, etc..

Analysis of the Data

- **Need to know**: what you want from the data i.e., phase analysis, fingerprinting, short-range ordering, full structure refinement (your analysis route may vary depending on what you want from your data)
- **Fingerprint/phase analysis**: basic graphing software such as Excel, Origin, GNUPlot will work fine
- **Small-box modelling**: TOPAS, PDFgui, diffPy-CMI…..
- **Large-box modelling**: EPSR, Dissolve, RMCProfile…

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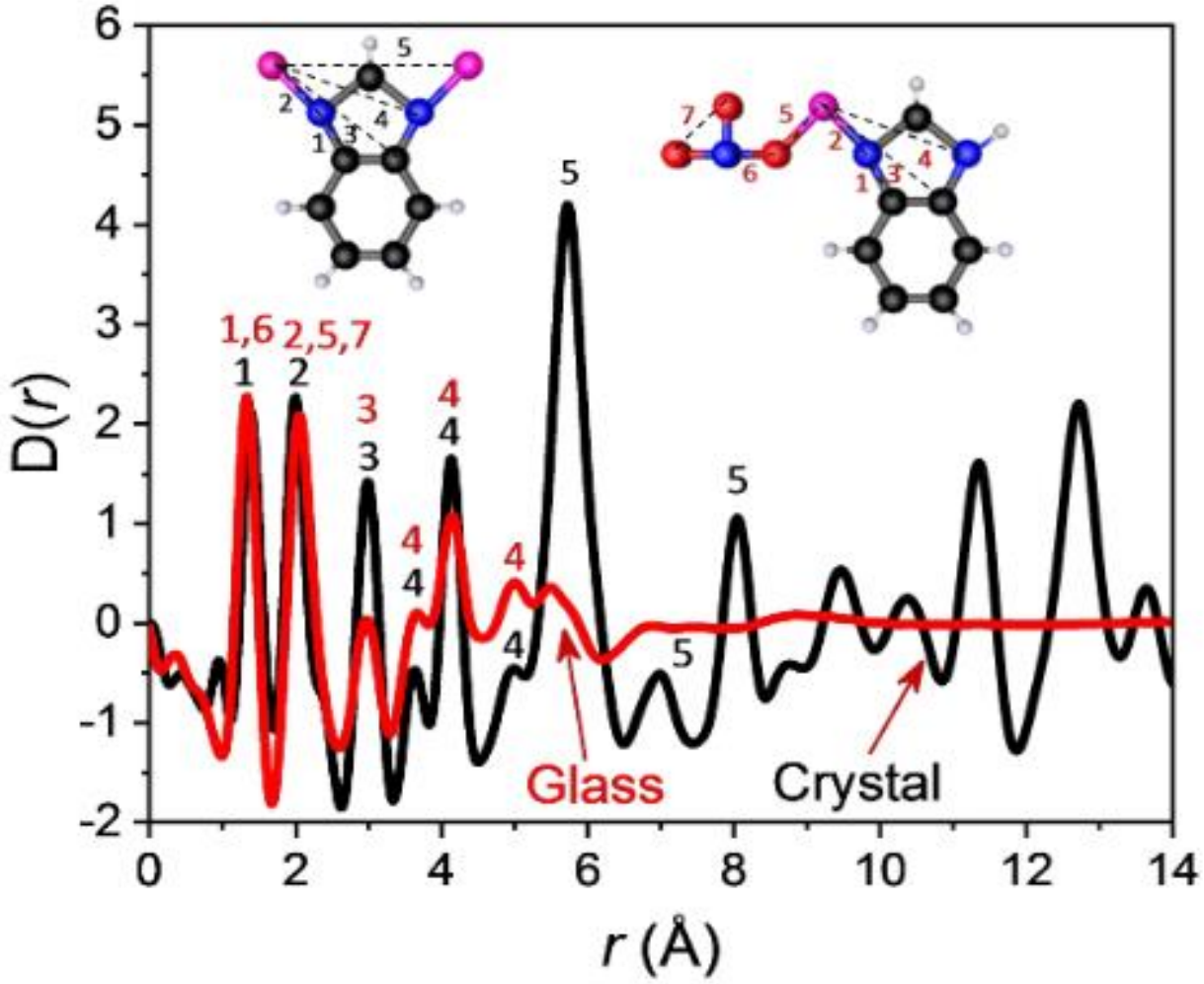
Current State of PDF Science

& Relevant Analysis Techniques

diamond

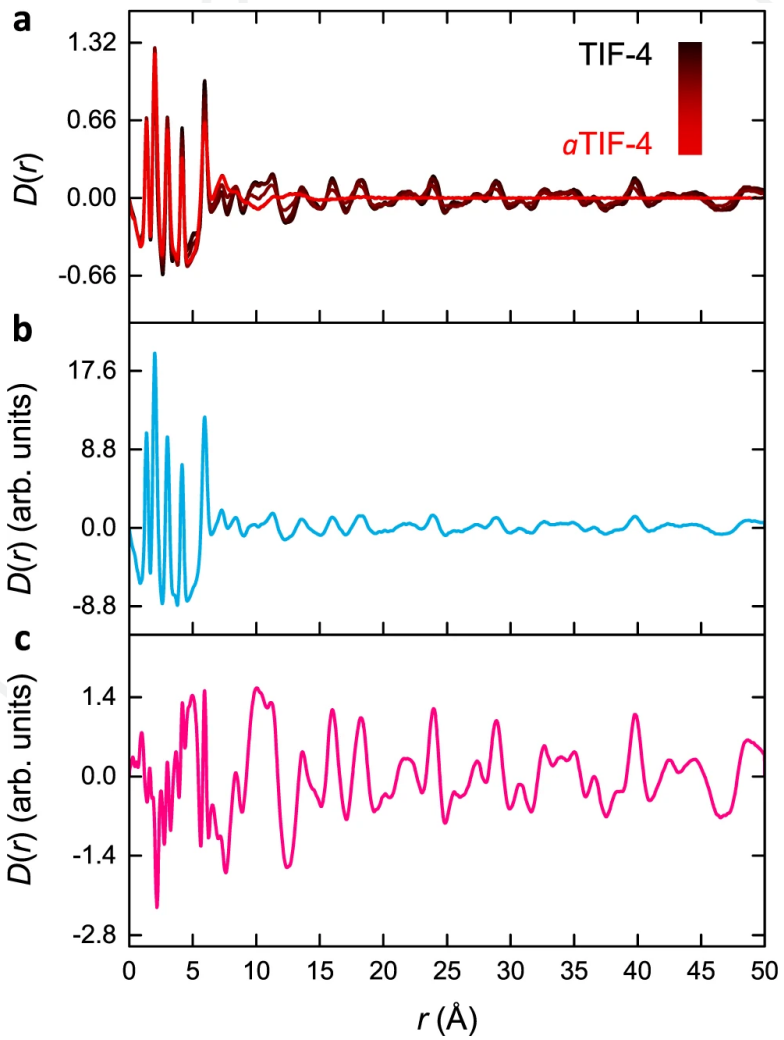
Metal-Organic Frameworks MOFs – Glass/Crystalline

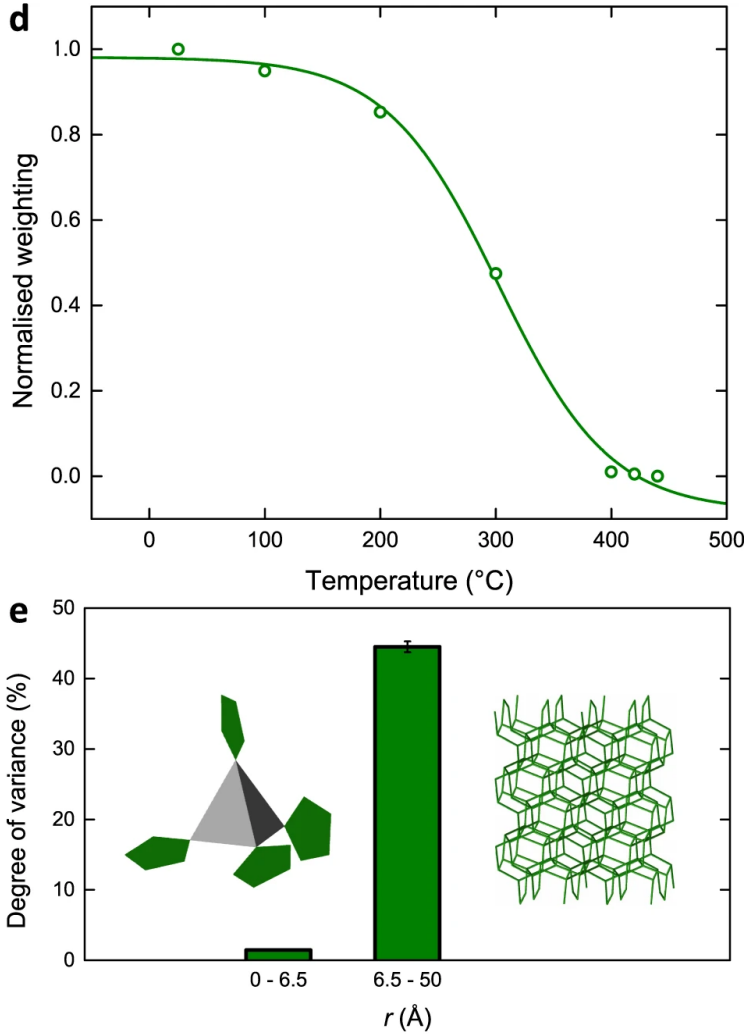
- Glassy MOFs can have additional physical properties compared to their crystalline counterparts
- Understanding what structural changes have (or have not) been implemented is key to property understanding
- Glassy materials cannot be verified by XRD, but can by PDF



M. A. Ali *et al., Angew. Chem. Int. Ed.,* **62** (2023), e202218094

Metal-Organic Frameworks MOFs – Melts and PCA

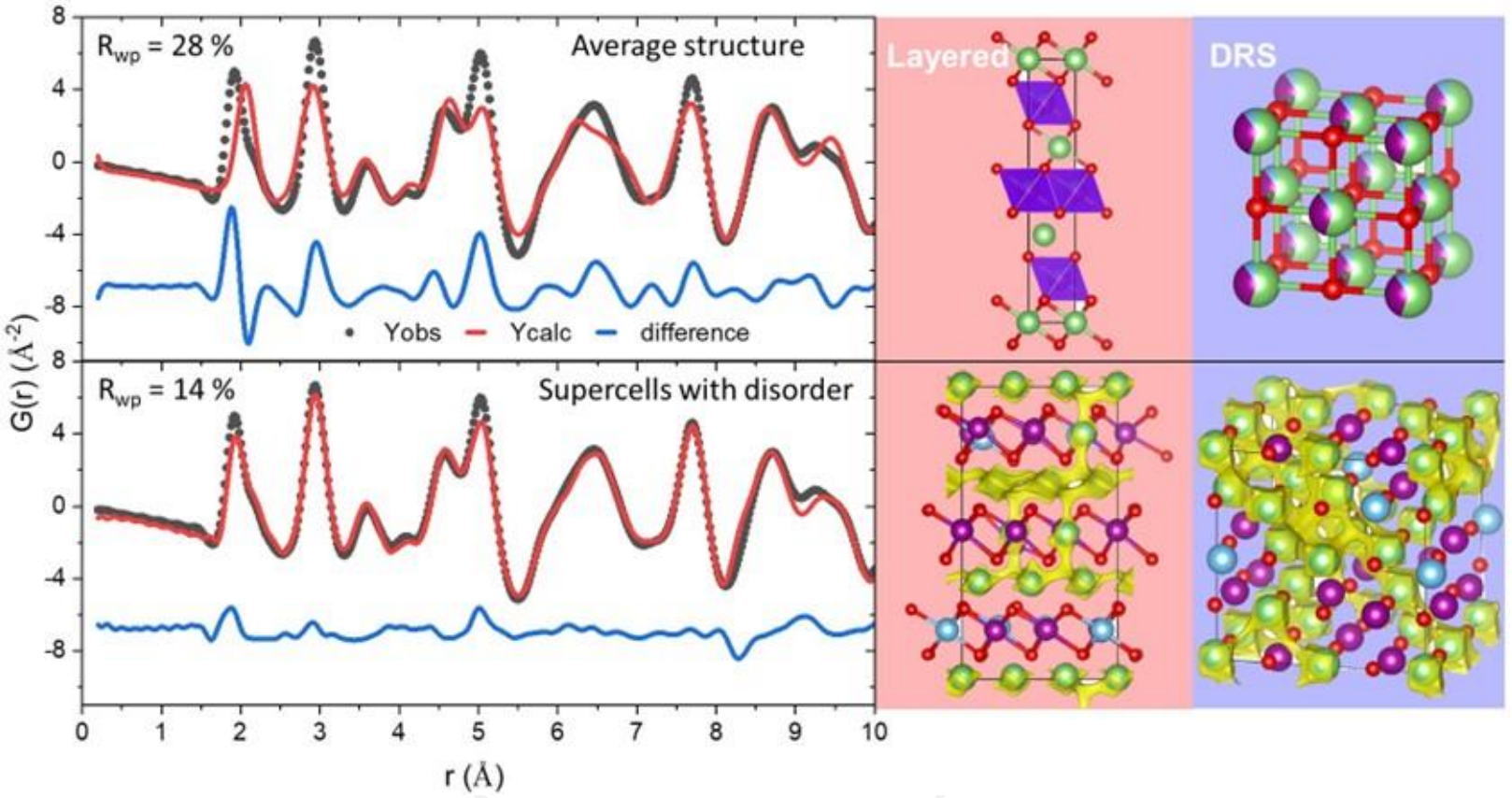




- MOF disorder gives a lot of their properties
- Understanding structures over physical properties unlocks information on tunability
- TIF-4 keeps it short range structure, even when fully melted
- PCA was used to understand what structure changes as a function of temperature

A. Sapnik *et al.,* *Nat. Comms.,* **13** (2022), 2173

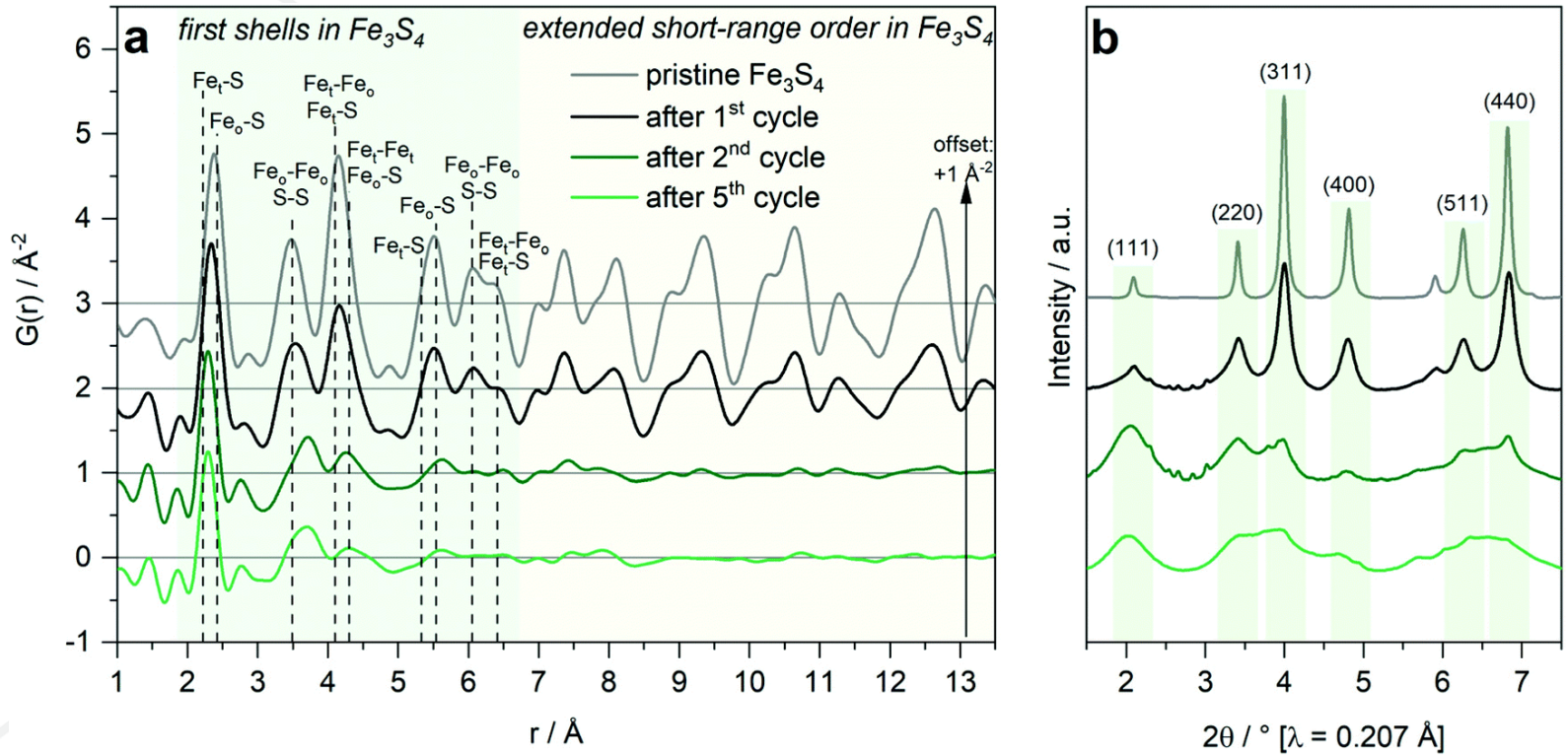
Battery Materials – Disordered Rock Salts



- Average structure achieved poor fit
- Introducing disorder allowed for much improved fit
- Li-disorder allows for high first charge capabilities

M Diaz-Lopez et al., ***J. Mater. Chem. A***, 2022,**10**, 17415-17423

Battery Materials – Fe_3S_4 nanoparticle & Na storage

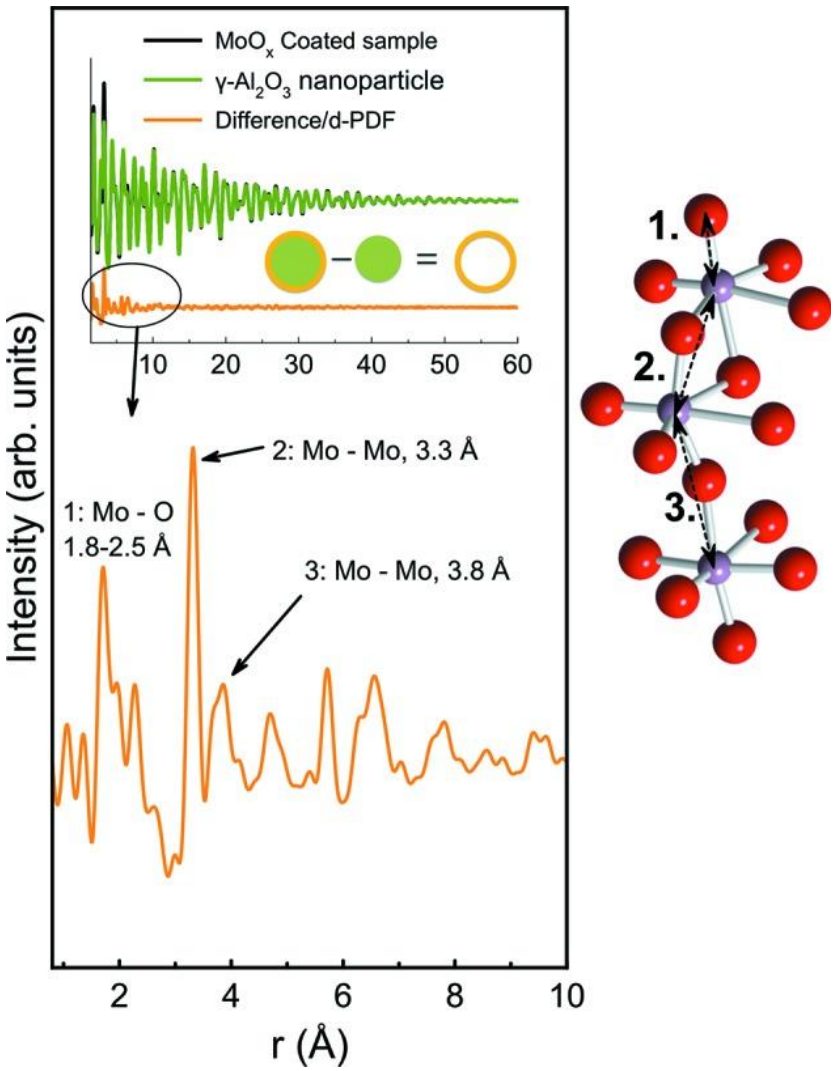


- Highlights the increasing loss of crystallinity after battery cycling, local structure remains
- Atom-atom correlations (Fe-S, S-S) are altered, observing an octahedral to tetrahedral local environment change
- Changes are reversible, and only observable via PDF due to nanoparticles

Hartmann et al., ***Nanoscale***, 2022,**14**, 2696-2710

Catalysis – MoO_X on Alumina Supports

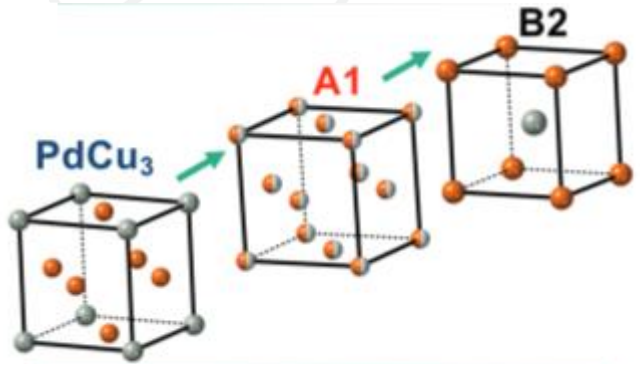
- Difficult to understand structure of the active material (MoO_X) when all scattering is dominated by alumina support
- By carefully measuring both elements, you can use differential PDF (dPDF) to extract more information
- Once alumina support has been subtracted, MoO_x octahedral cluster fragments can be found and often forming chains
- Changing the support changes the length of these chains

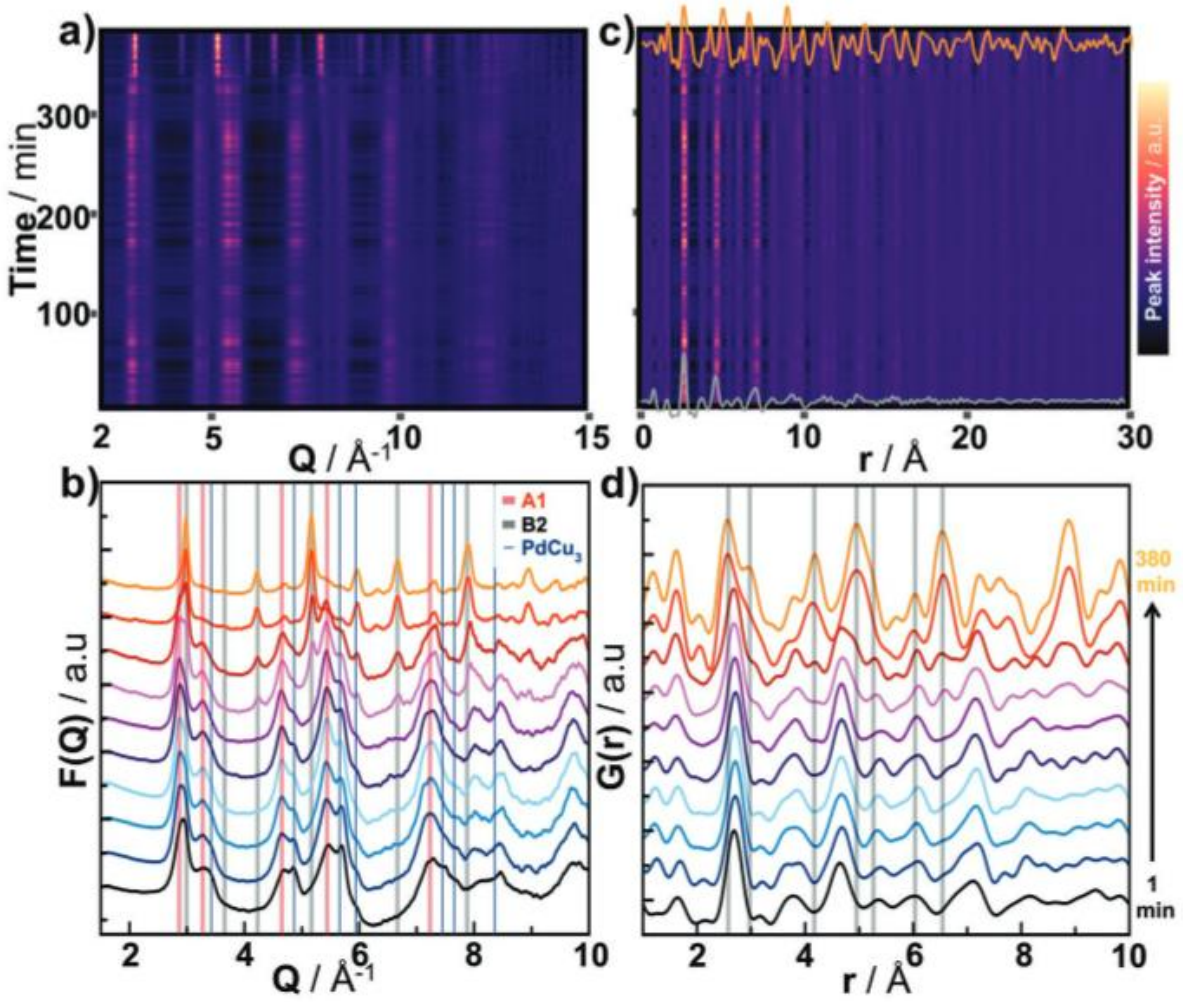


Christiansen et al**., J Appl Crystallogr**. 2020 Feb 1; 53(Pt 1): 148–158

Nanoparticles – $PdCu_3$ Hydrothermal Formation

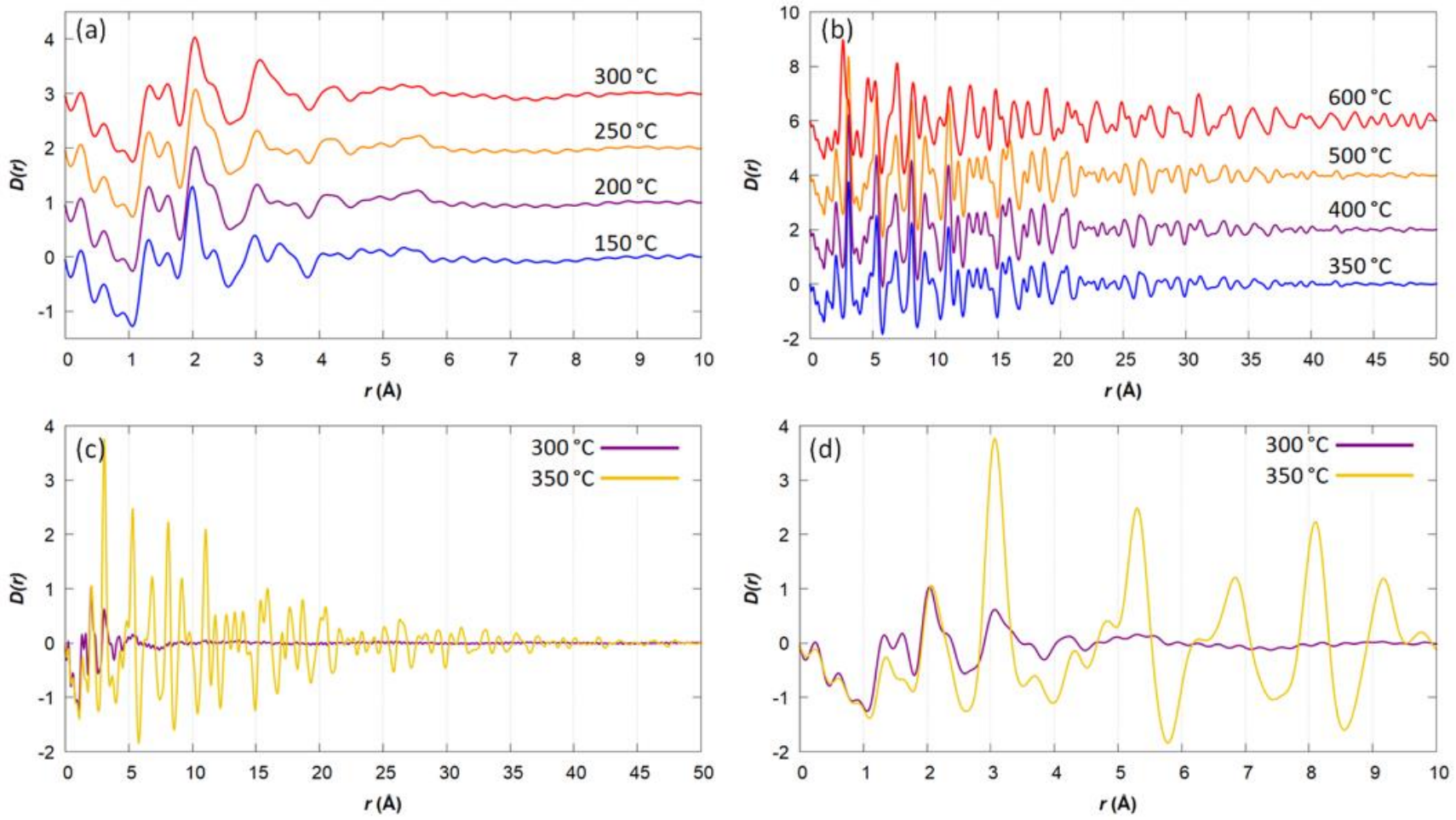
- Hard to characterise nanoparticles with XRD
- Shows the hydrothermal formation of $PdCu_3$ which unexpectedly goes through various intermediates
- Highlights PDF as being able to visualise this whilst unlocking previously unknown structures





J. K. Mathiesen et al., **Small Methods**, 6 (2022), 2200420

Nanoparticles – Sol-gel Fe_3C Synthesis

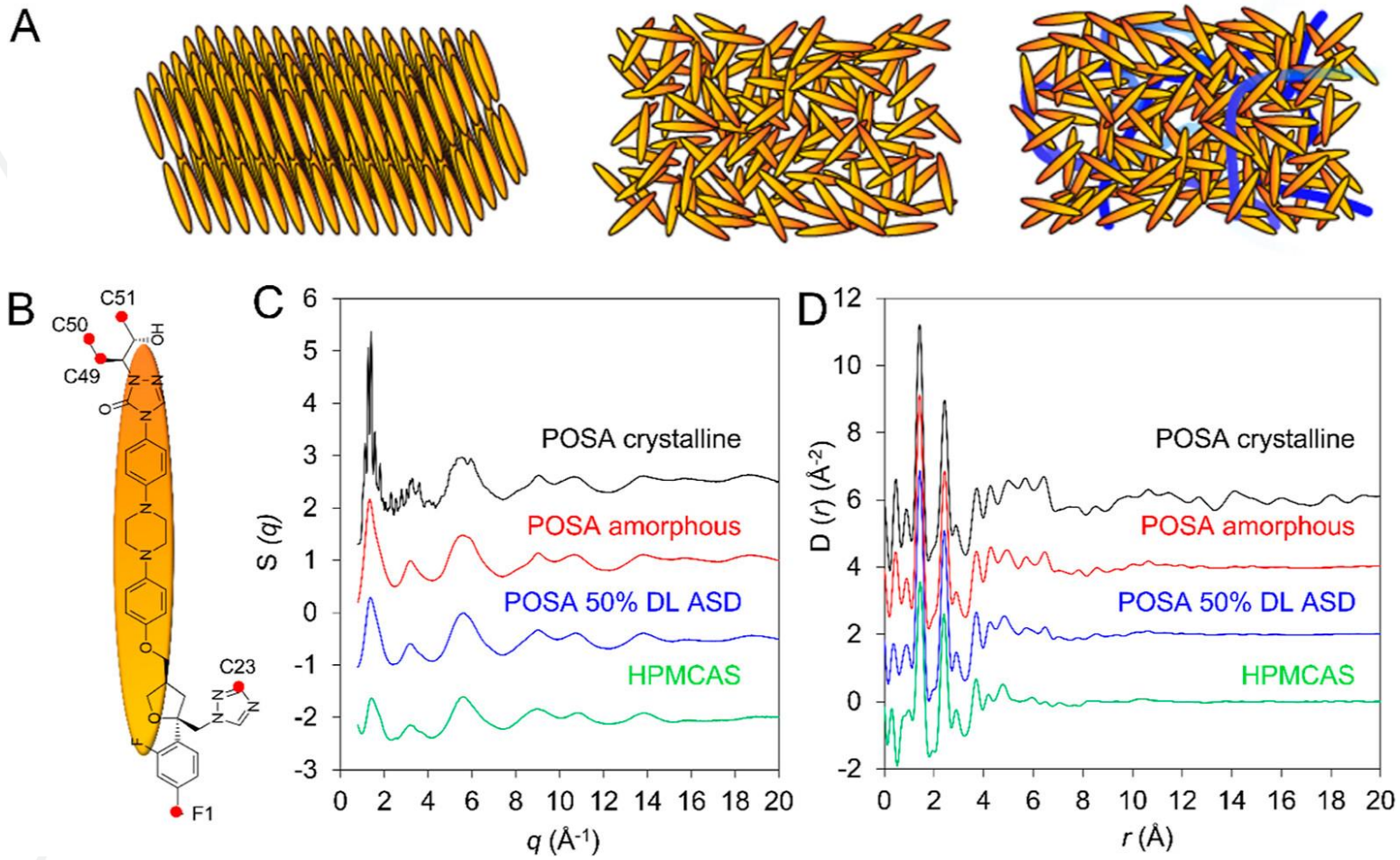


- Similar discovery of intermediate phases between amorphous Fe_3O_4 precursor and Fe_3C NPs
- FeO_X nanoparticle formation at ~350 °C
- Larger Fe_3N formation between 500-600 °C with some N/C substitution found via distortions

J. K. Mathiesen et al., **Small Methods**, 6 (2022), 2200420

Pharmaceuticals – Amorphous Pharm

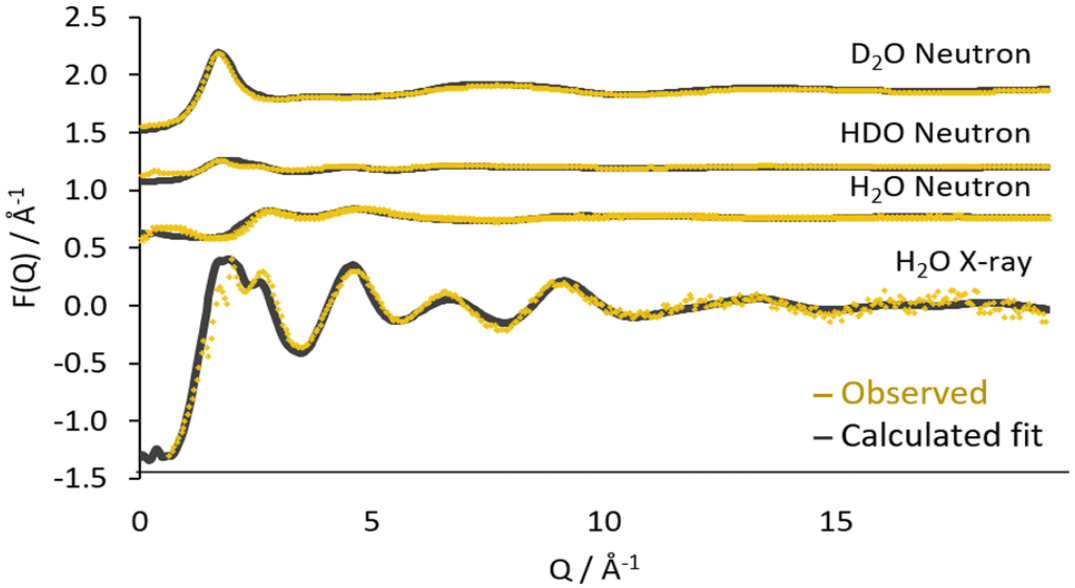
- Many modern developments in pharma have a focus on amorphous-solid dispersions forms due to increased solubility and bio uptake
- Posaconazole (POSA) is one such drug for fungal infections
- Understanding whether the drug has changed is crucial for safety
- This study found there is a rigid conformation of POSA and that the molecular structure does not change

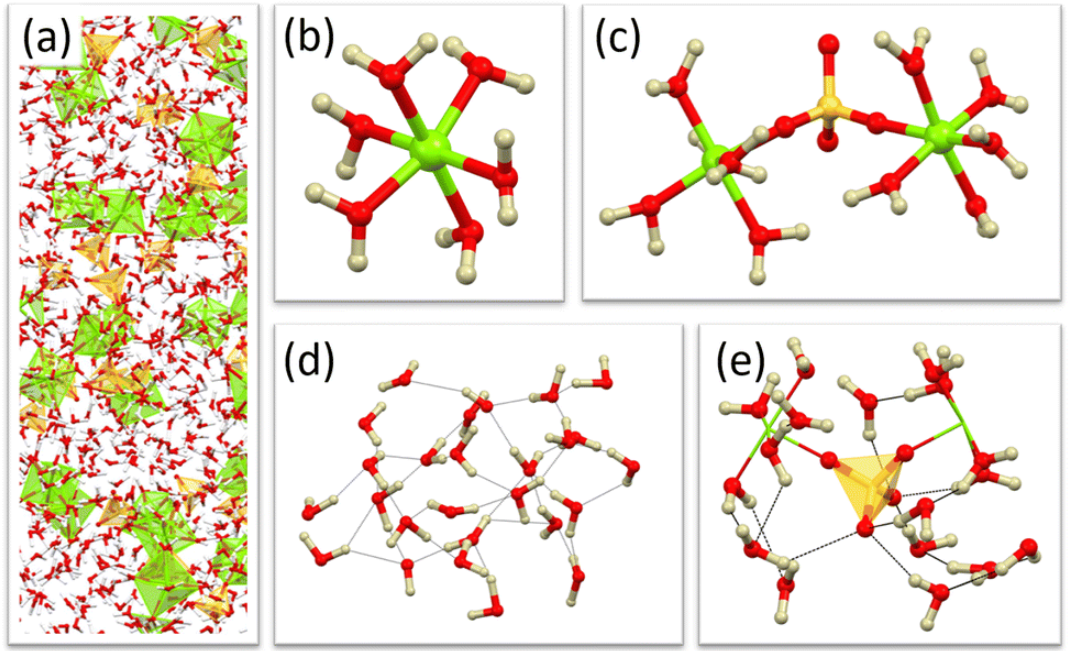


Chen et al., Molecular Pharmaceutics **2023** *20* (11), 5763-5777

Liquids – Aqueous $MgSO_4$ Structure

- Total scattering can also be used for fully disordered systems, such as salts in water
- Combination X-ray/neutron study using large-box modelling elucidated structure in a fully disordered system
- Observation of octahedral MgO_6 ($Mg\text{-}H_2O/SO_4$) structures
- Observation of longer-range chains and rings

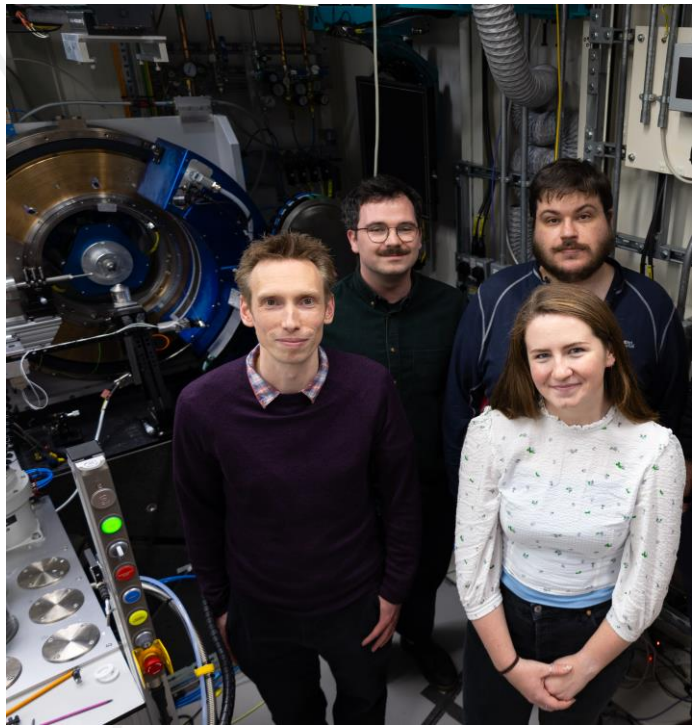




Irving et al., **Phys. Chem. Chem. Phys**., 25 (2023), 14898 - 14906

Thank you for your attention!

e-mail: xpdf@diamond.ac.uk



Twitter: @xpdfdls

Any Questions?