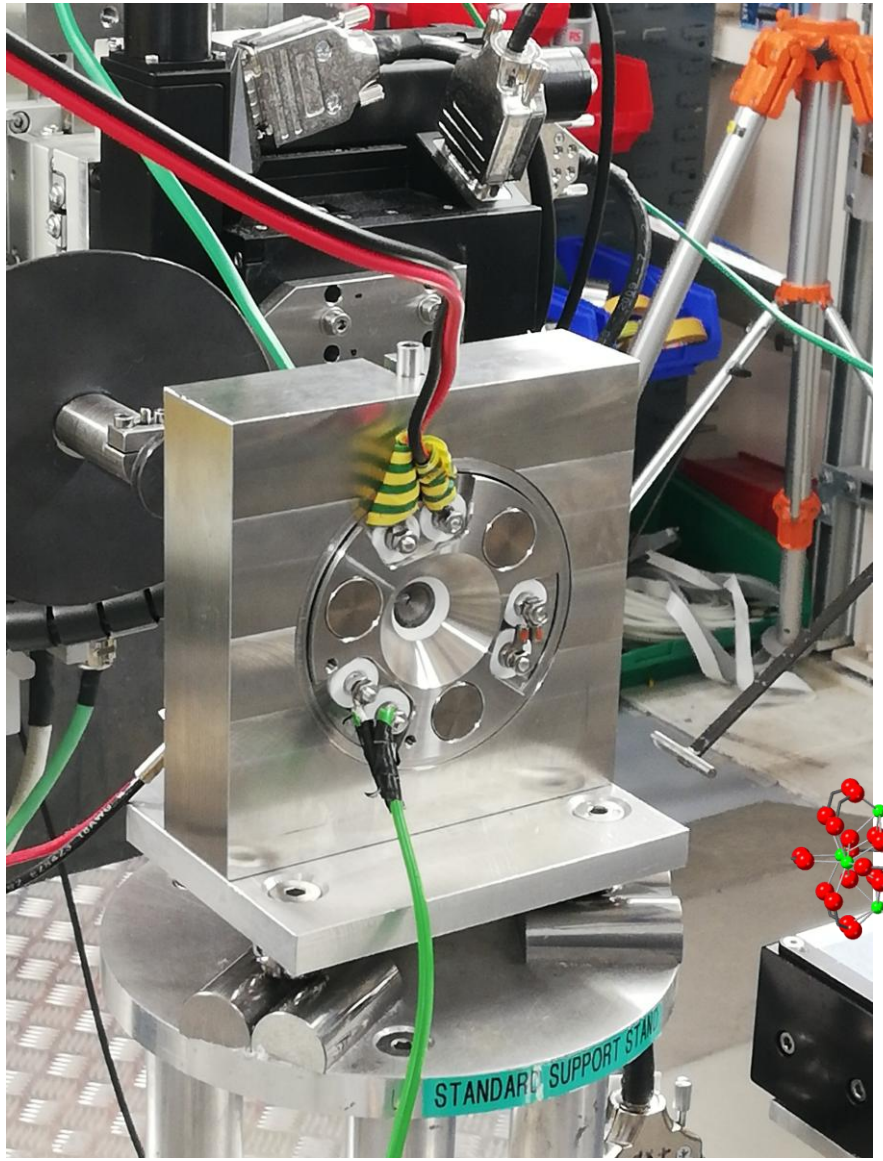

Challenges in XPDF Analysis of High Pressure-Temperature Metal-Organic Frameworks

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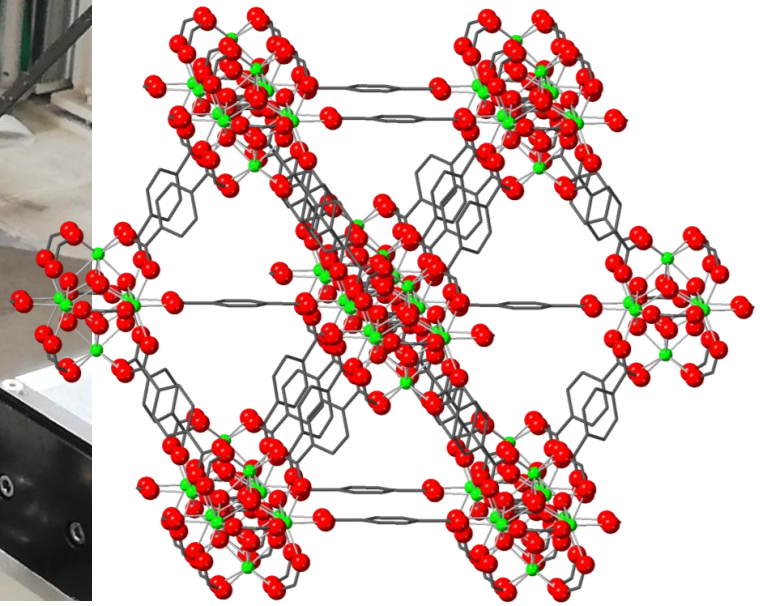
Georgina Robertson



PIONEERING SYNCHROTRON SCIENCE

ESRF
The European Synchrotron

30 years of science

CONTENTS

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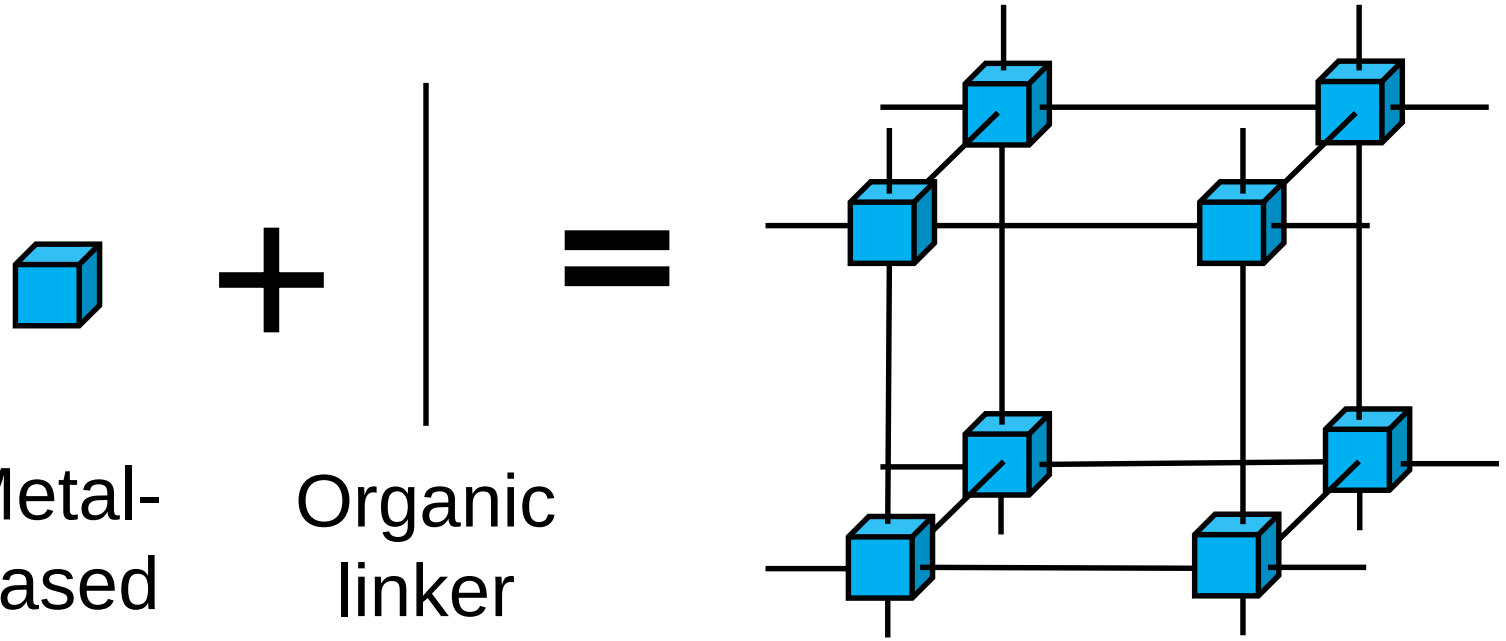
METAL-ORGANIC FRAMEWORKS

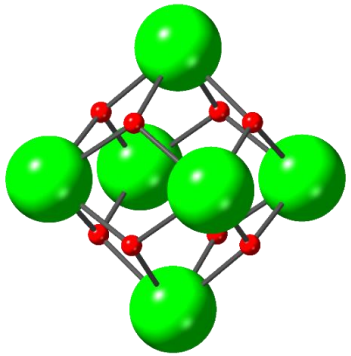


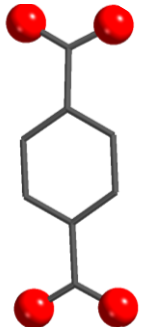
Metal-based node

Organic linker

MOF unit cell, simplified

METAL-ORGANIC FRAMEWORKS





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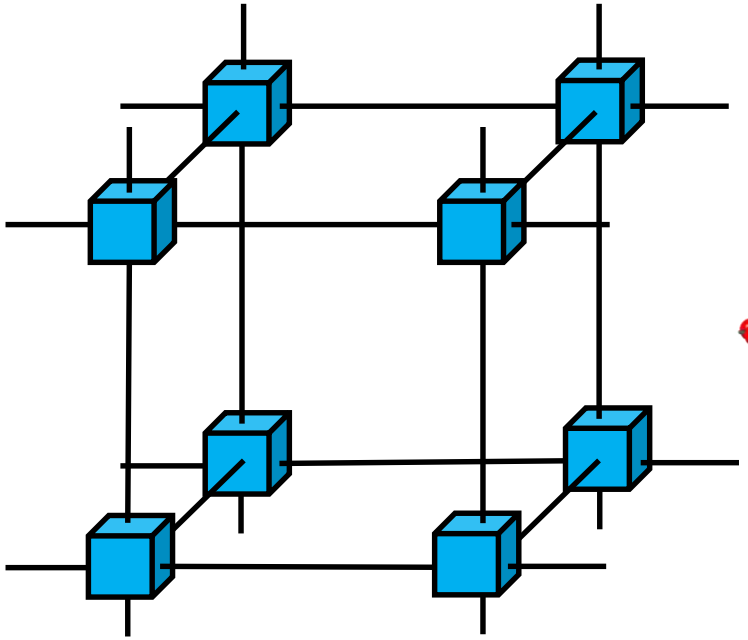
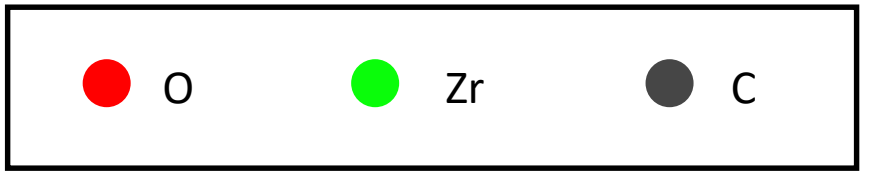
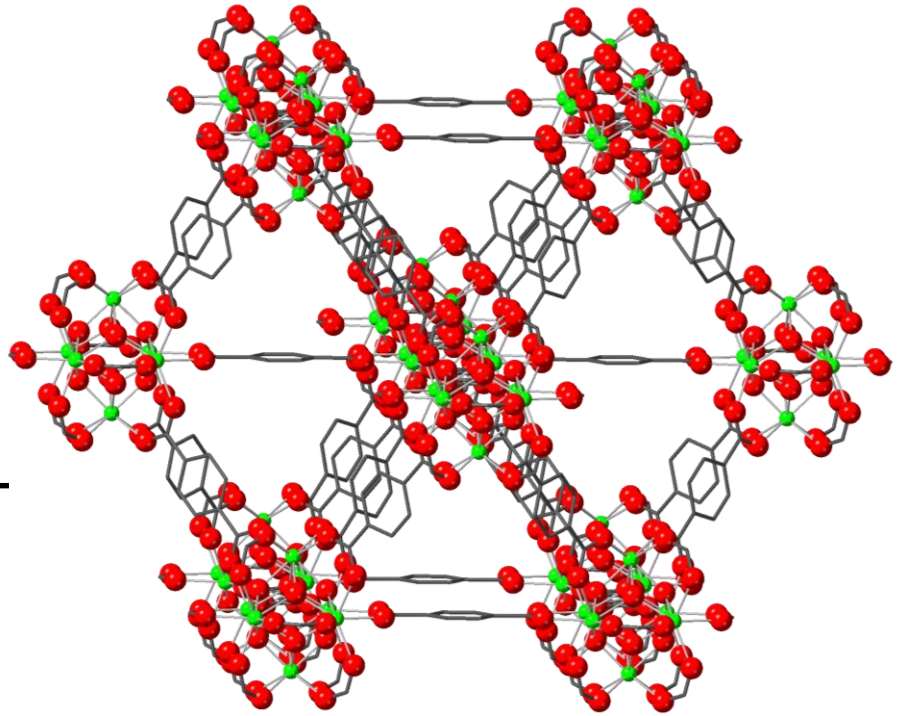
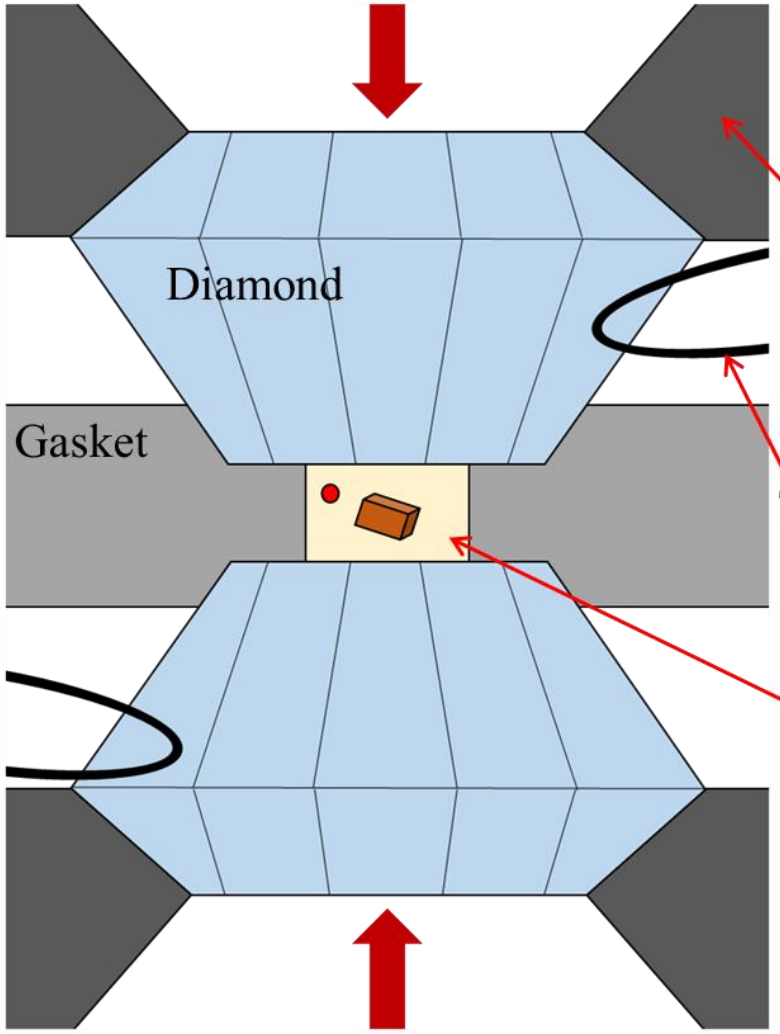


MOF unit cell, simplified





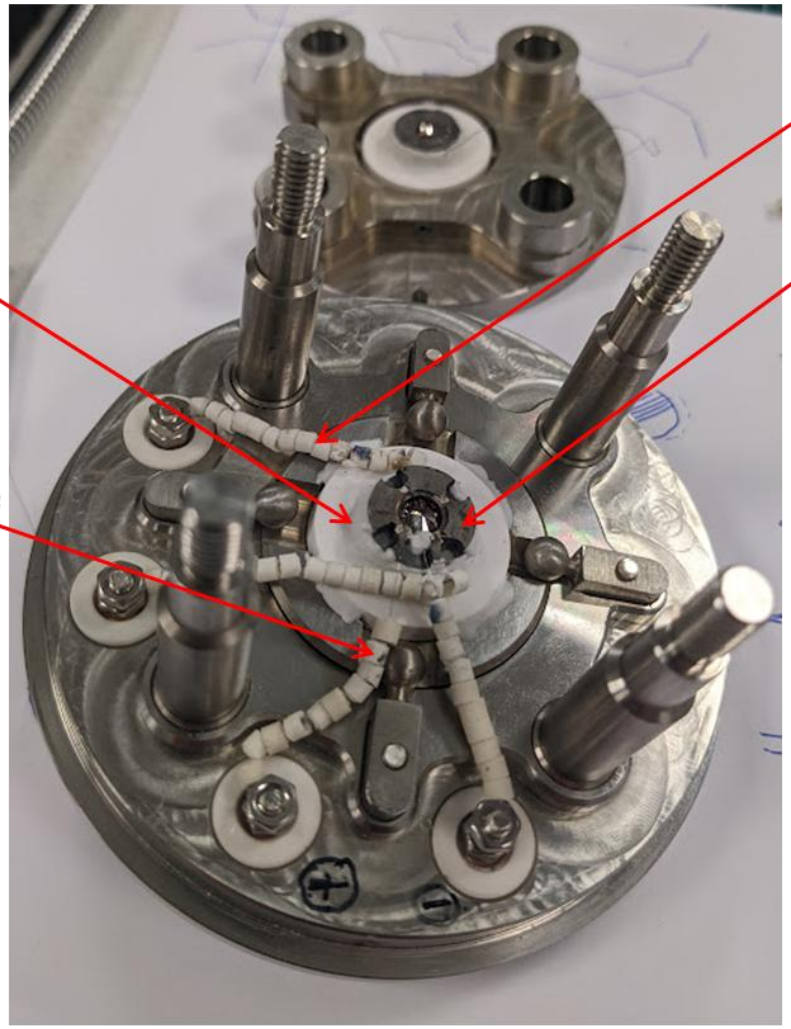
HIGH PRESSURE SETUP



Diamond seat

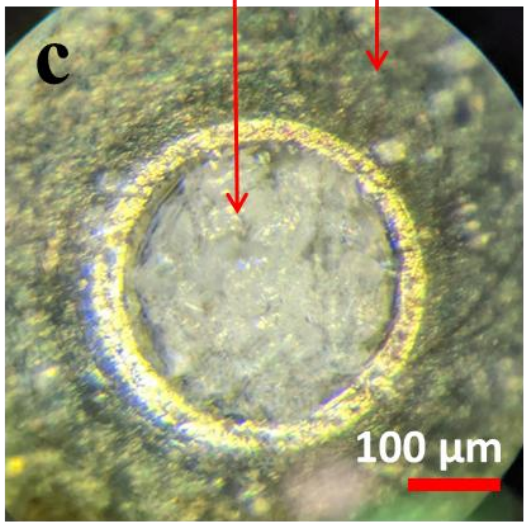
Thermocouple

Sample + PTM + calibrant



Power supply

Gasket holder



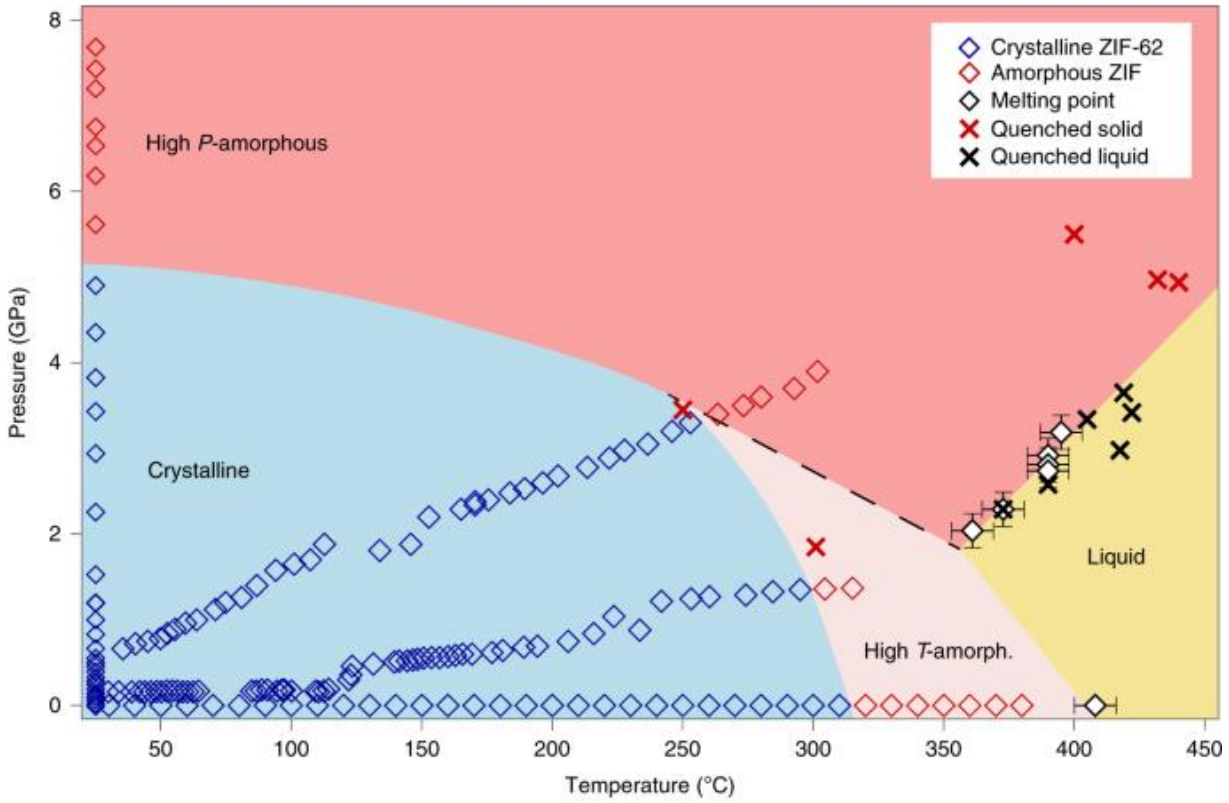
CHALLENGES

Challenges:

1. Metal-organic framework
   a. Low scattering
   b. PTM effect on structure

2. High pressure/temperature setup
   a. ‘Equilibrating’ the system
   b. Beam path clutter
   c. Changes in geometry

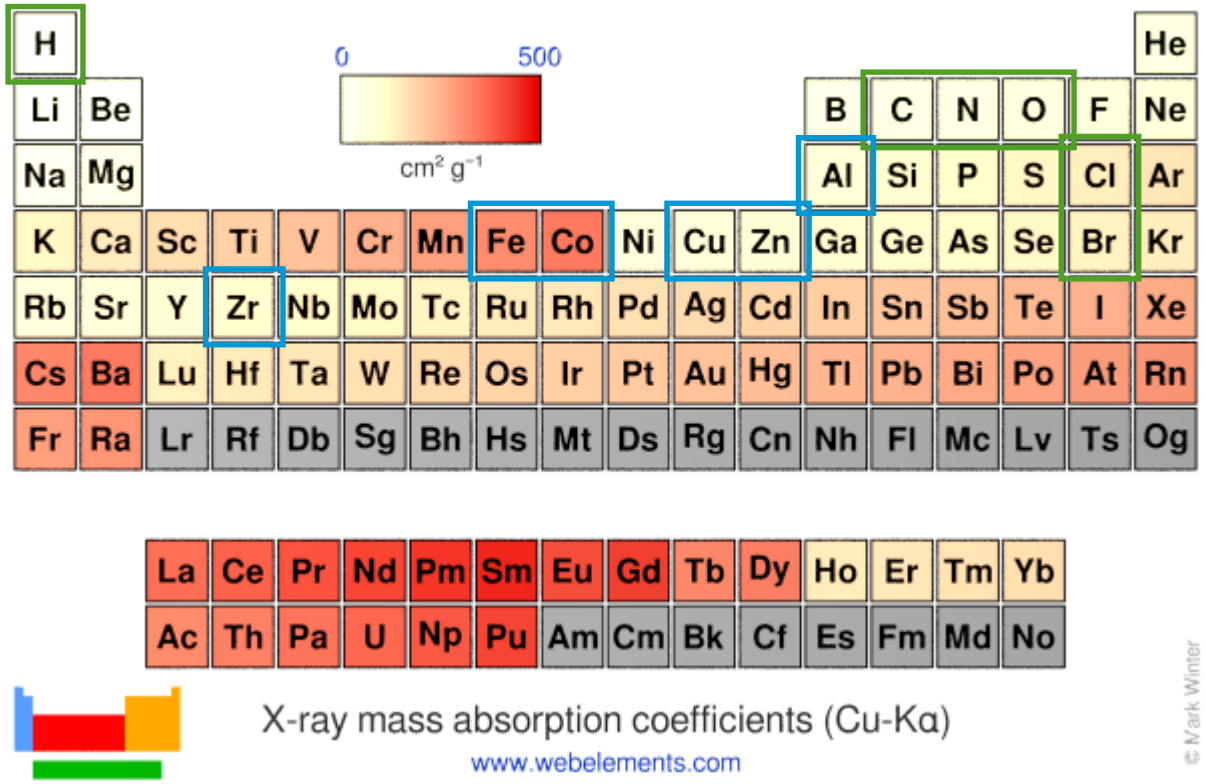
3. Processing & Analysis
   a. Processing software
   b. Phase purity
   c. Choosing a background
   d. Processing a series
   e. Isolating PTM effects

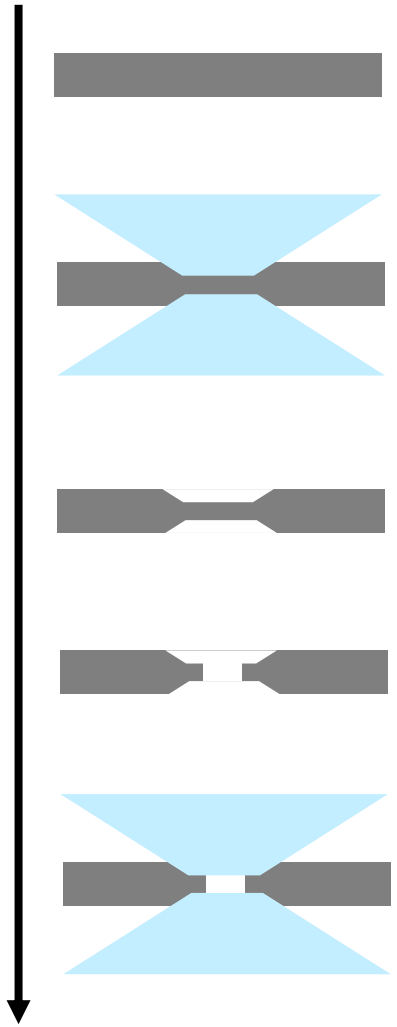


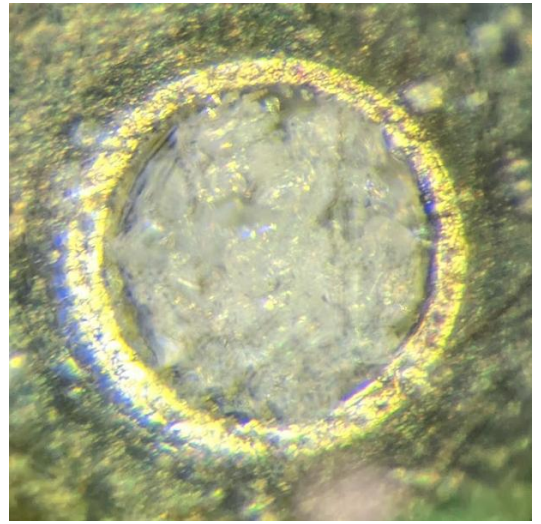
Phase diagram of ZIF-62 (Zn and imidazole-based framework)

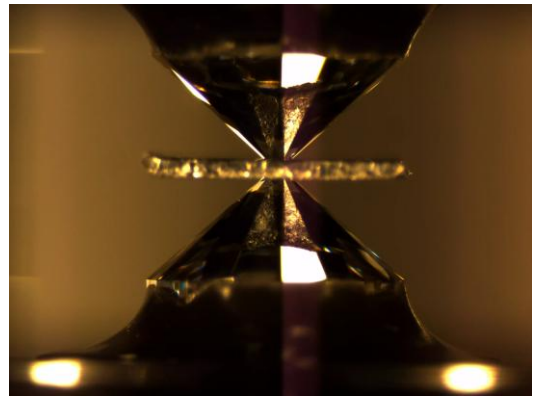
Widmer et al. ***Pressure promoted low-temperature melting of metal-organic frameworks.*** *Nature Materials, 2019, 18, 4, 370-376*

LOW SCATTERING OF MOFS









serc.carleton.edu/NAGTWorkshops/mineralogy/mineral_physics/diamond_anvil.html

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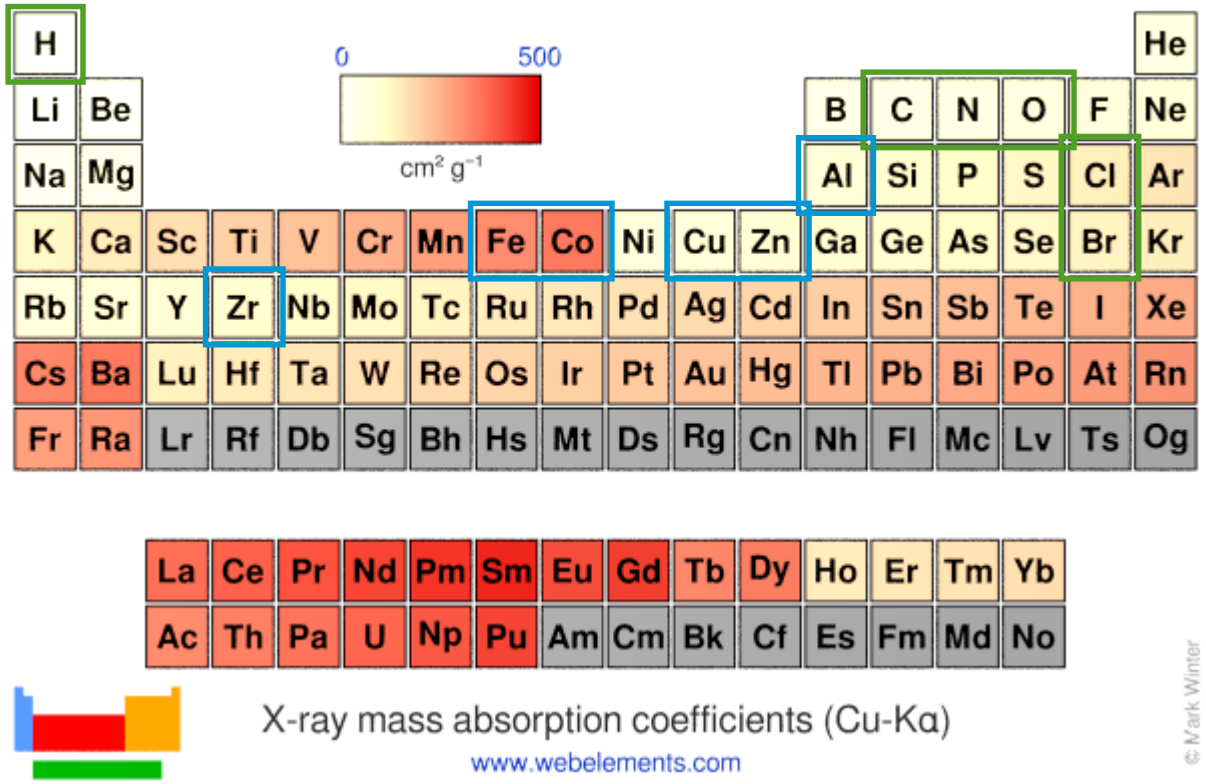
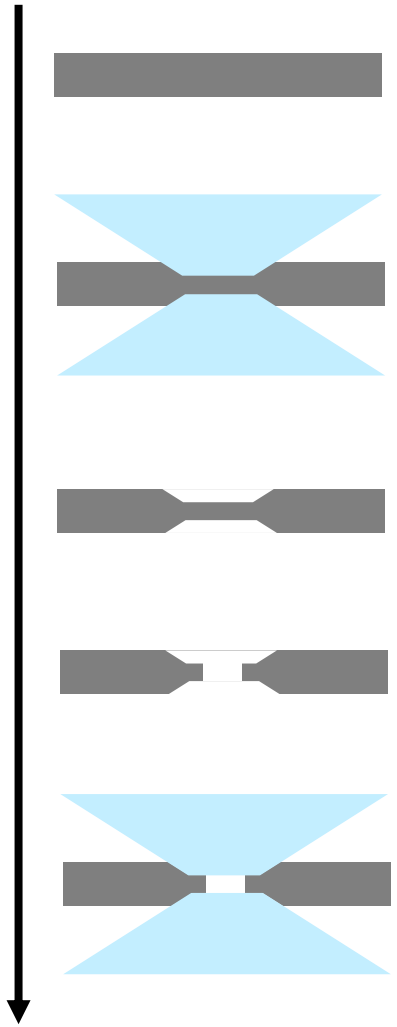
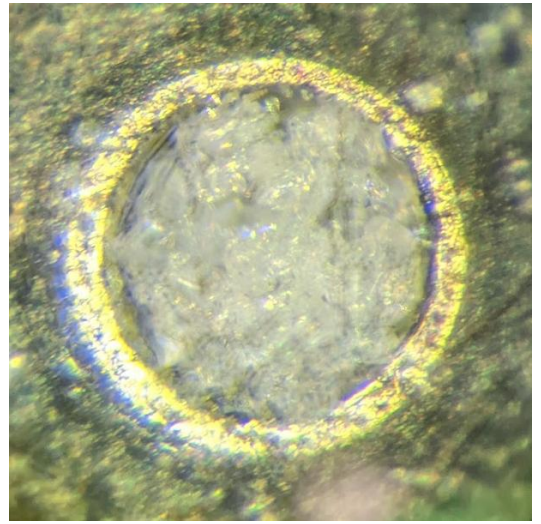
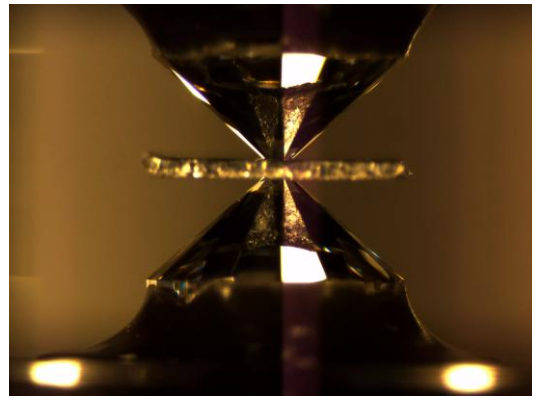
LOW SCATTERING OF MOFS









serc.carleton.edu/NAGTWorkshops/mineralogy/mineral_physics/diamond_anvil.html

Solution: More sample in the beam path

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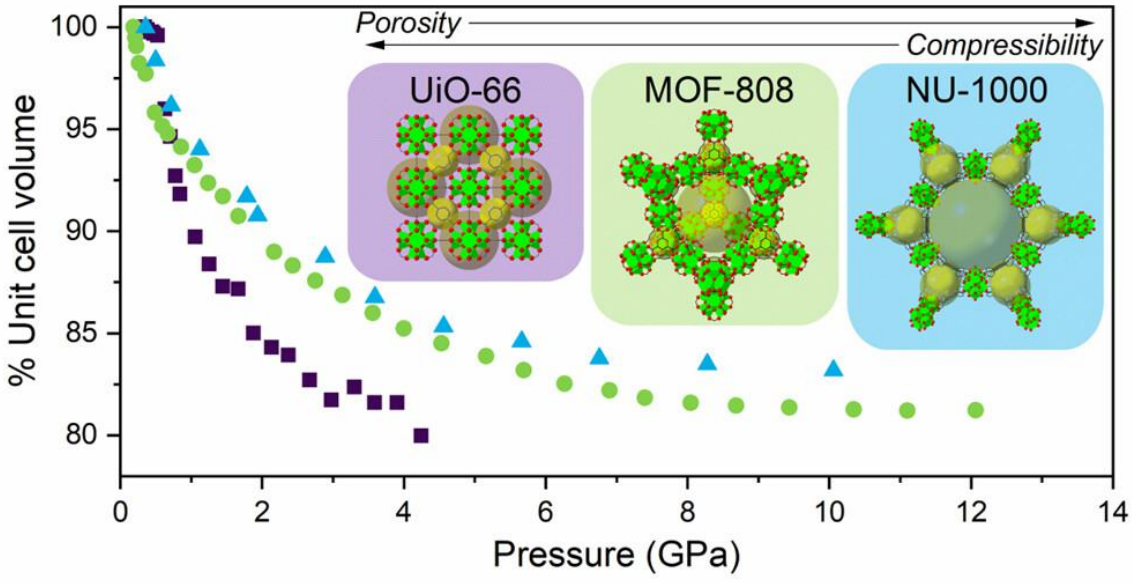
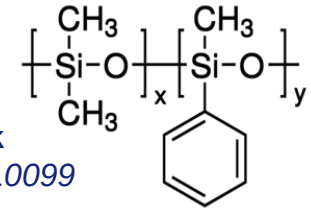
PTM EFFECT ON MOF STRUCTURE

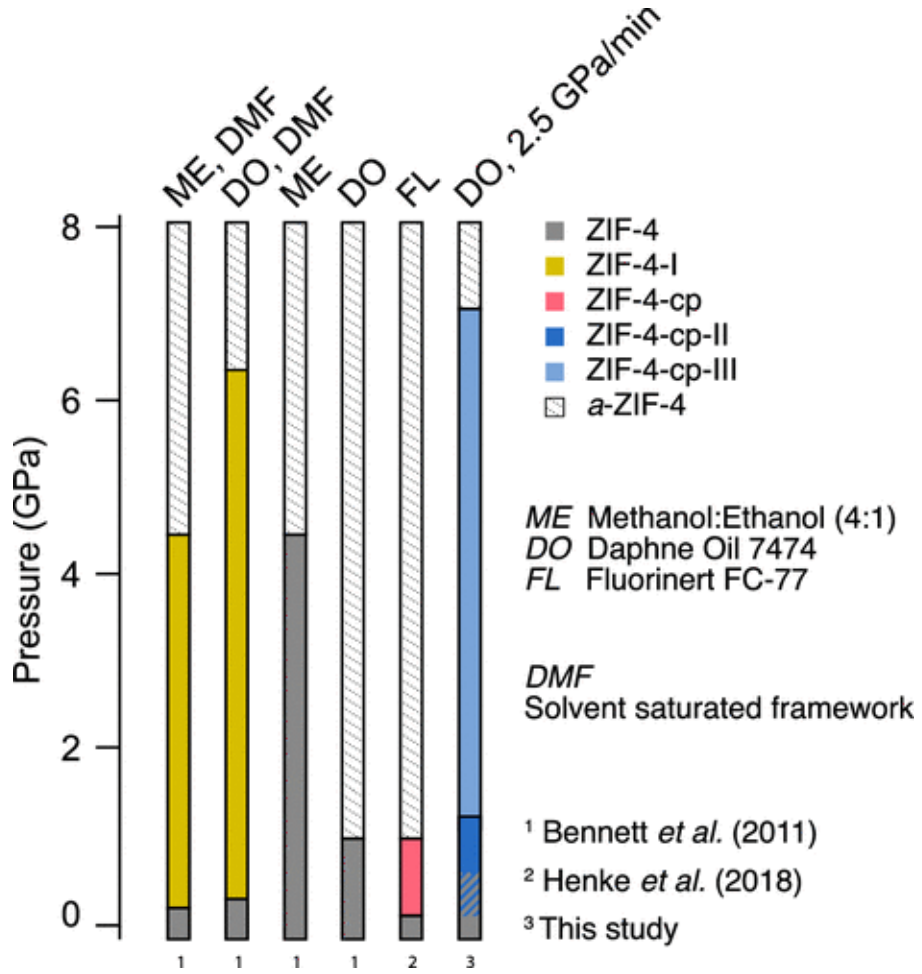
Effect on:

- Pressure thresholds of phase transitions
- Phases formed
- Compressibility





Robertson et al. **Survival of Zirconium-Based Metal–Organic Framework Crystallinity at Extreme Pressures.** *Inorganic Chemistry, 2023, 62, 26, 10092-10099*



Widmer et al. **Rich Polymorphism of a Metal–Organic Framework in Pressure–Temperature Space.** *J. Am. Chem. Soc. 2019, 141, 23, 9330-9337*

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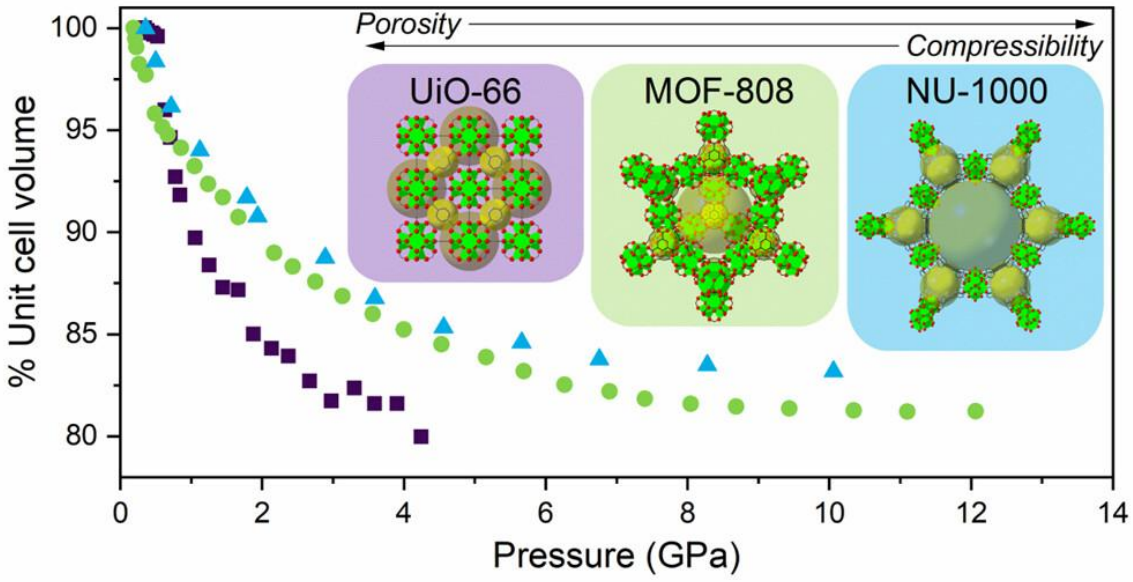

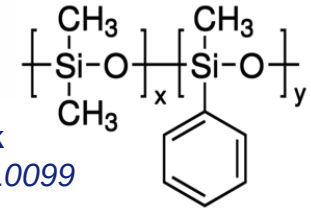

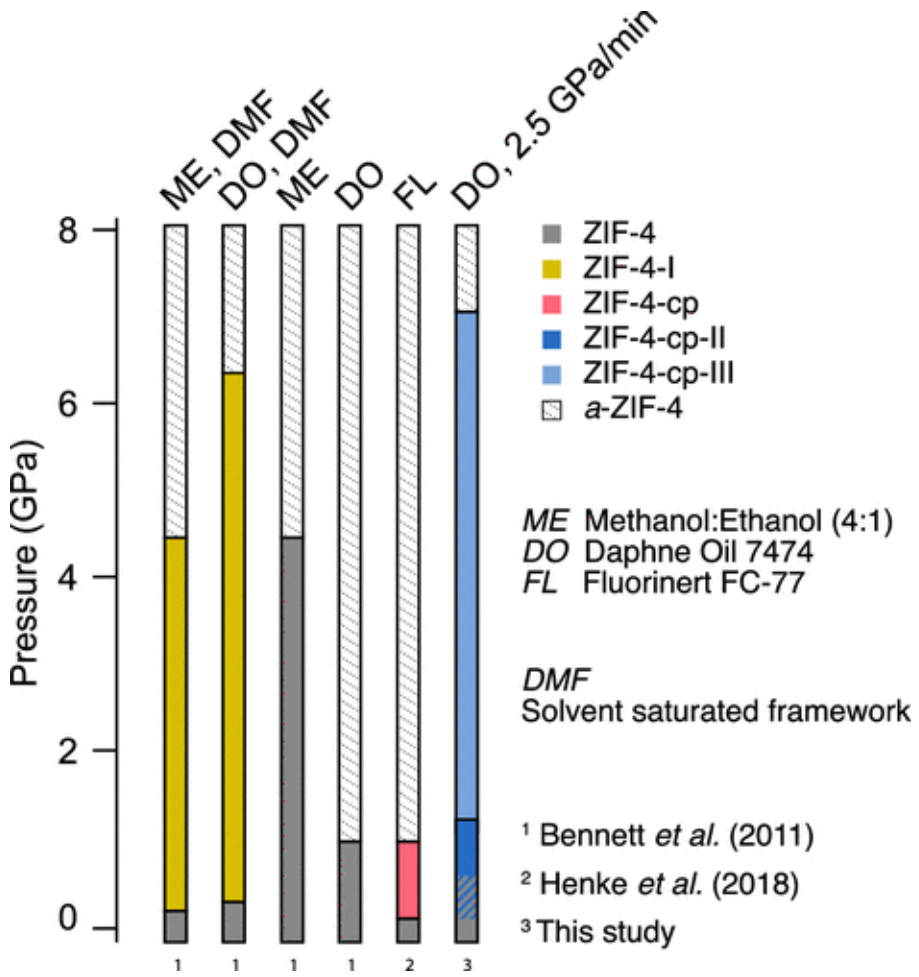

Widmer et al. **Rich Polymorphism of a Metal–Organic Framework in Pressure–Temperature Space.** *J. Am. Chem. Soc. 2019, 141, 23, 9330-9337*

Solution: Careful selection and testing of PTM

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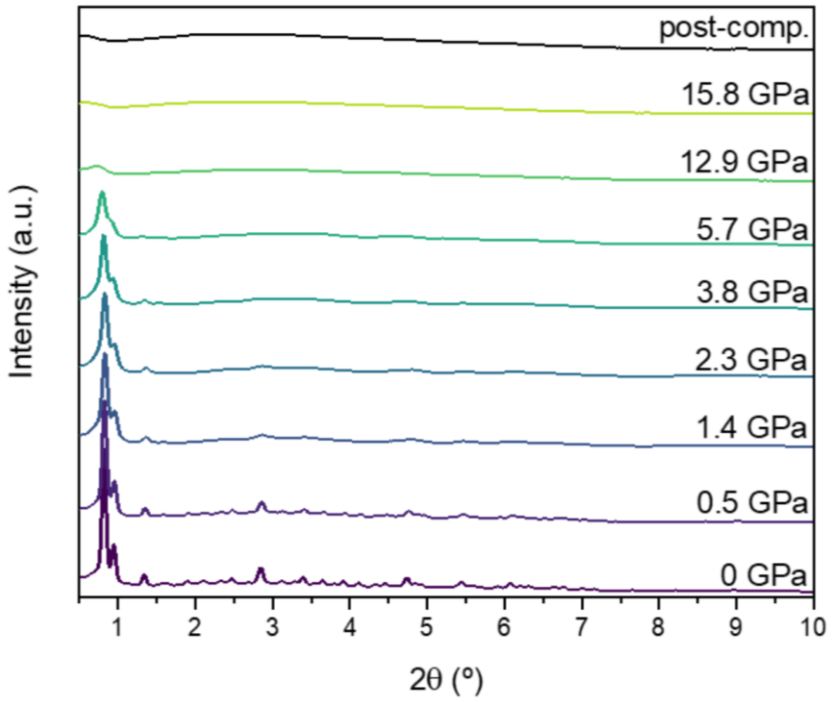
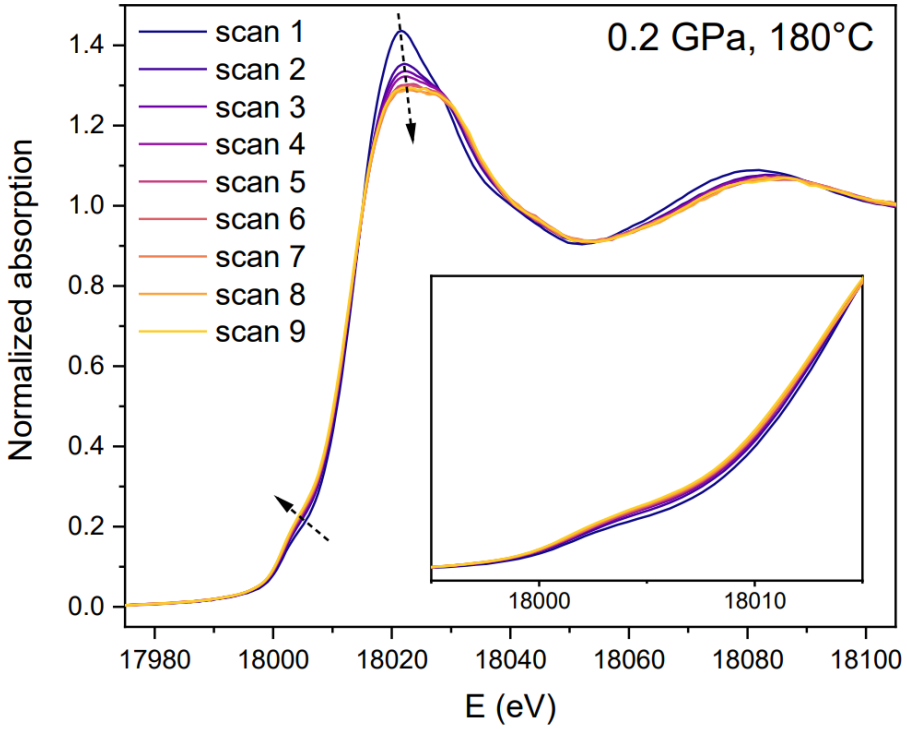
‘EQUILIBRATING’ THE SYSTEM



XRD data for UiO-66 at high pressure, 1 hour per measurement

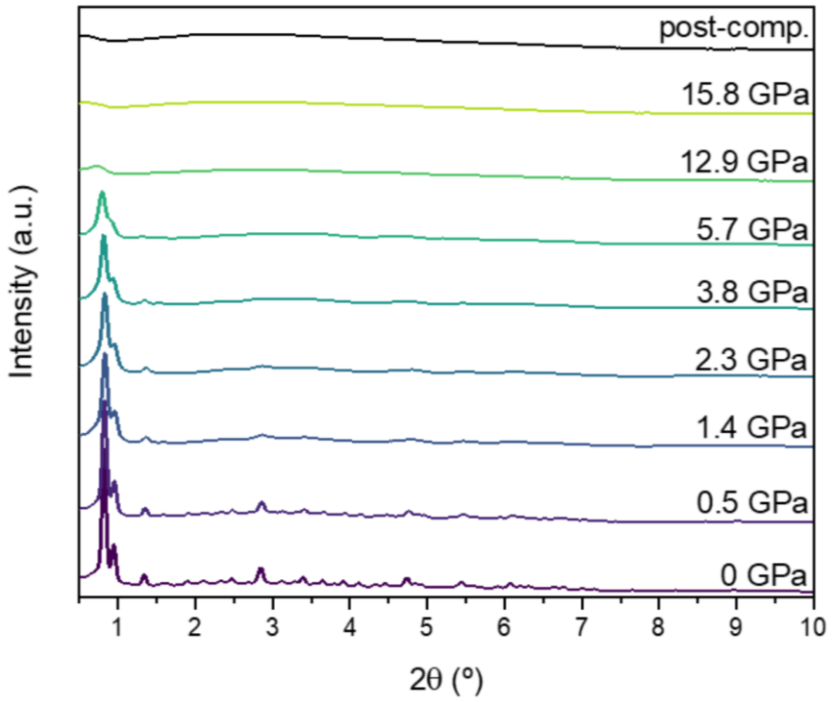
P before (GPa)	P after (GPa)	
0	0	=
0.4	0.47	↑
1.28	1.42	↑
2.07	2.34	↑
3.81	3.81	=
5.59	5.68	↑
12.69	12.86	↑
15.84	-	
1.23	-	

- Kinetic effects within the sample
- Deformation of the high pressure chamber



XANES data for UiO-66 at high pressure-temperature conditions, 30 min per scan

‘EQUILIBRATING’ THE SYSTEM



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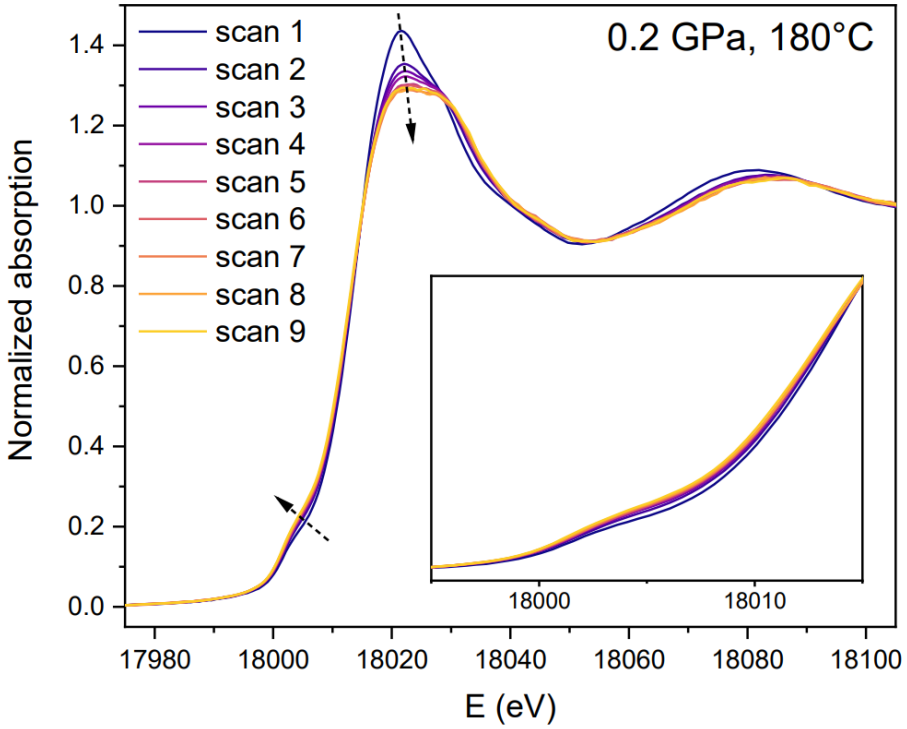
Solution: Test the equilibration time and allow it

- Kinetic effects within the sample
- Deformation of the high pressure chamber



XANES data for UiO-66 at high pressure-temperature conditions, 30 min per scan

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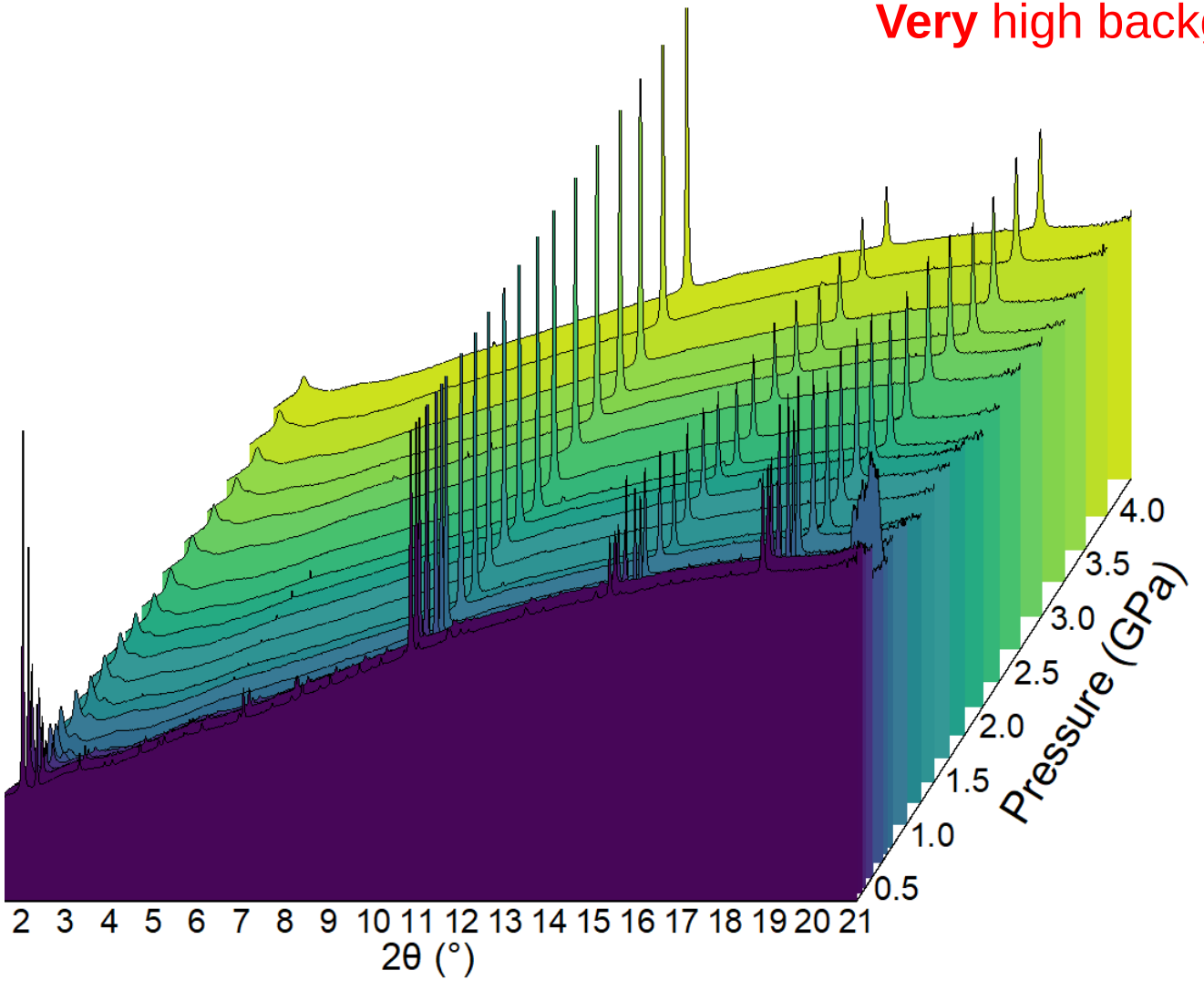
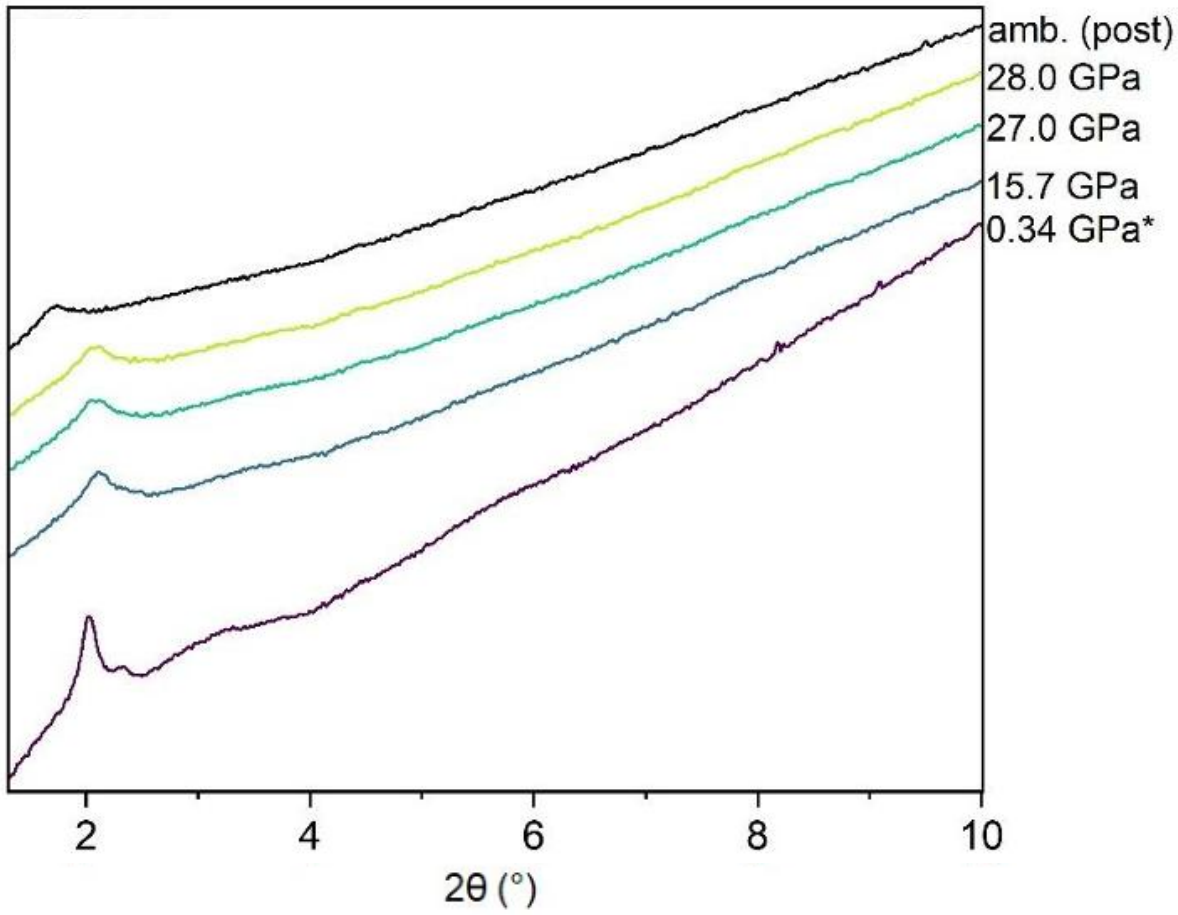
BEAM PATH CLUTTER

Very high background





BEAM PATH CLUTTER

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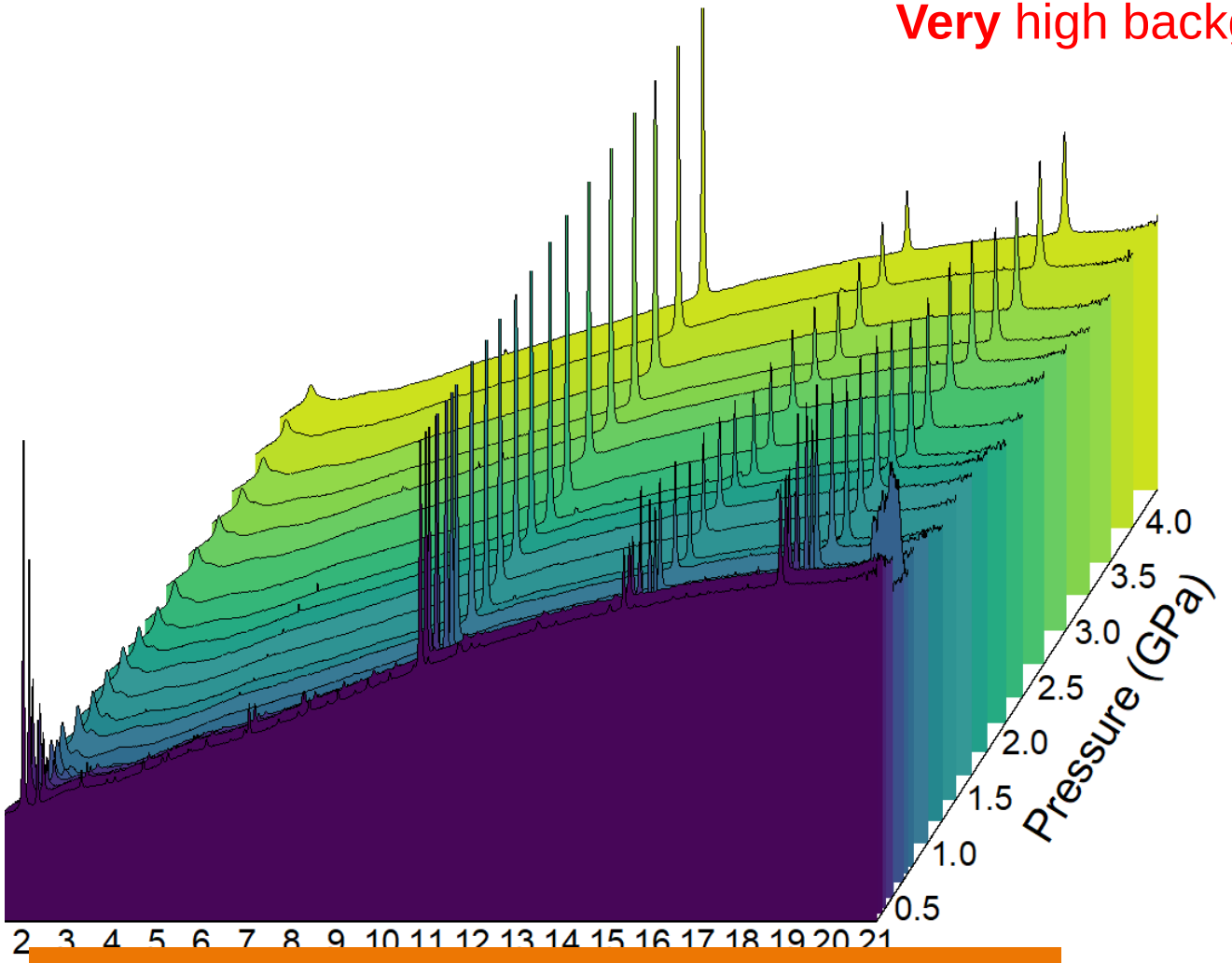
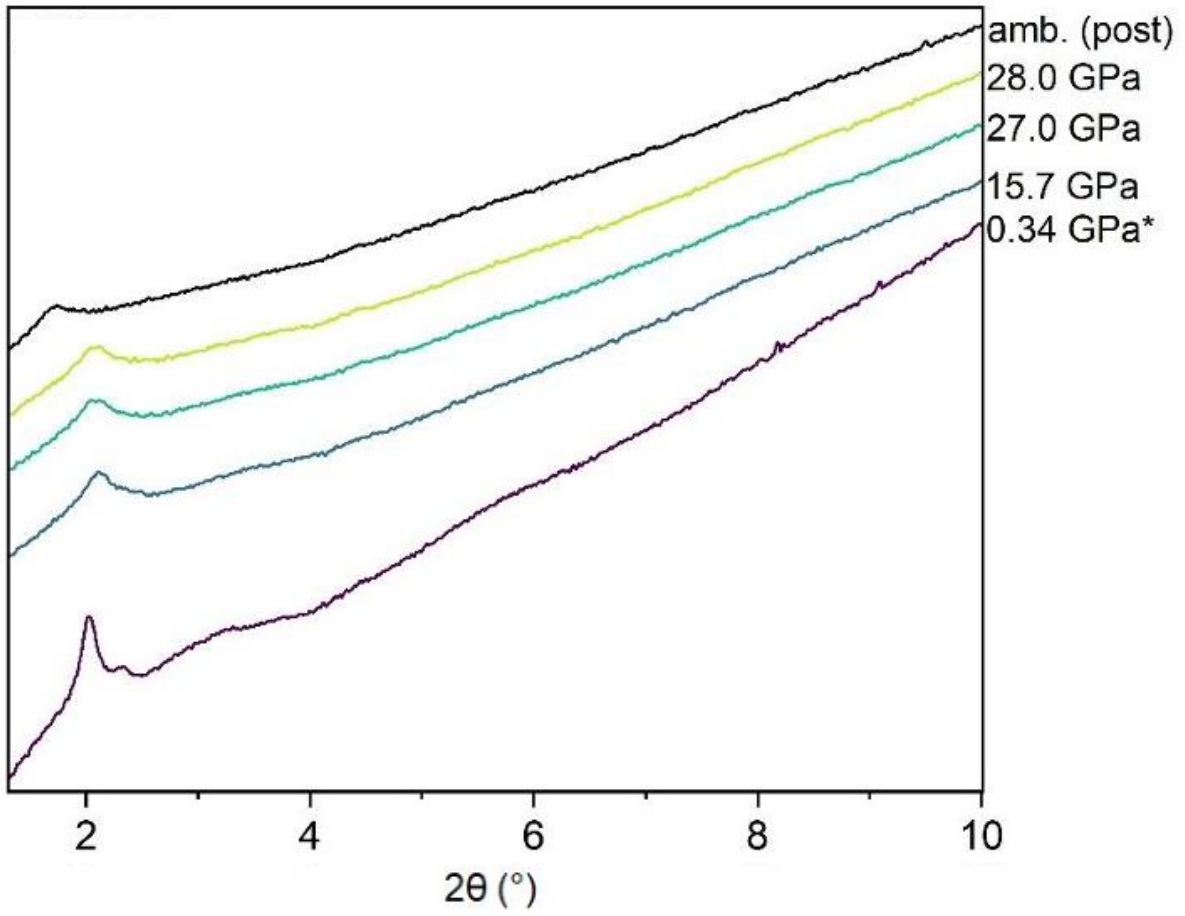
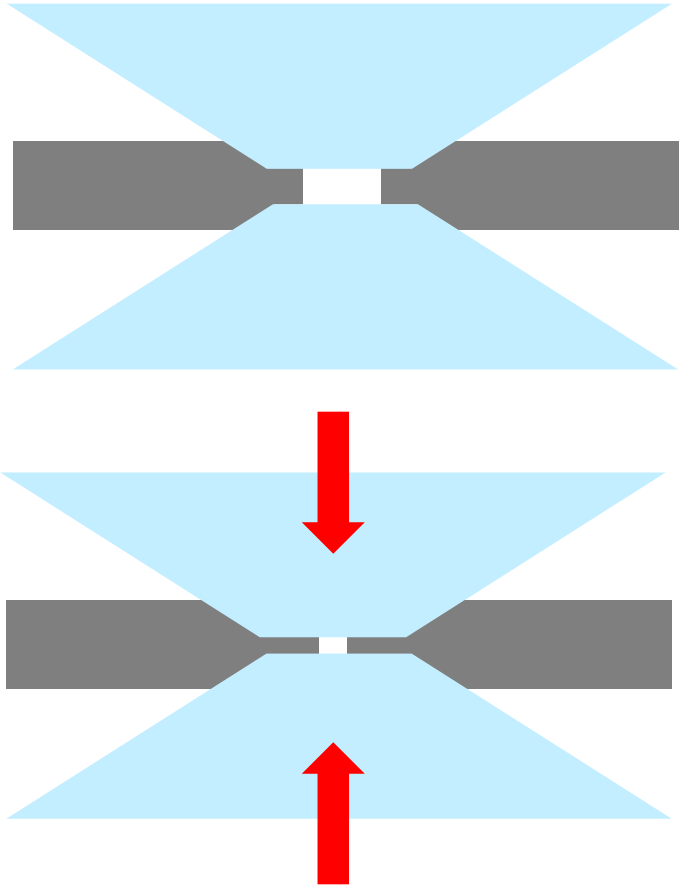


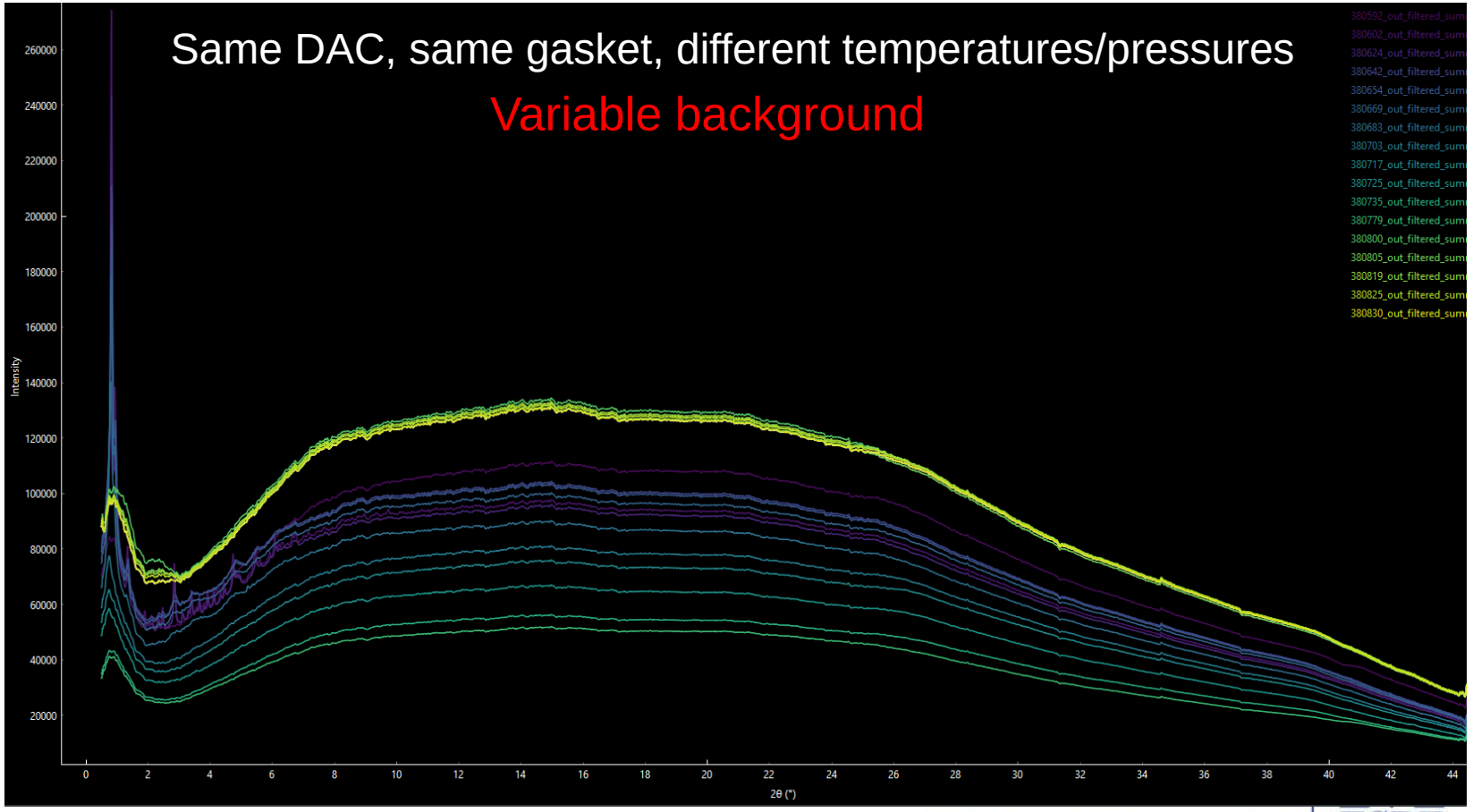


Solution: ?

CHANGES IN GEOMETRY

- Soft materials, changes in pressure and temperature
- Downside of a large sample chamber (i.e. thick gasket)





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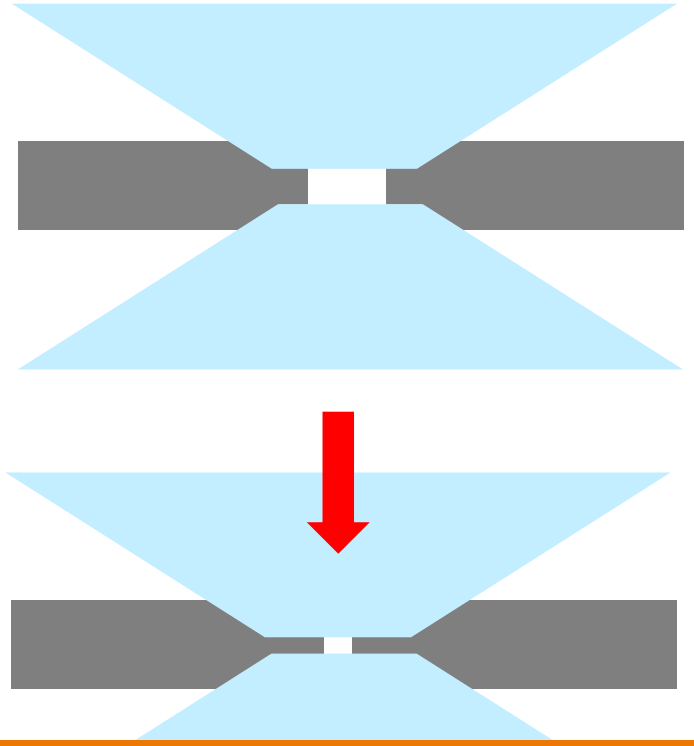
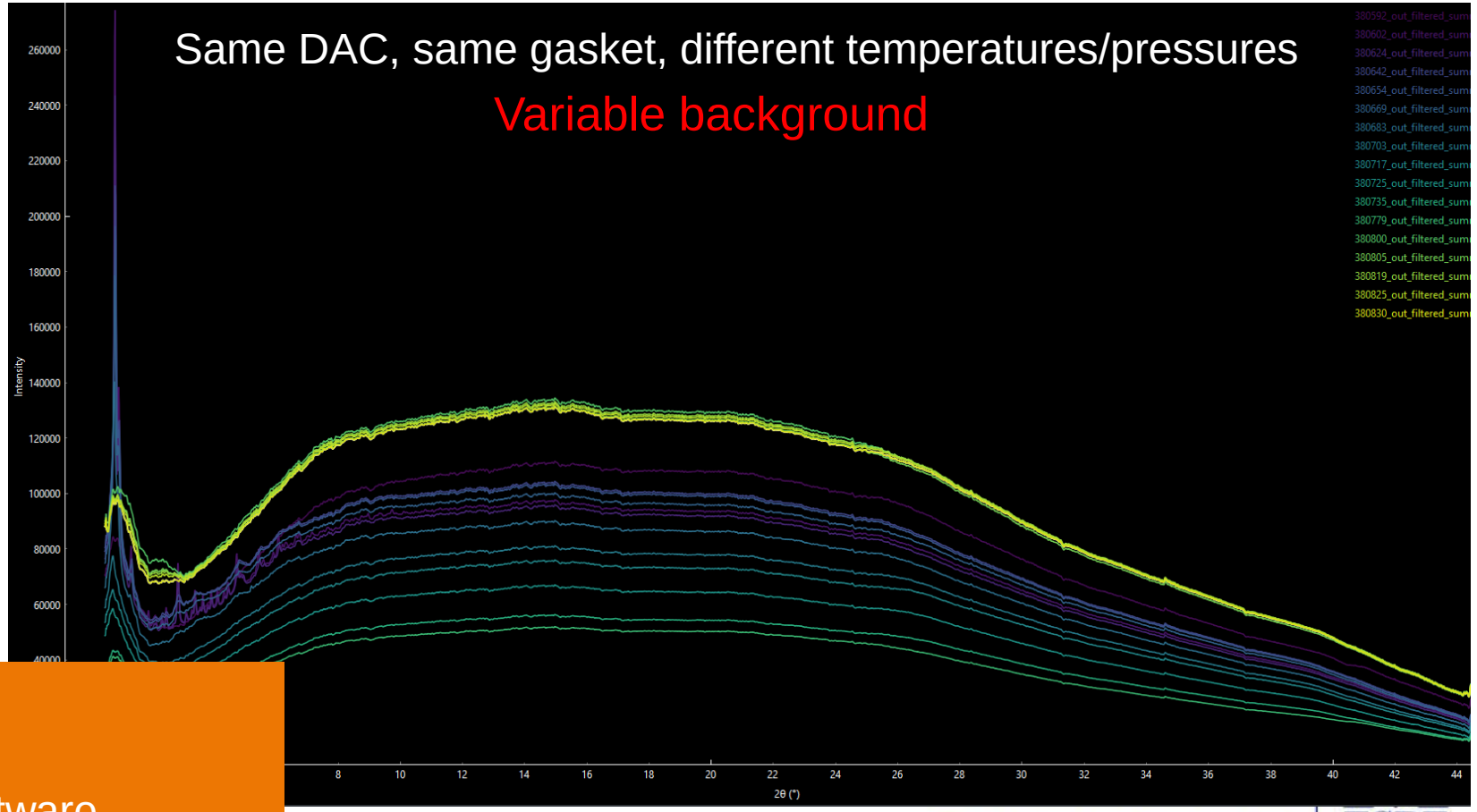




Solutions:
Hard gasket material
Selection of processing software

PROCESSING SOFTWARE

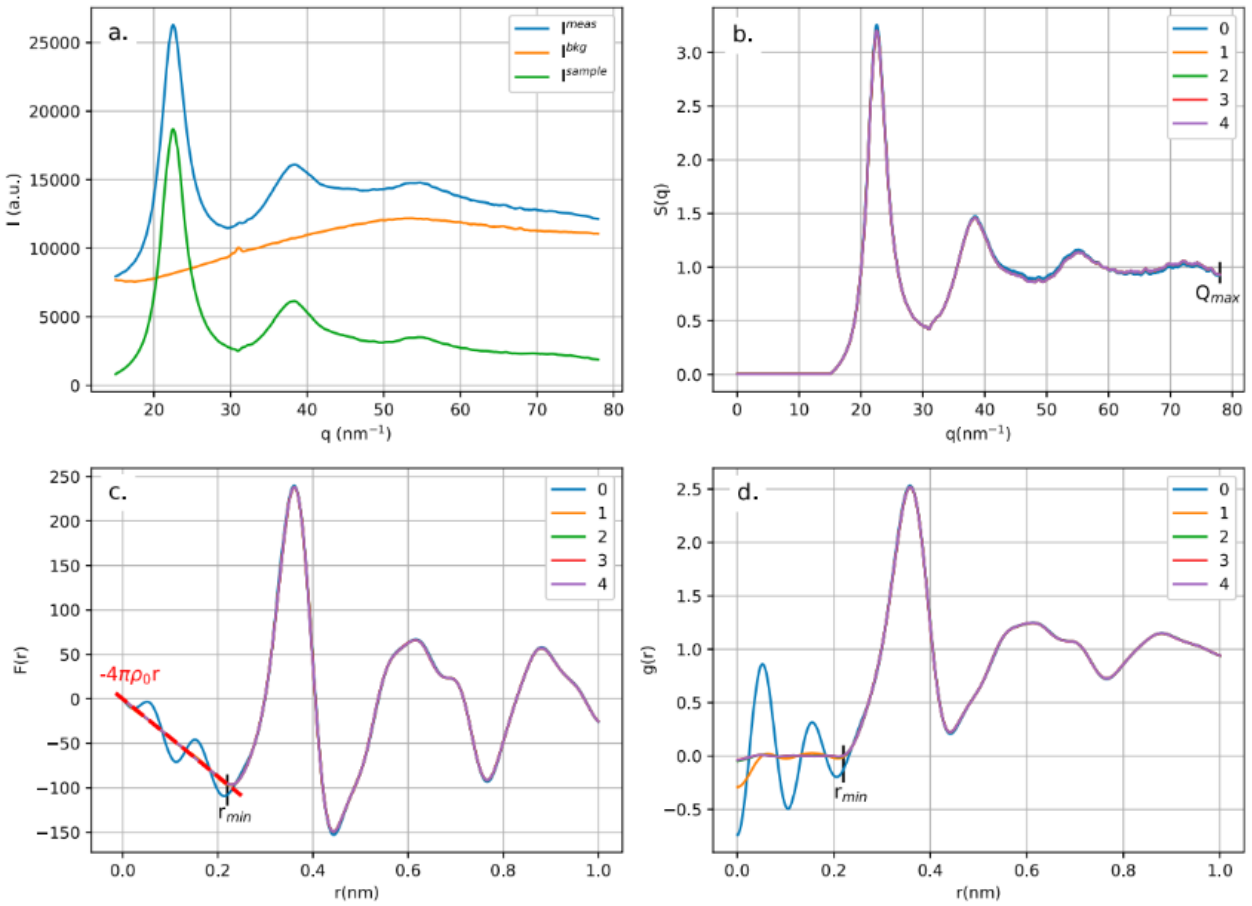
Amorpheus minimizes a figure of merit - integral of the distribution function *F(r)* below the minimum considered real space distance r_{min}, which depends on factors including the density ρ_0

- Background scale factor
- Density determination

$$\chi^2(r_{min}, Q_{max}, \rho_0, b) = \int_0^{r_{min}} [\Delta F(r)]^2 \mathrm{d}r$$

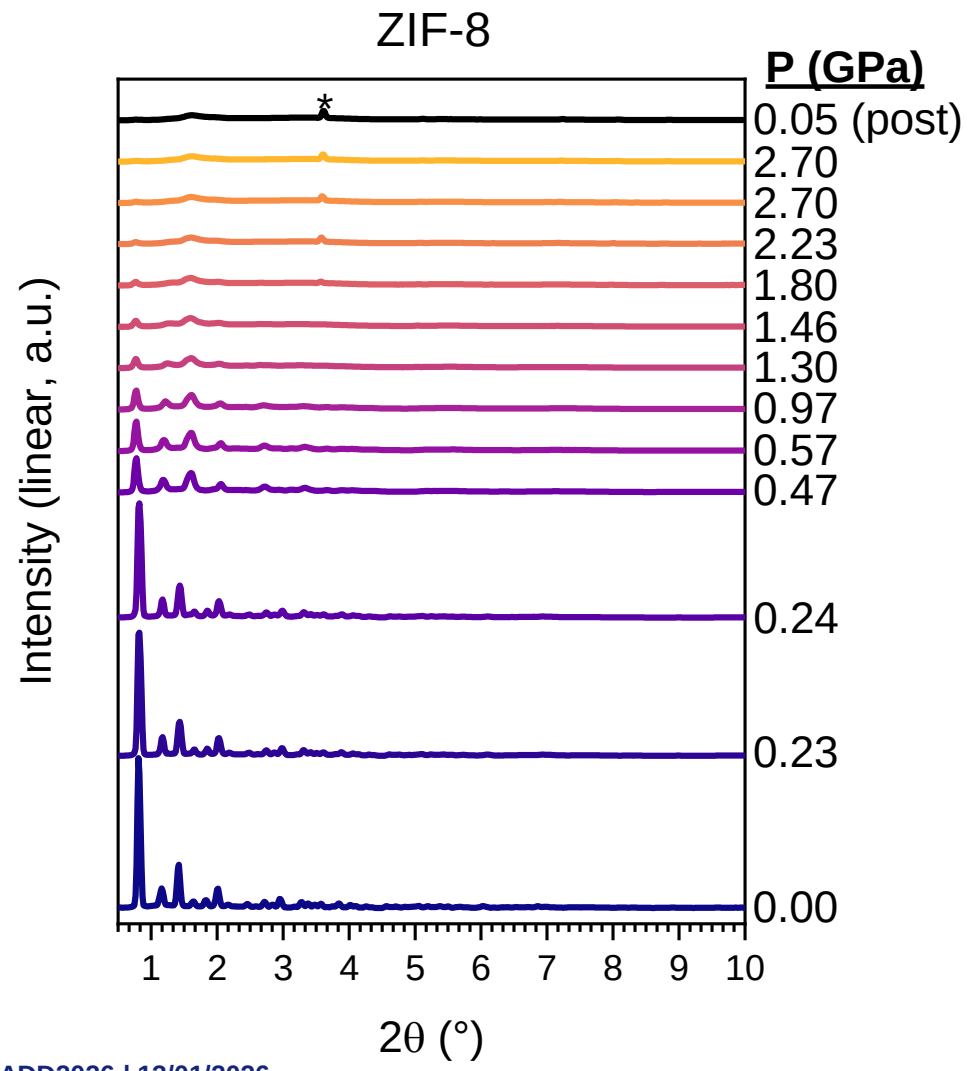
a. Background subtraction
b. Iterations of S(q)
c. Iterations of F(r)
d. Iterations of g(r)

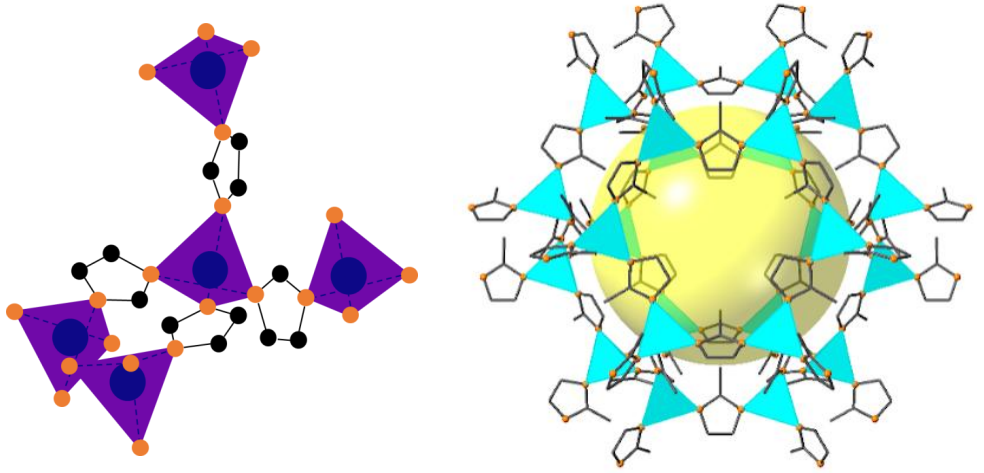
Boccato et al. **Amorpheus: a Python-based software for the treatment of X-ray scattering data of amorphous and liquid systems,** High Pressure Research, *2022,* 42:1, 69-93

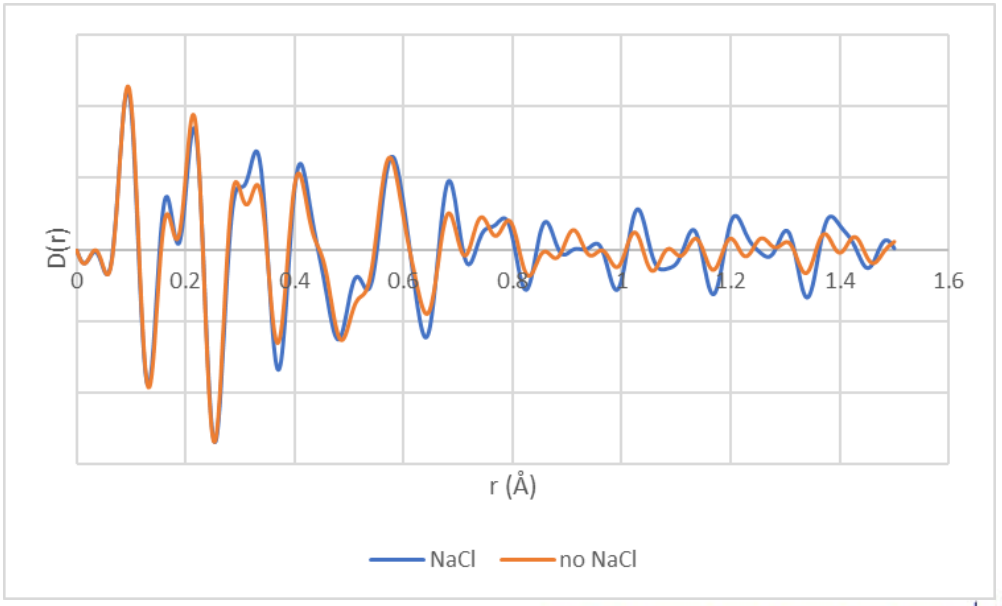


PHASE PURITY

Need to be very sure that calibrant material is not affecting measurement







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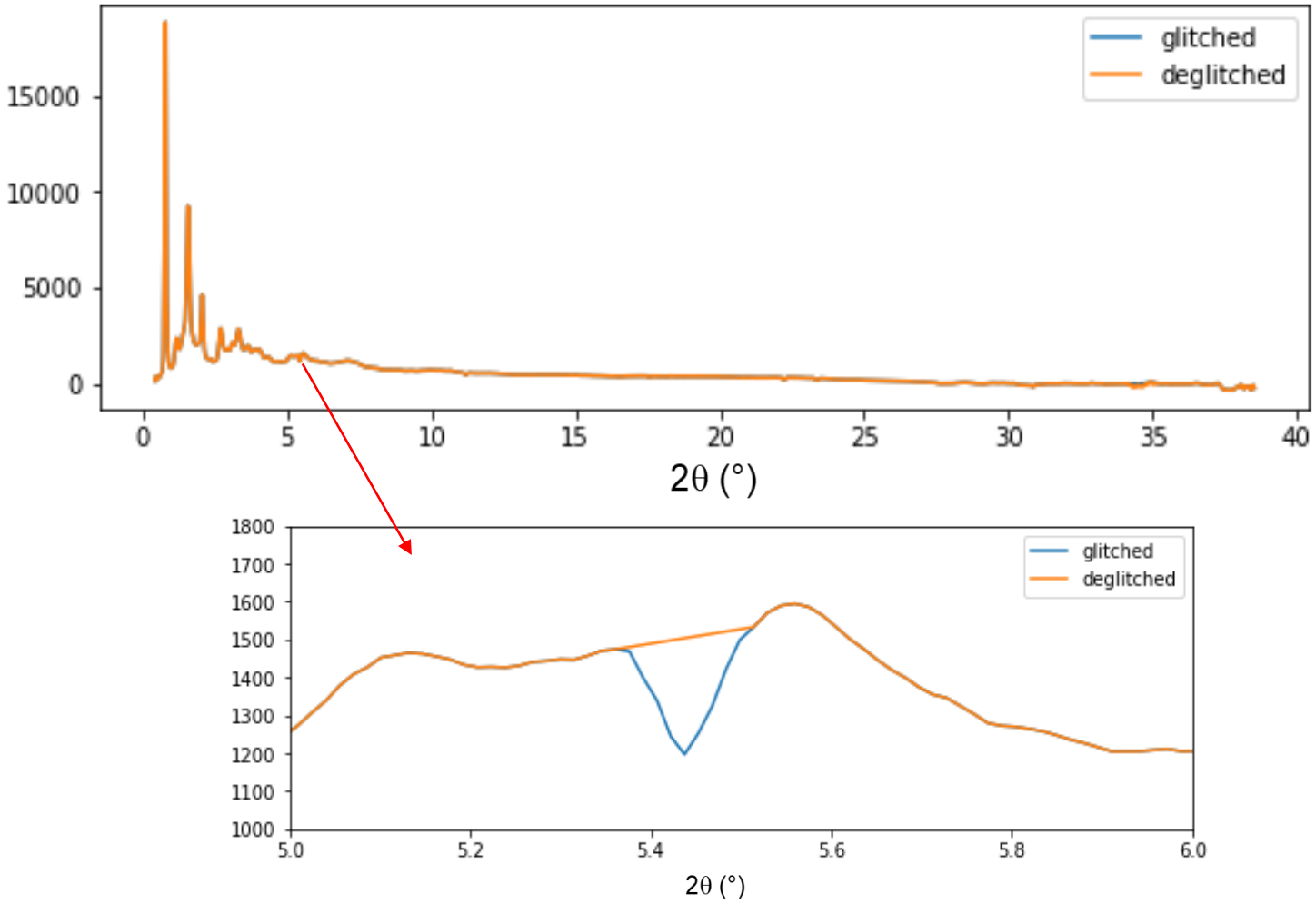

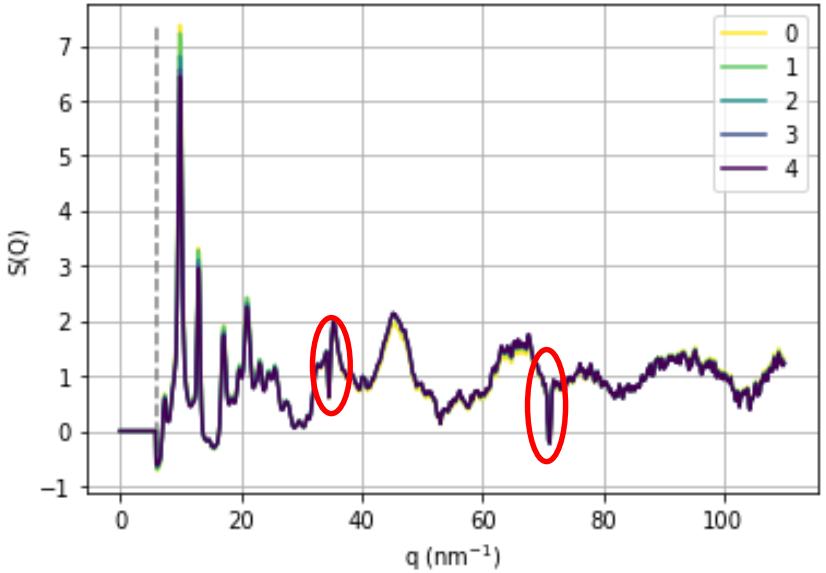

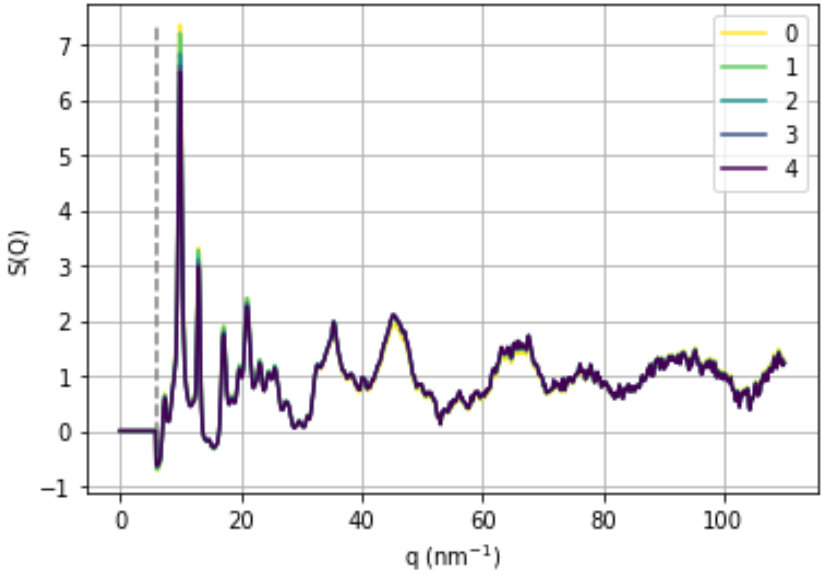

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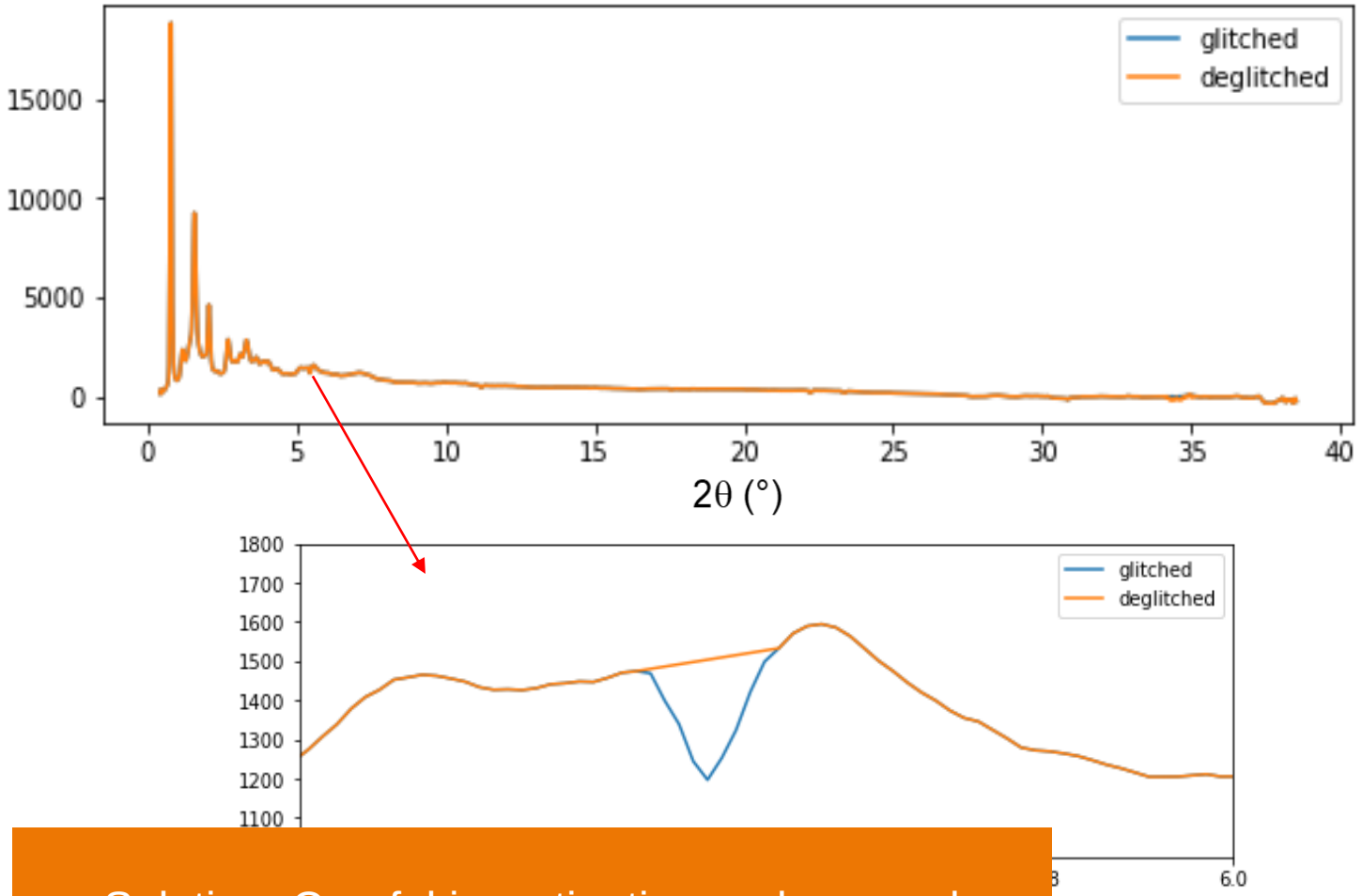

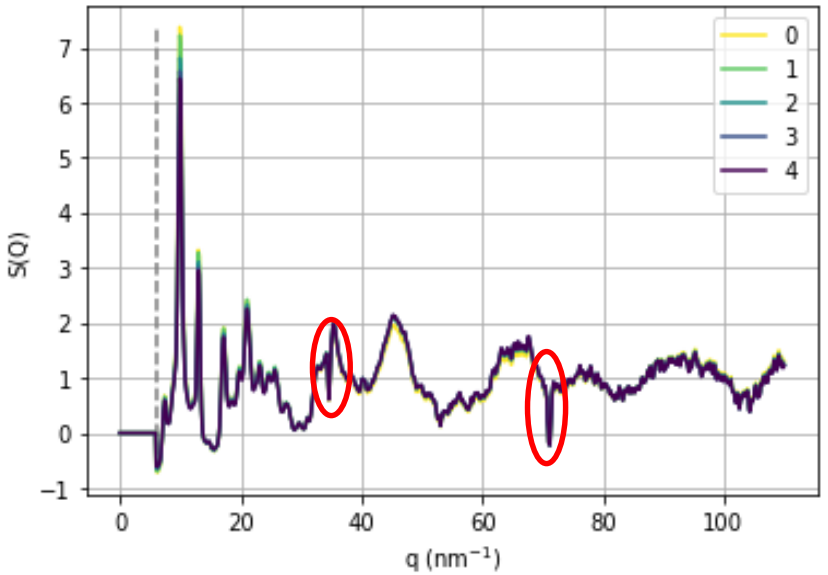

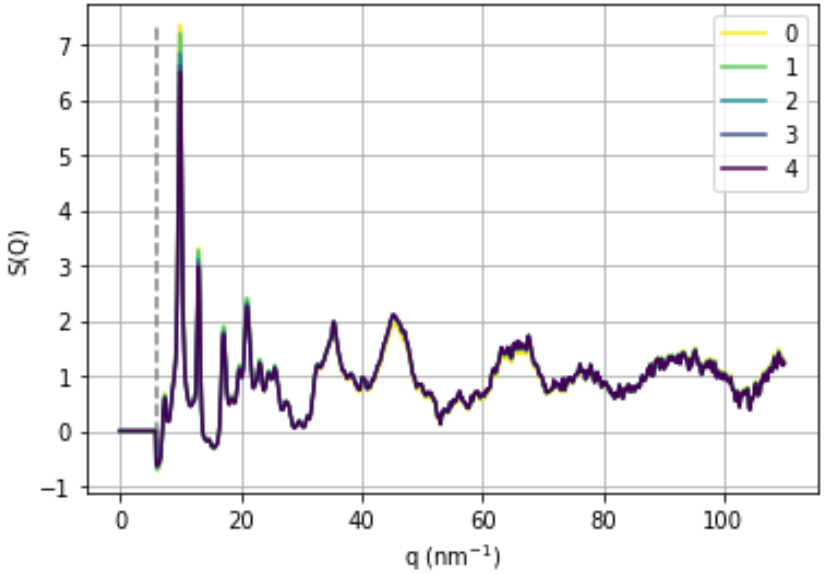

Solution: Careful investigation and removal

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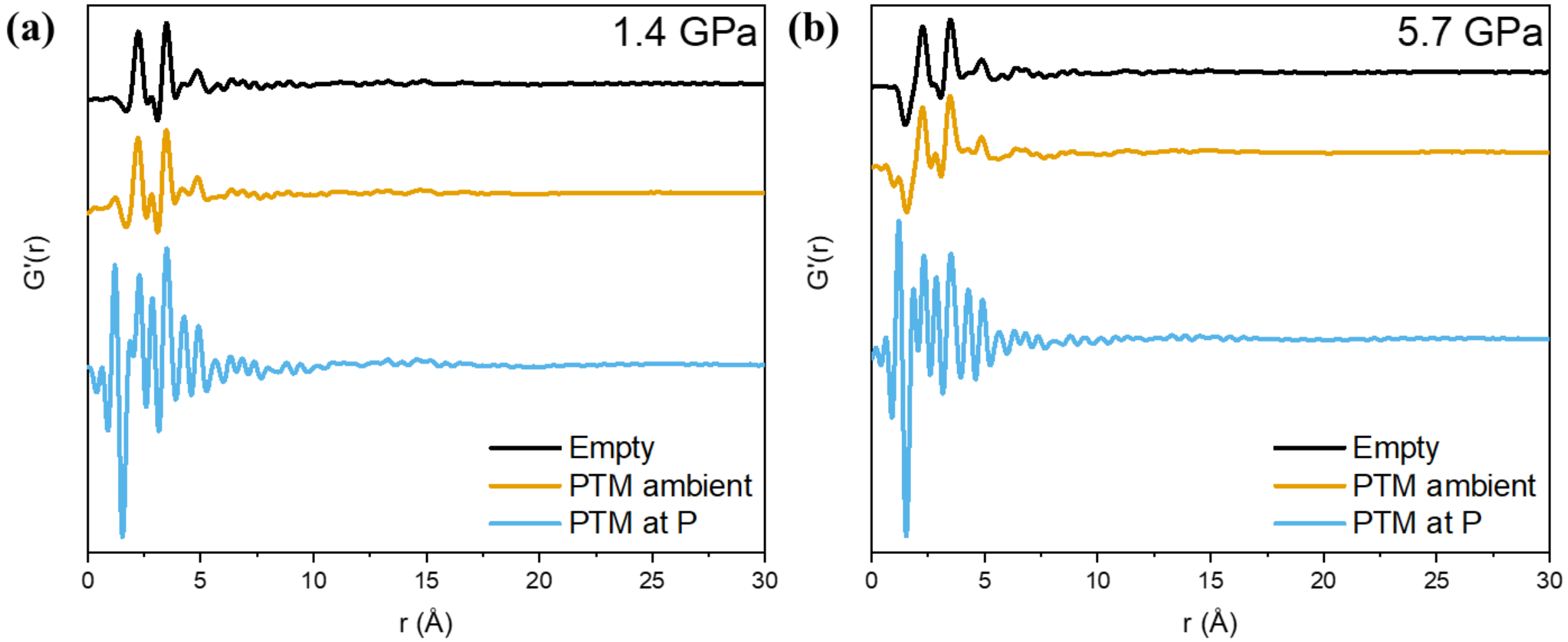
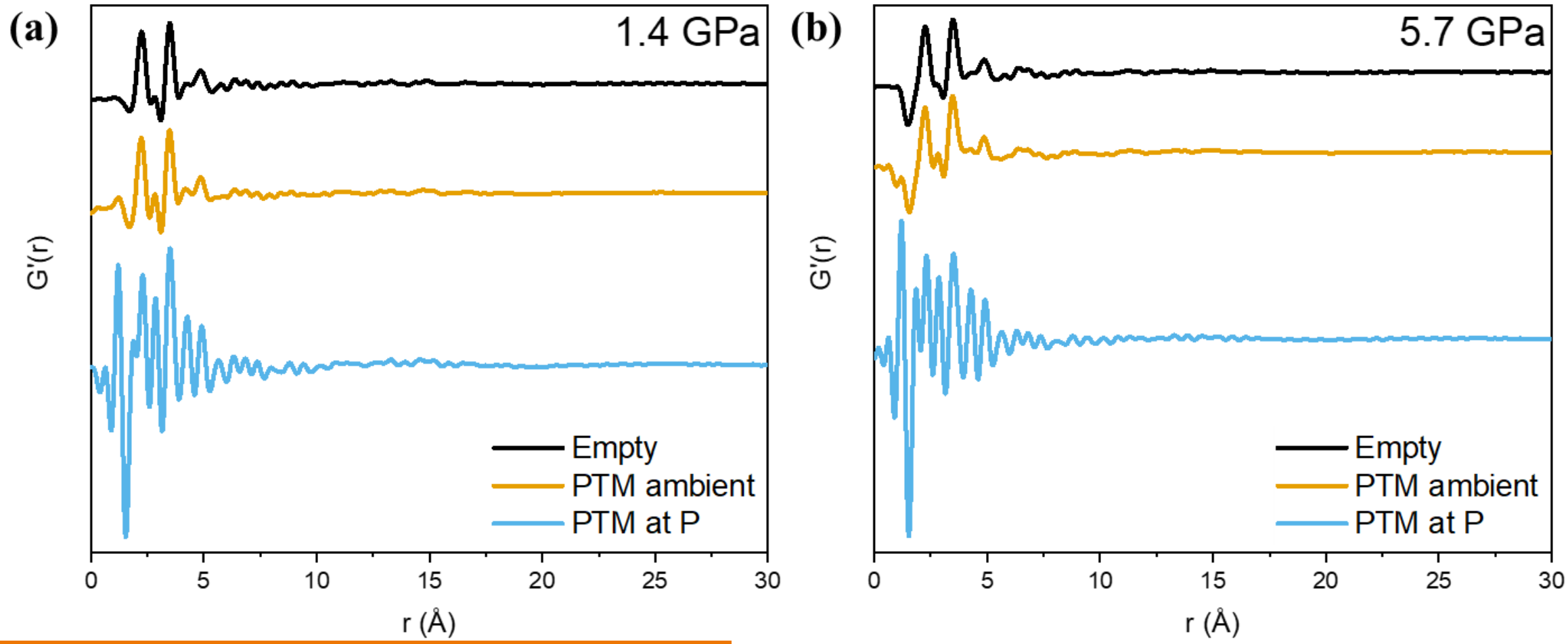
CHOOSING A BACKGROUND



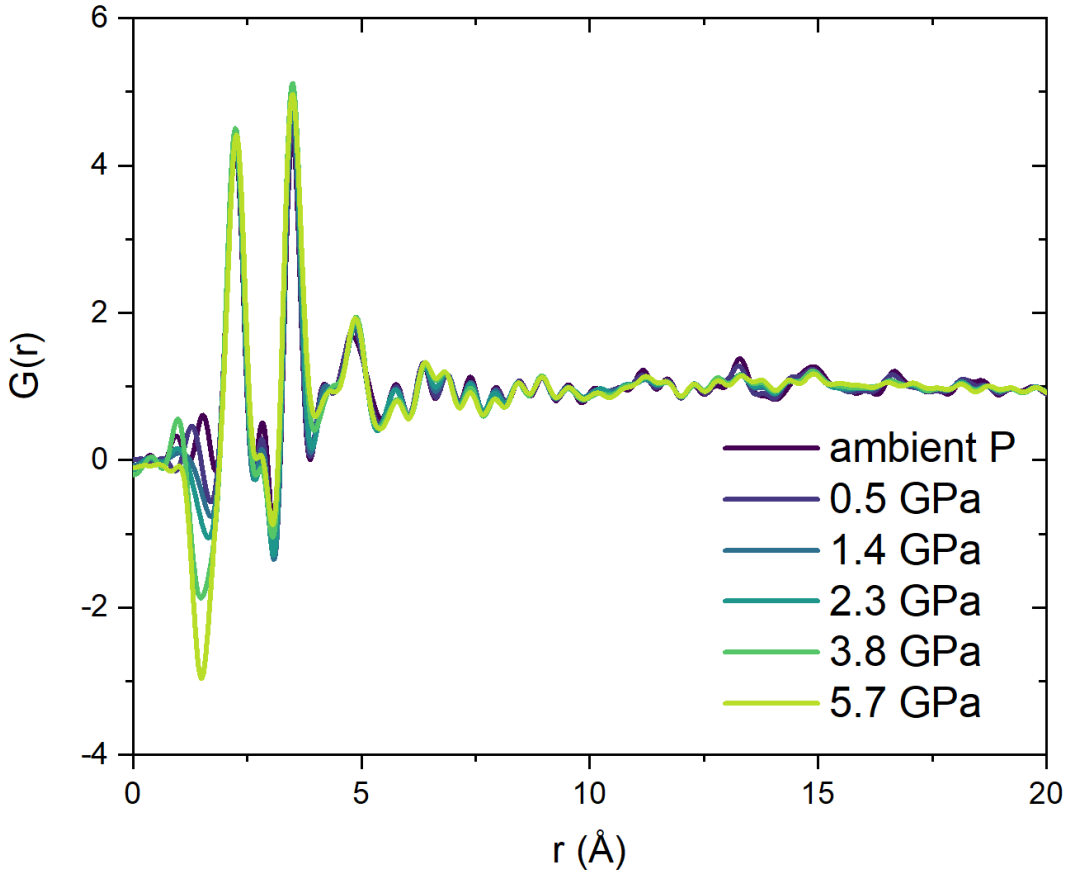
CHOOSING A BACKGROUND



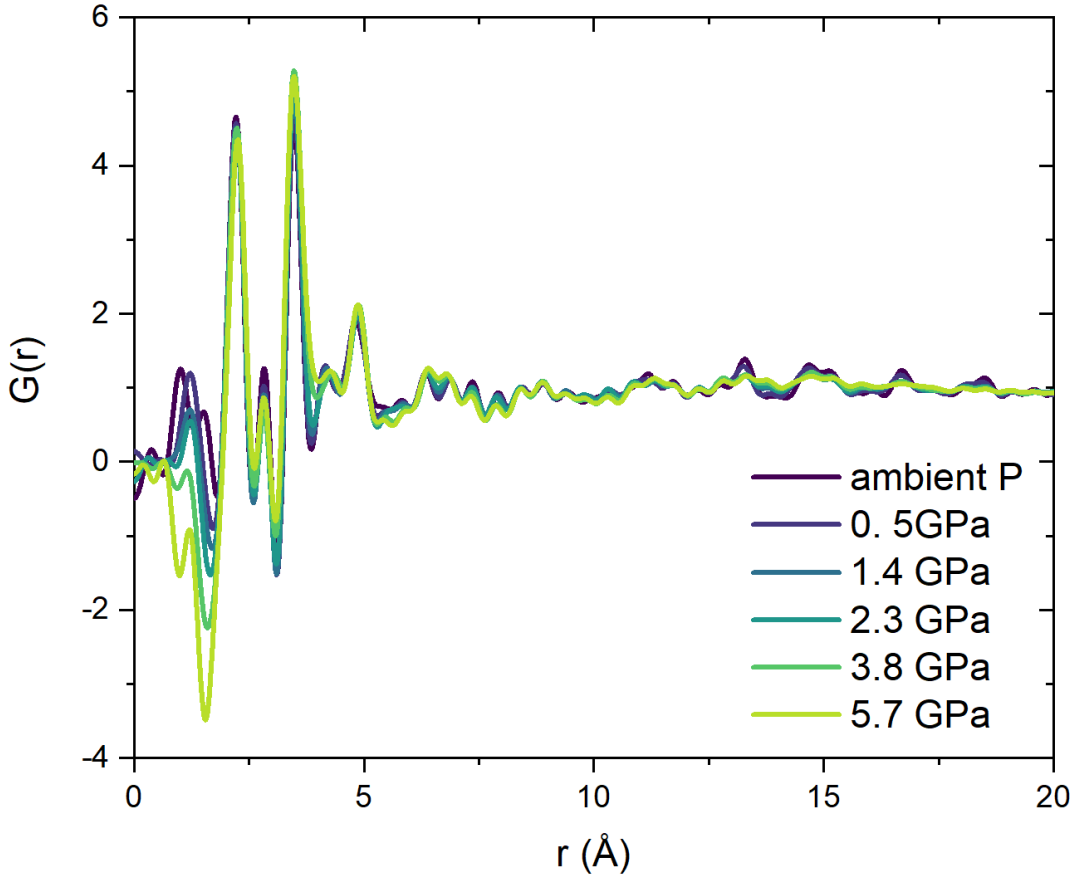
Solution: Use empty or PTM-full cell at ambient conditions, test both

CHOOSING A BACKGROUND

Empty cell (ambient conditions) as background



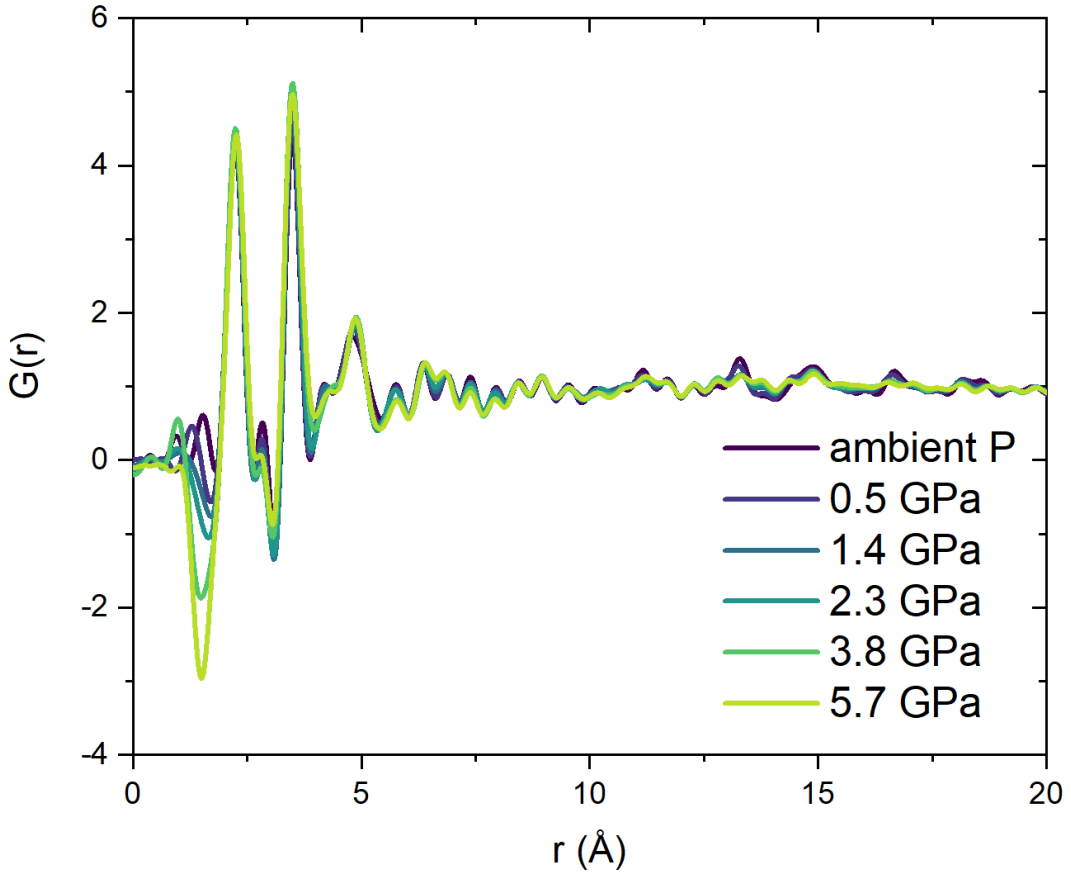
PTM-full cell (ambient conditions) as background



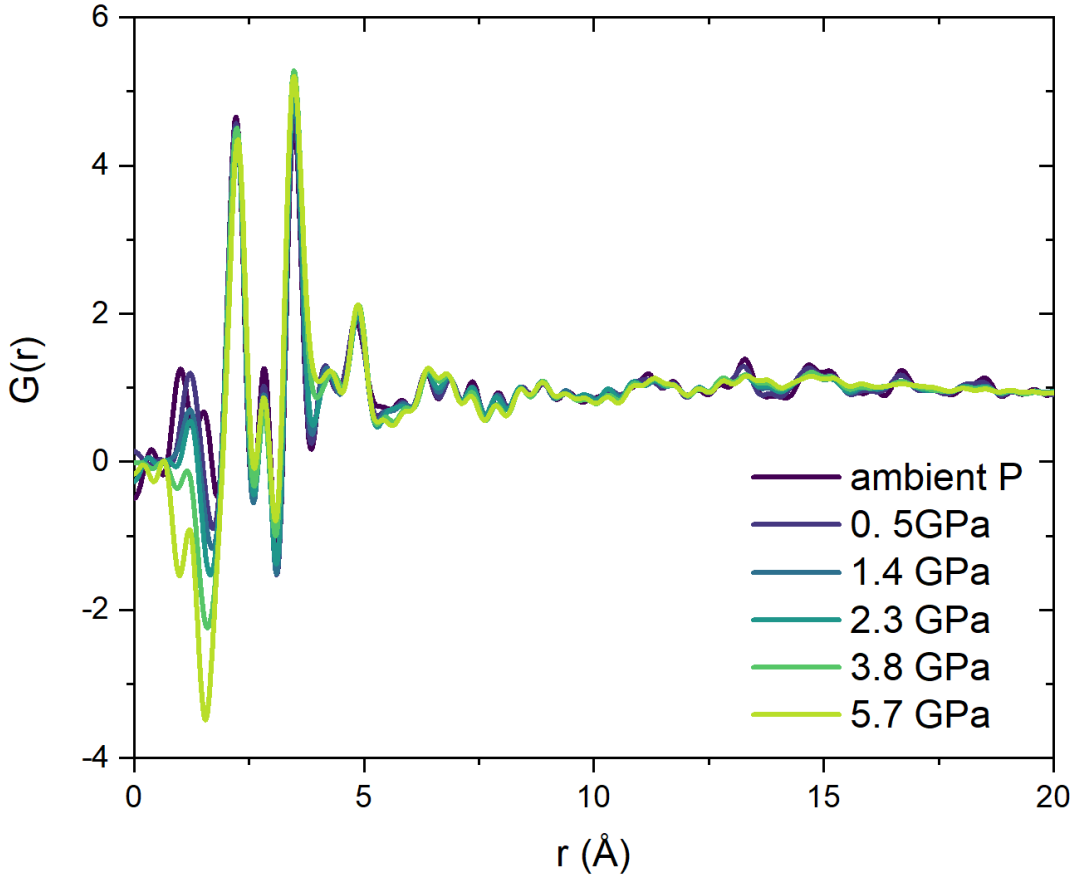
A single background measurement should be used to evaluate a series, too much variation in low-*r* region to hand-pick the best background measurement for each sample measurement

CHOOSING A BACKGROUND

Empty cell (ambient conditions) as background



PTM-full cell (ambient conditions) as background



A single background measurement should be used to evaluate a series, too much variation in low-*r*

nd measurement for each sample measurement

Solution: Decide between low-r oscillations and PTM information

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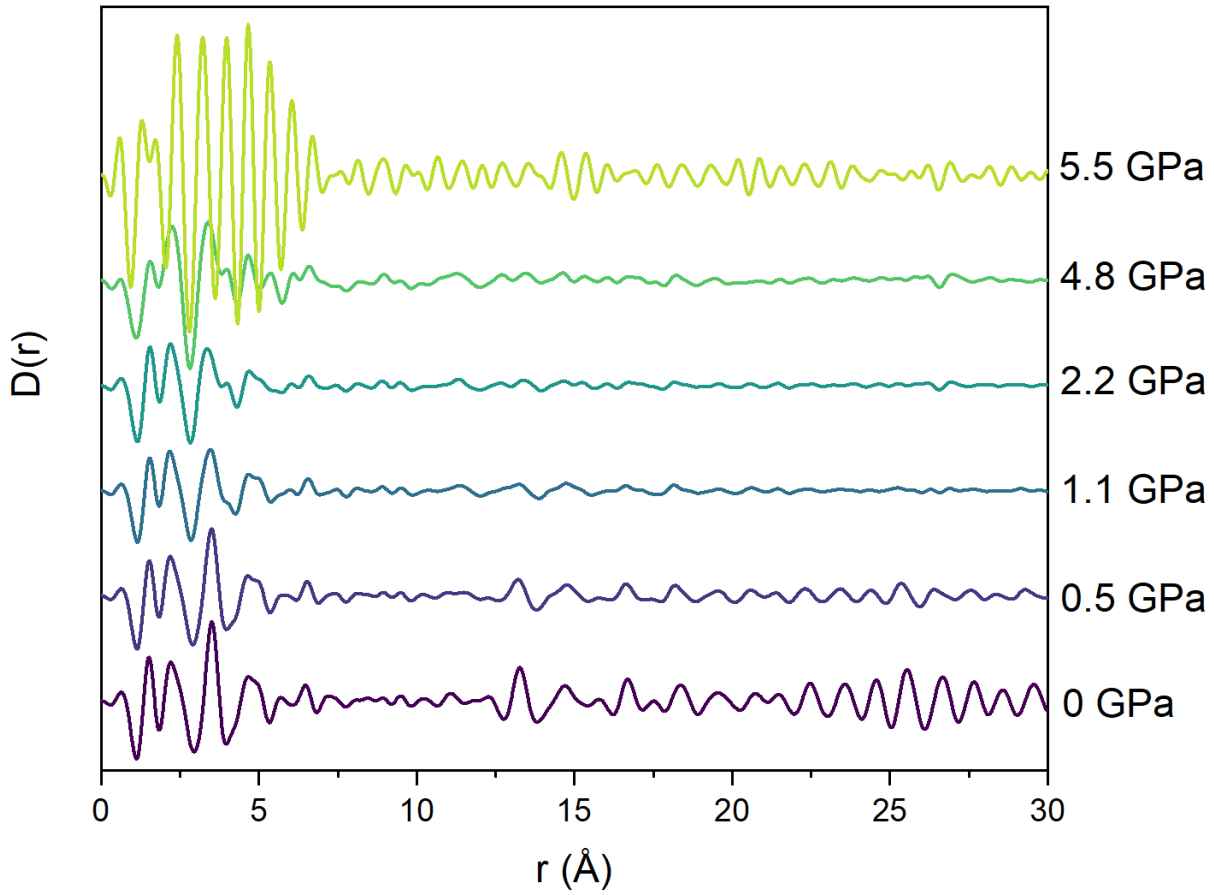
PROCESSING A SERIES

- Same background measurement subtracted each time (varying scaling factor)
- Still doesn't always give comparable data

UiO-66 at 250°C, Same background used for all (empty cell post-compression)



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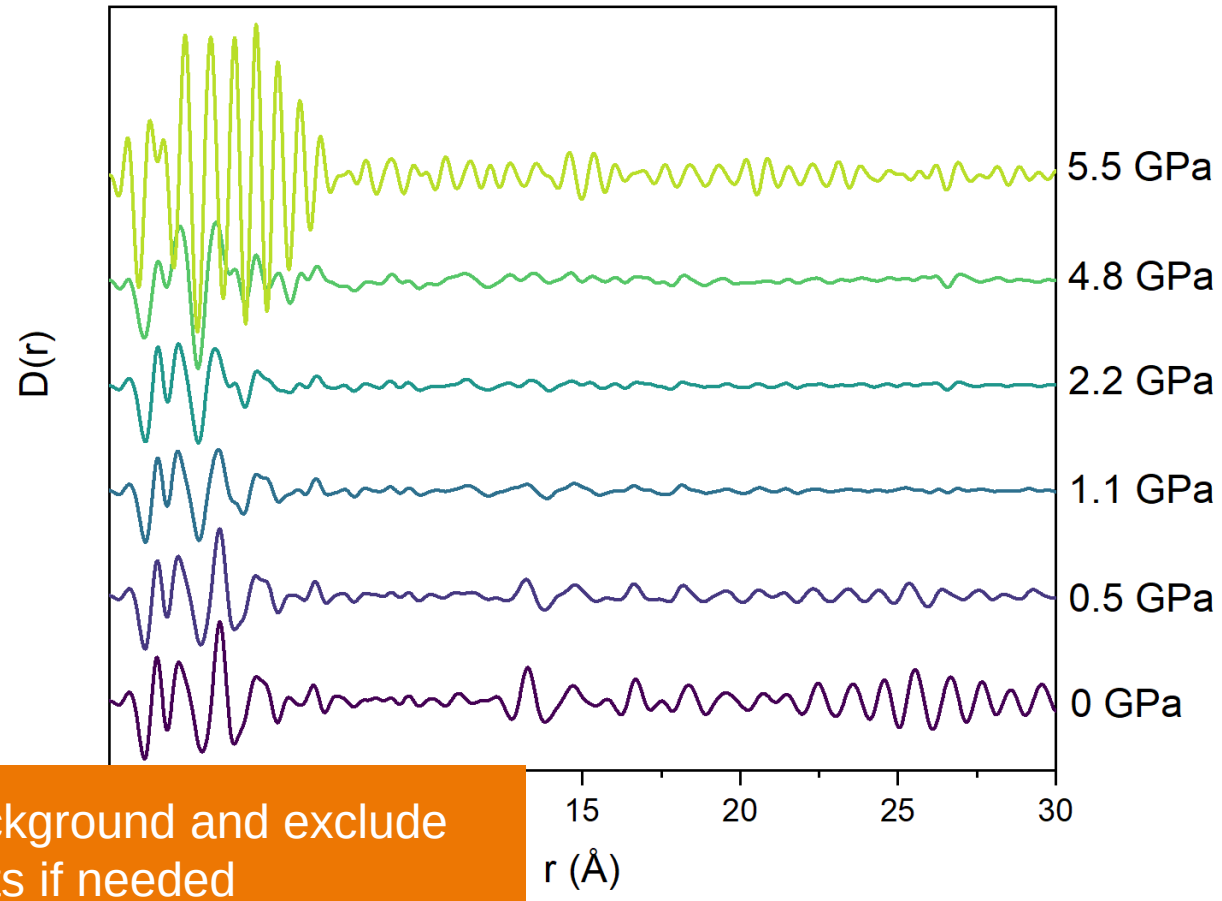
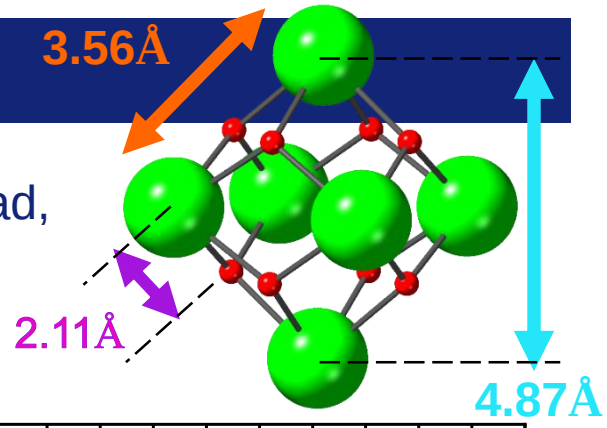
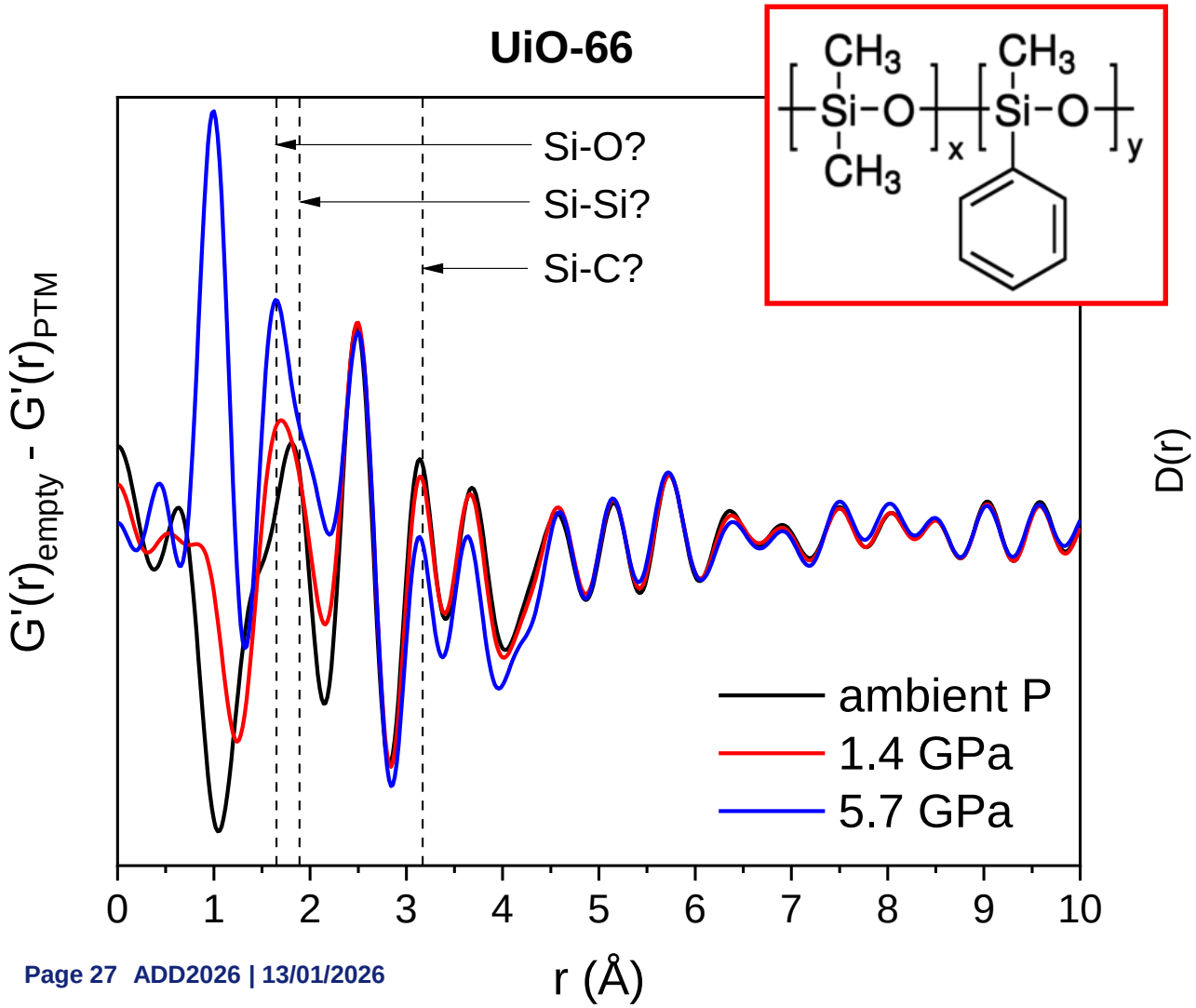


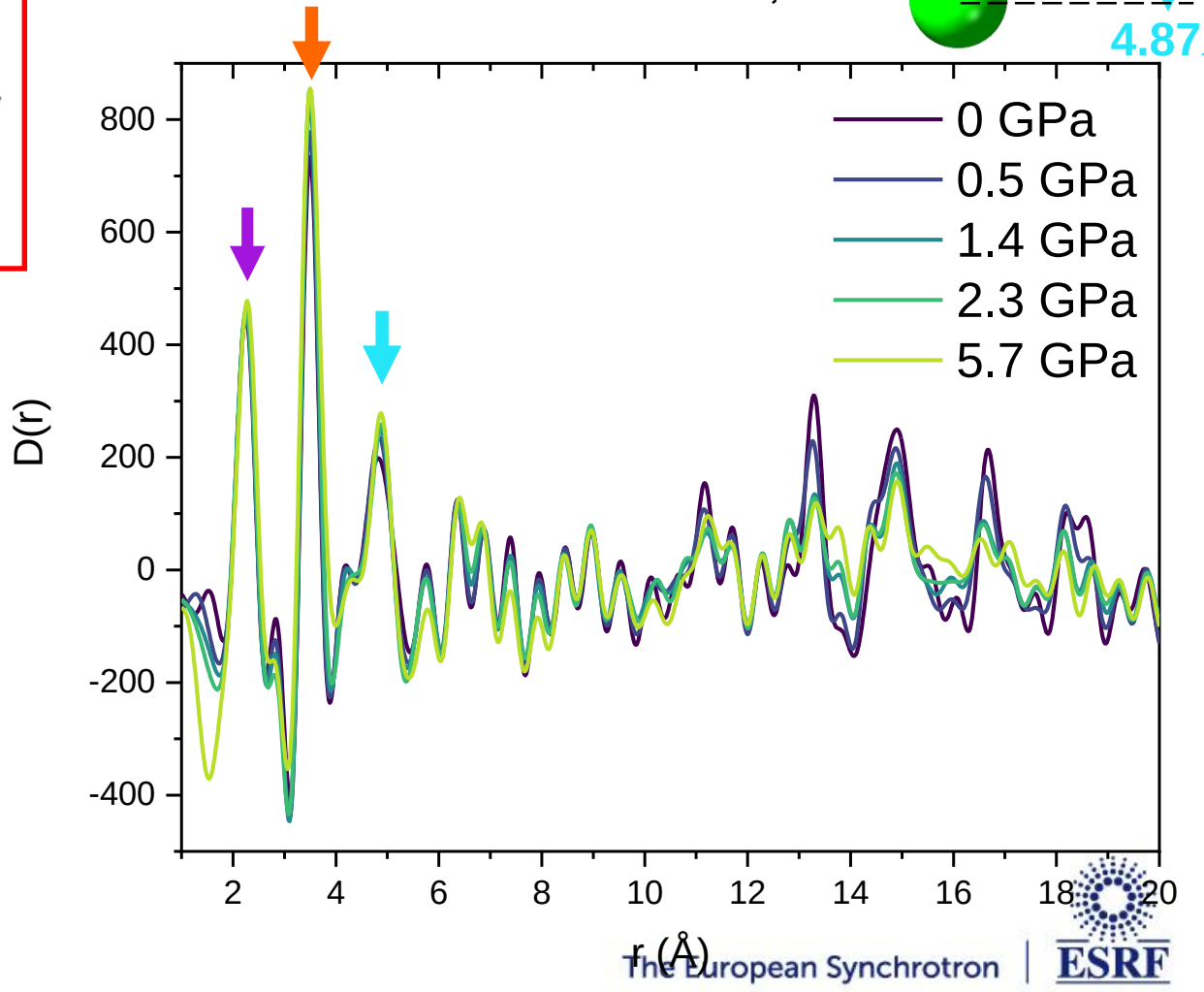
Solution: Use same background and exclude measurements if needed

ISOLATING PTM EFFECTS

True differential PDFs (i.e. difference between with and without PTM) not possible. Instead, testing effect of background. ‘PTM’ indicates the background includes the PTM.







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SUMMARY

Challenges:

1. Metal-organic framework
   a. Low scattering – high packing of sample (but watch out!)
   b. PTM effect on structure – balance h-static limit and pore size

2. High pressure/temperature setup
   a. ‘Equilibrating’ the system – test, note rest time
   b. Beam path clutter – careful background subtraction
   c. Changes in geometry – hard gasket material

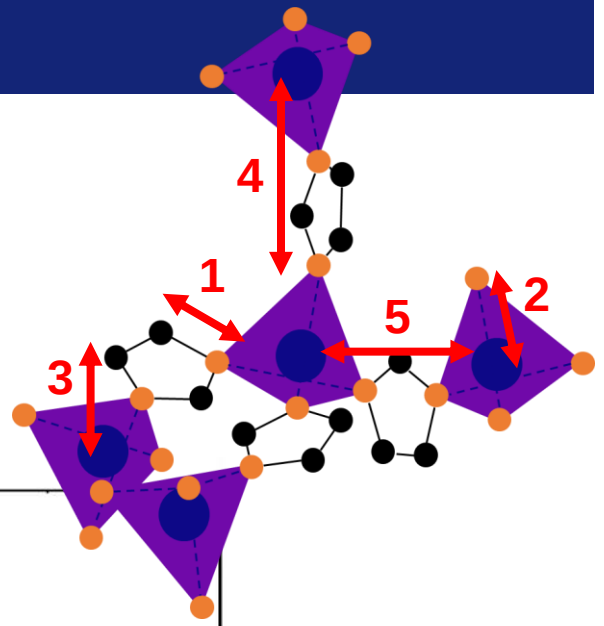
3. Processing & Analysis
   a. Processing software – choose carefully
   b. Phase purity – remove unwanted peaks
   c. Choosing a background – measure multiple and compare them
   d. Processing a series – requires the same background data
   e. Isolating PTM effects – differential PDF & other comparison methods

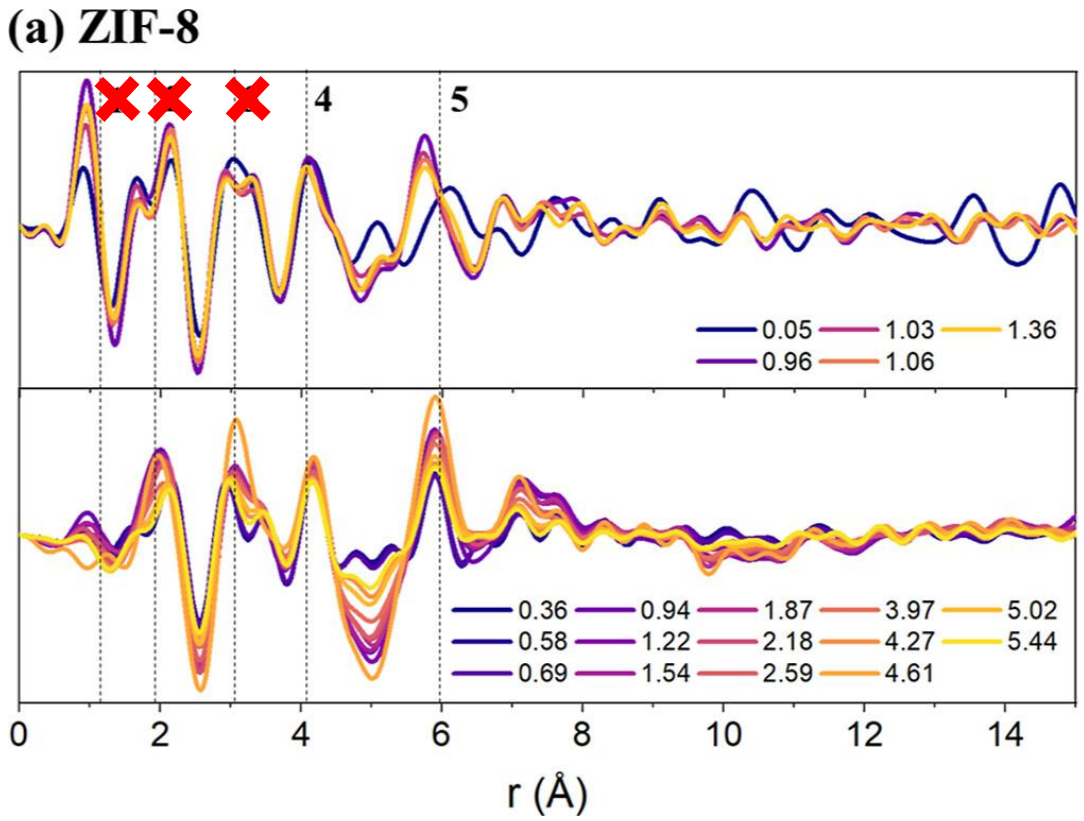
Issue

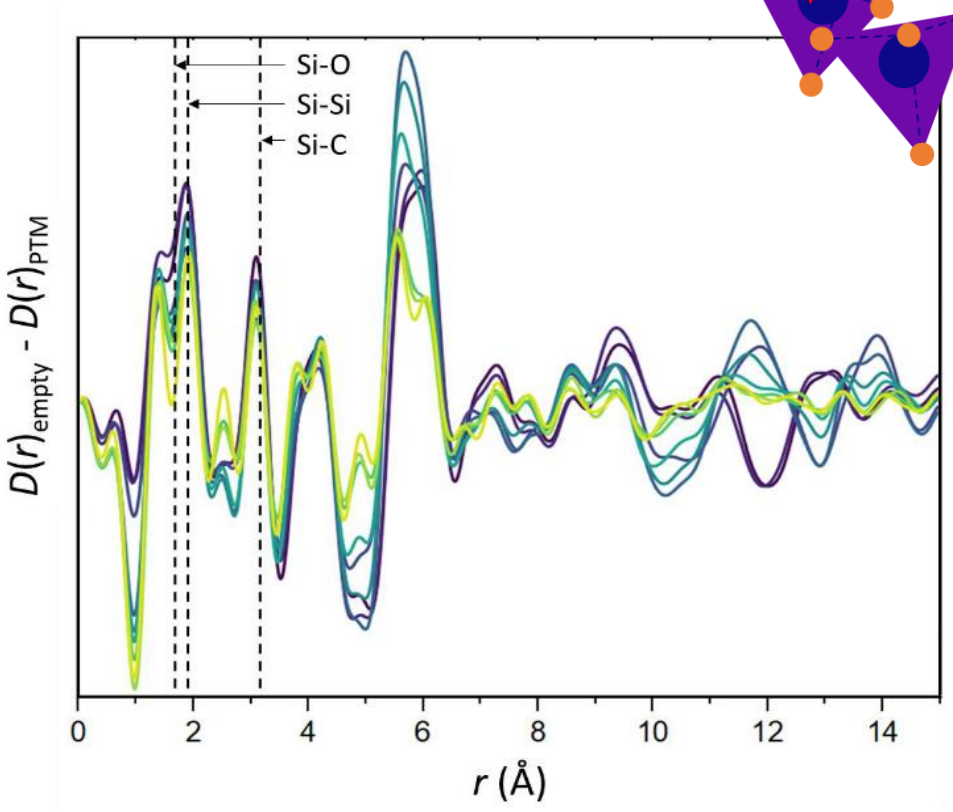
Solution

BEING REALISTIC ABOUT YOUR DATA

- How useful is it actually?

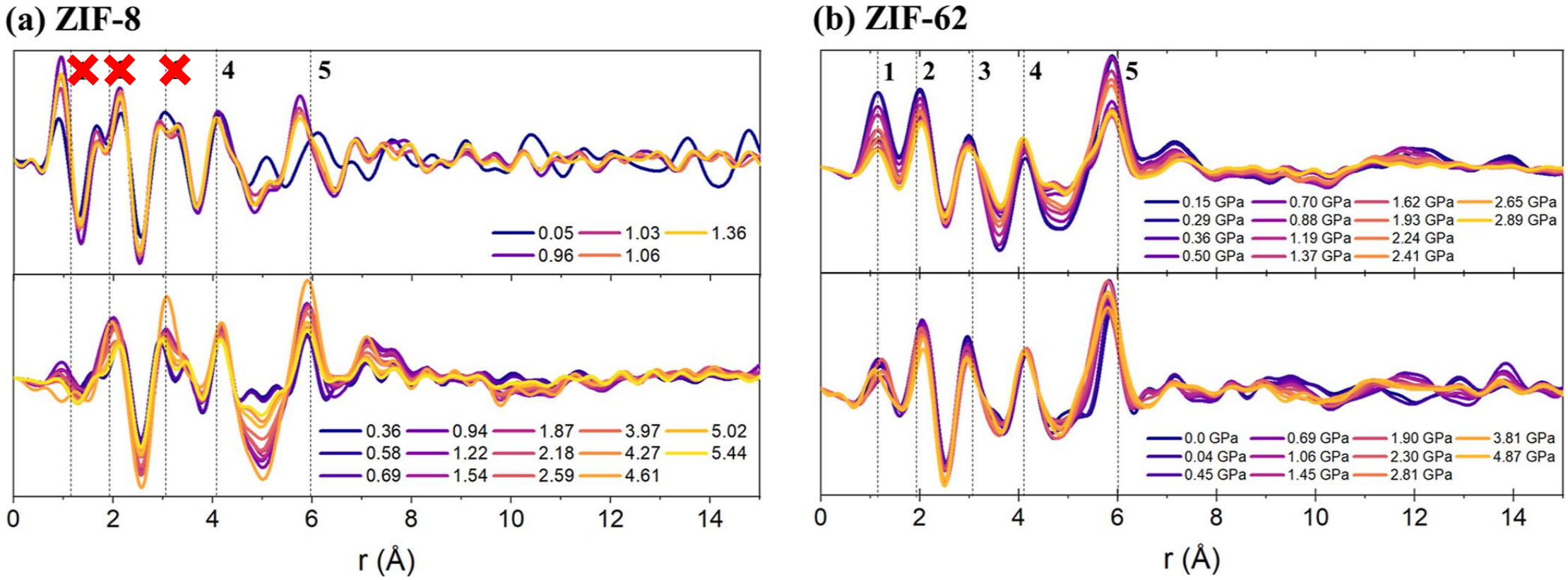






BEING REALISTIC ABOUT YOUR DATA

- How useful is it actually?
- Is it reproducible?



BEING REALISTIC ABOUT YOUR DATA

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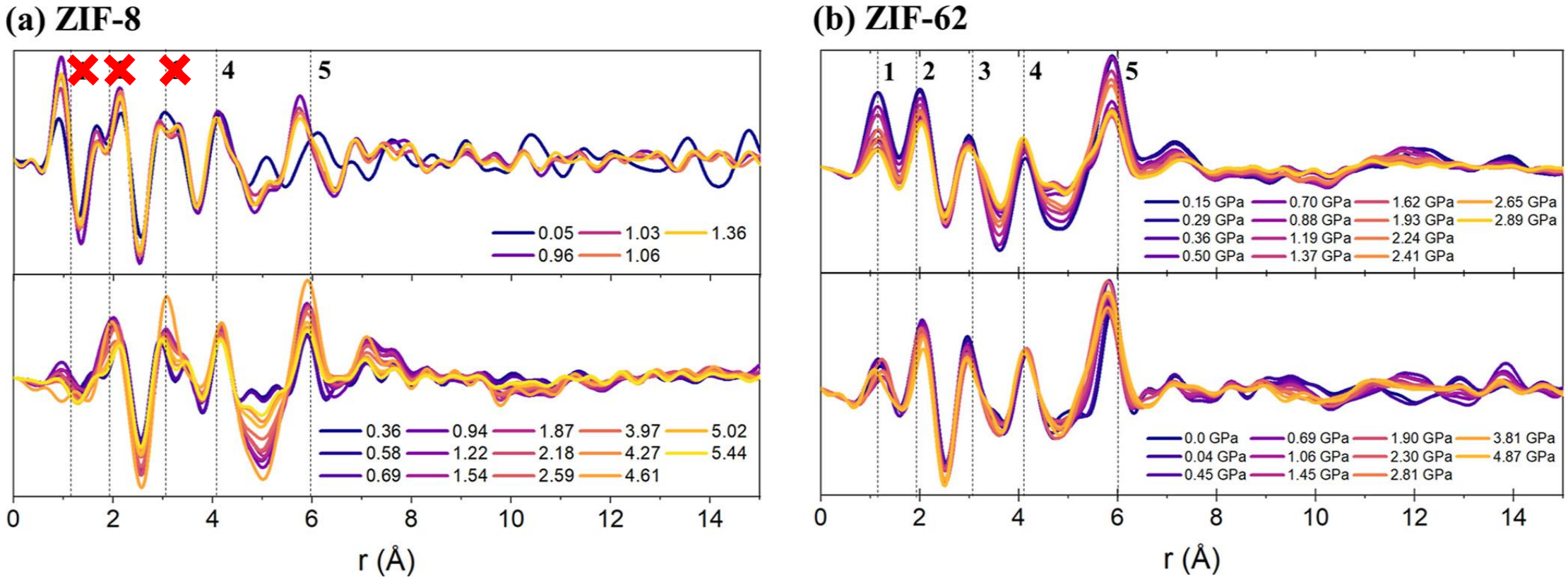

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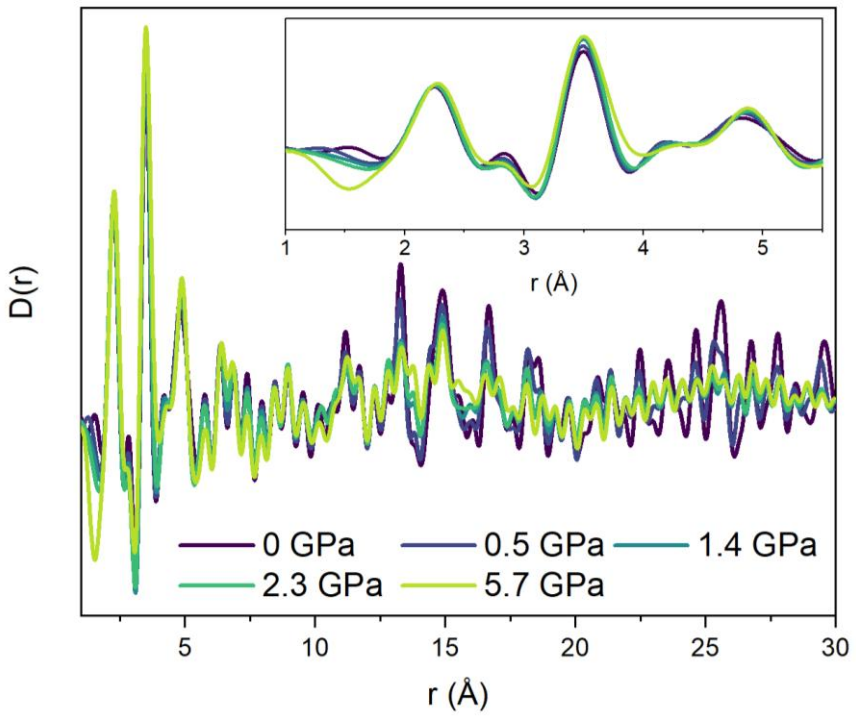

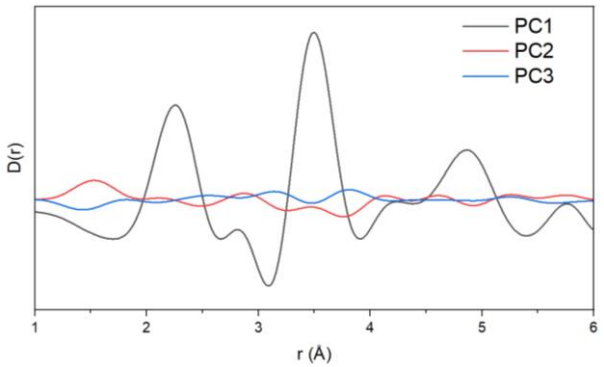

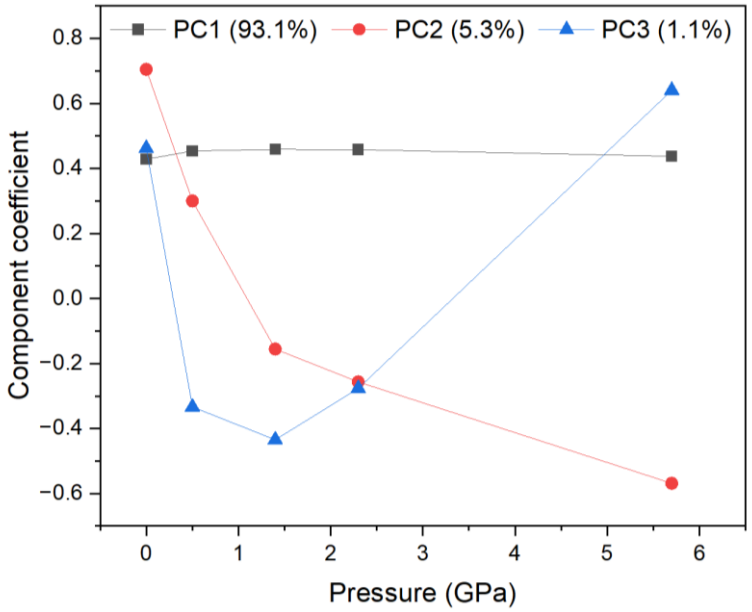

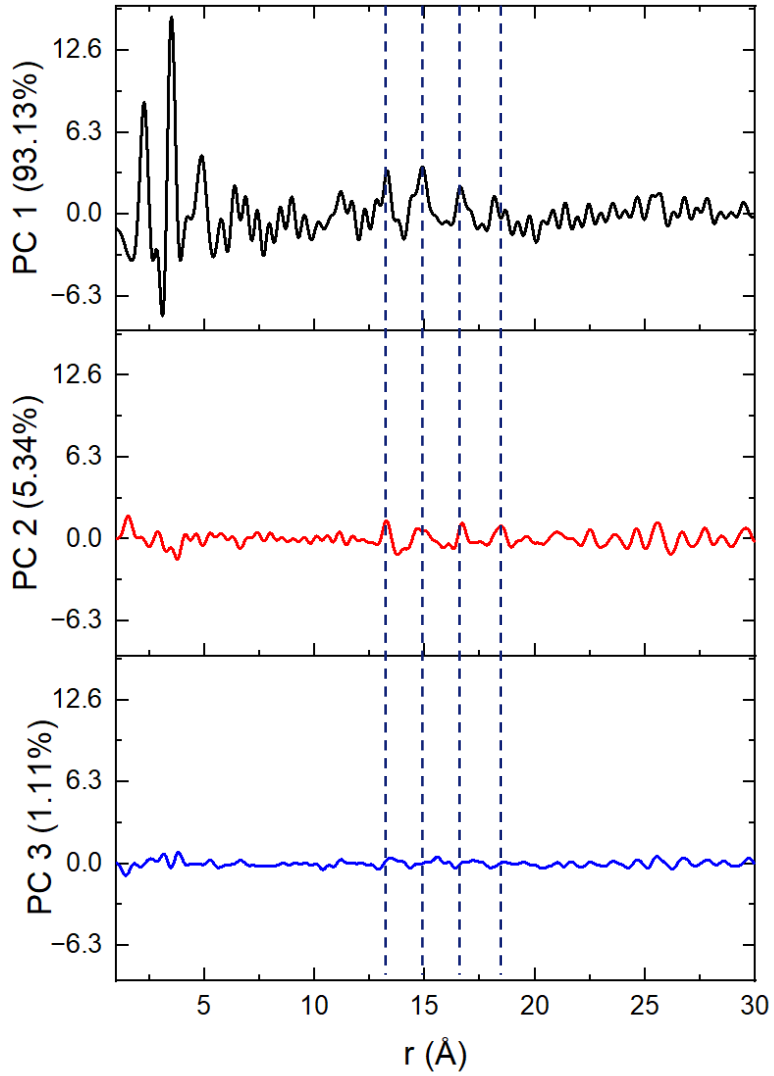

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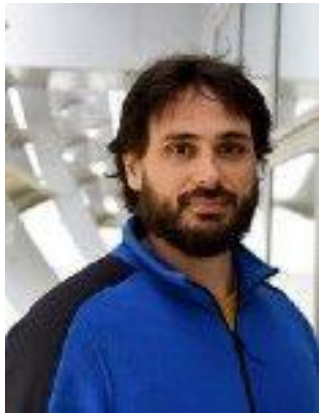

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UNIVERSITY OF CAMBRIDGE

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UKRI Engineering and Physical Sciences Research Council

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THANK YOU FOR YOUR ATTENTION