IAEA-CN301-179

SWIFT HEAVY ION MODIFIED MATERIALS

APPLICATIONS AND CHARACTERISATION USING SYNCHROTRON SMALL ANGLE X-RAY SCATTERING

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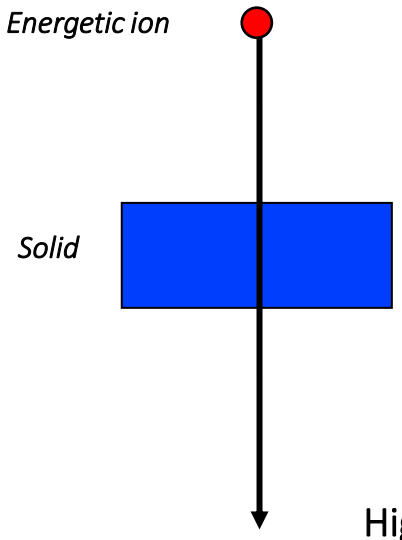
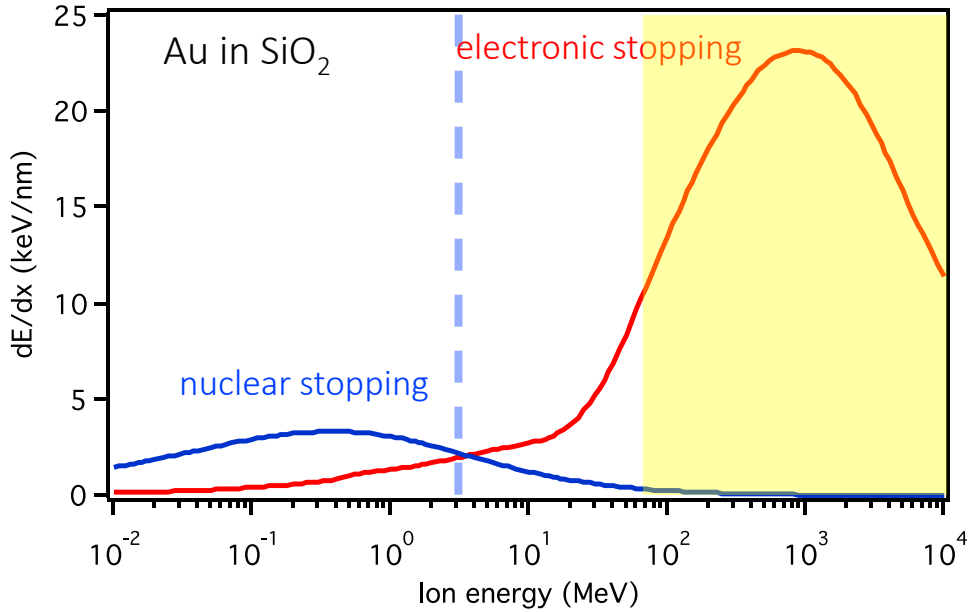
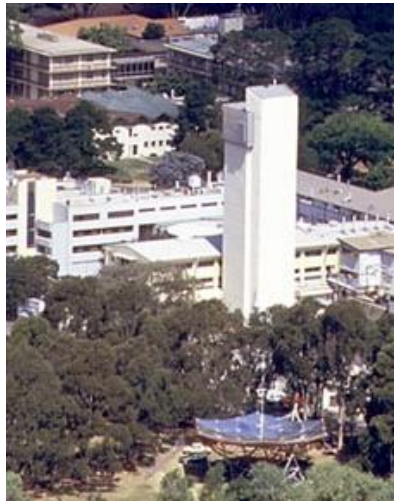
Ion Irradiation of Materials





ANU Heavy Ion Accelerator Facility



< 200 MeV

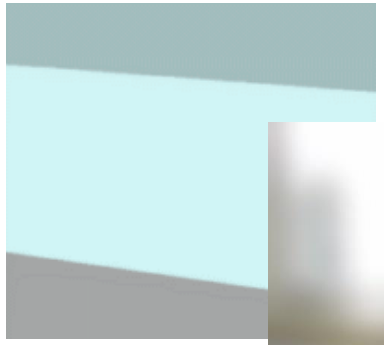
UNILAC Accelerator at GSI, Germany

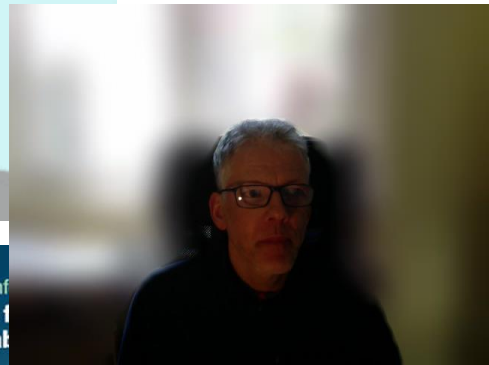
< 500-2600 MeV

Highly energetic ions:

- electronic energy loss dominant
- high energy deposited in a narrow region around the ion path
- can lead to long (µm), narrow (nm) defect regions, *"ion tracks"*

Tracks often show increased chemical etching

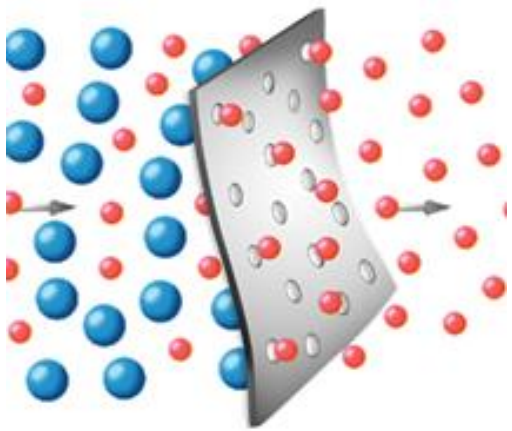




Nanopore membranes

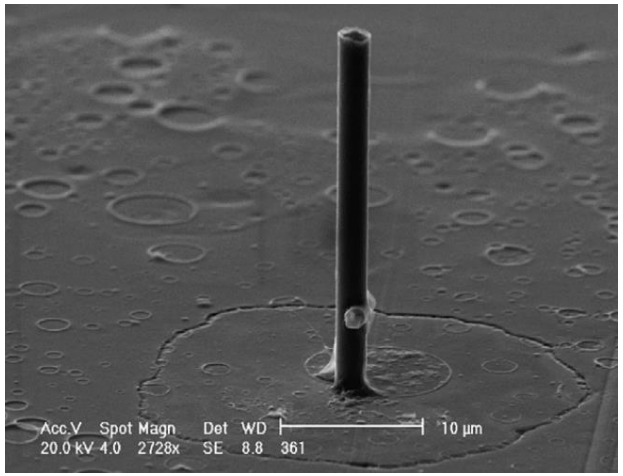
Single pore or multi-pore track etched membranes

Filtration



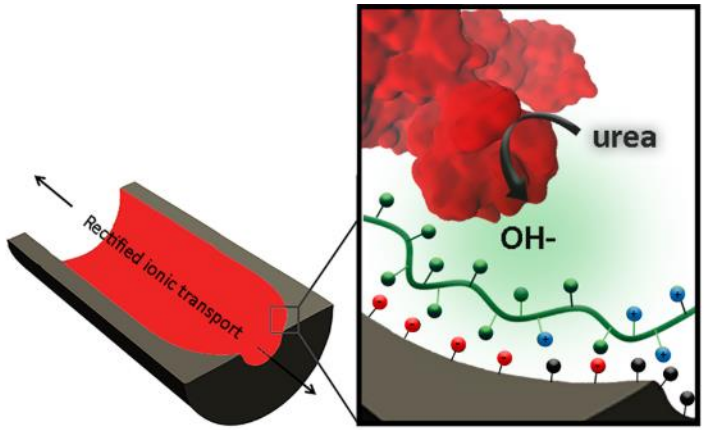
Aperture Games, (available at https://aperturegames.com/8205/global-polymeric-membrane-for-separation-market-2017-2022/).

Nanowire templates



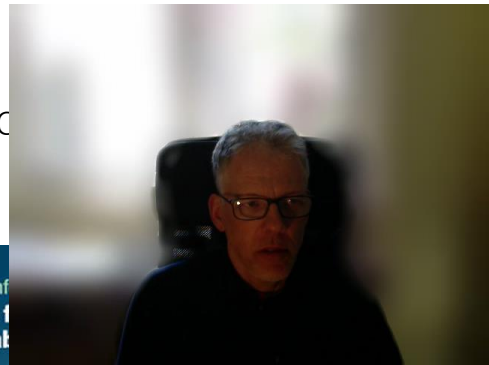
Man et al., *Nucl. Instruments Methods Phys. Res. Sect. B*. **265**, 621–625 (2007).

Sensing of single ions, molecules and biomarkers



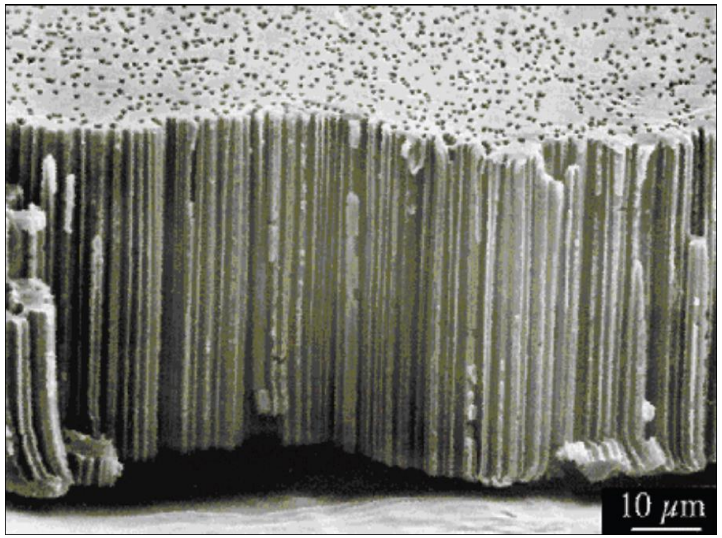
Pérez-Mitta et al., *Nano Lett.* **18**, 3303–3310 (2018).

Track etched membranes are generally made from polymers, predominantly PC

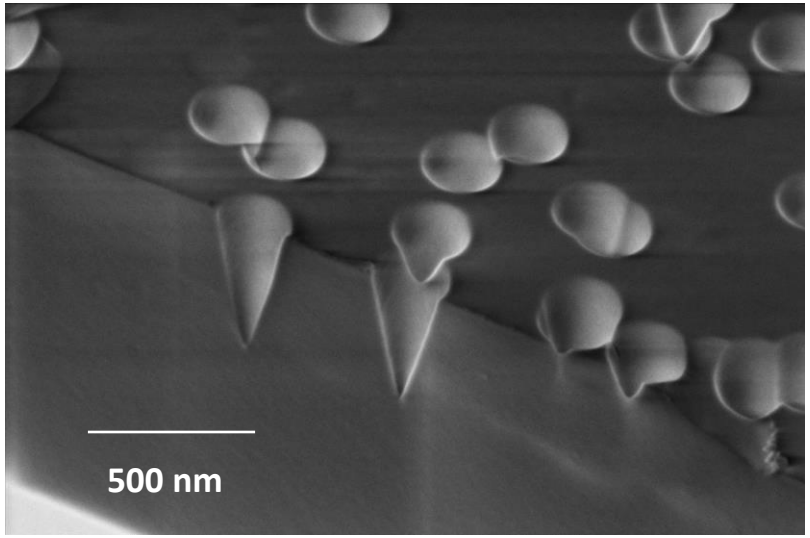


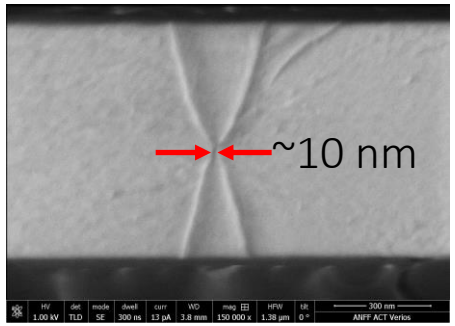
Track etched nanopore membranes

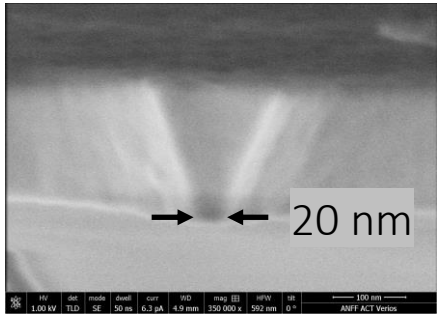
- **Cylindrical nanopore in PC**



- **Conical nanopores in SiO_2**



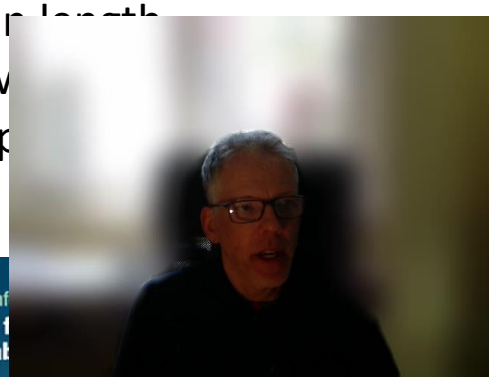




Ability to produce pores with different shapes and sizes controlled by:

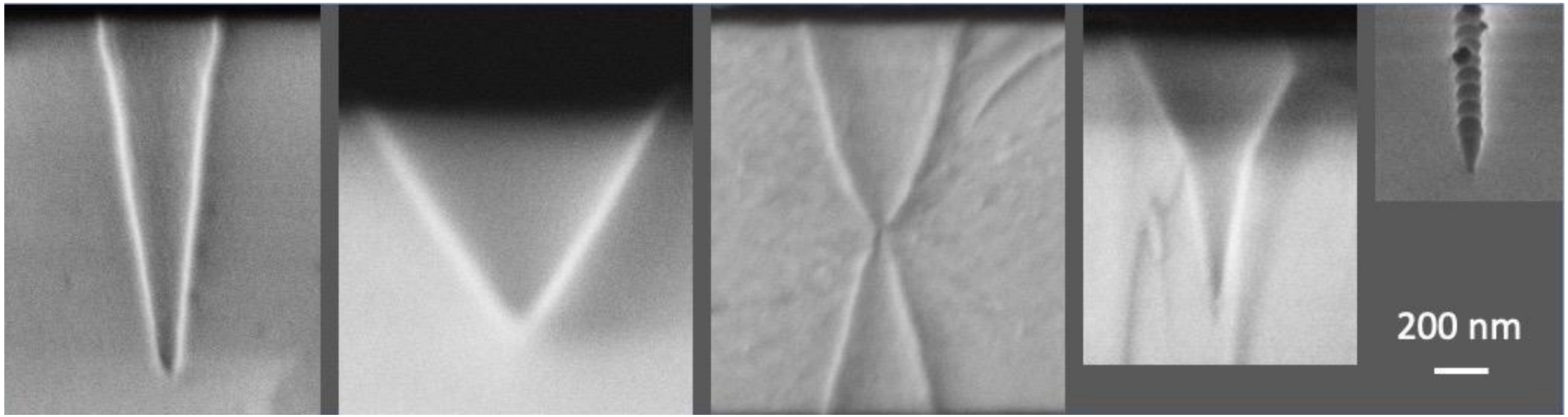
- Irradiation conditions
- Etching parameters (time, temp, concentration, etchant)
- Membrane material
- One sided/two sided etching
- Membrane bias

- Tuneable cone angle (10° – 30°)
- 200 nm to 1 µm in length
- Tip diameter dow
- Single pores or up



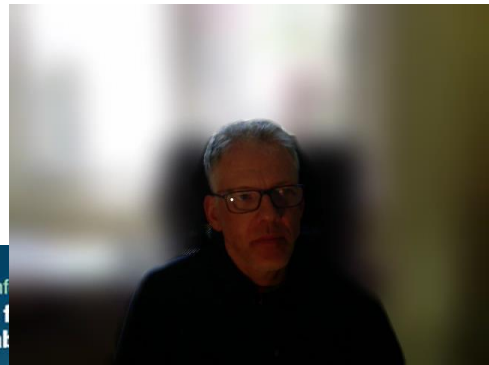
Track etched nanopore membranes

Nanopores in silicon oxynitrides

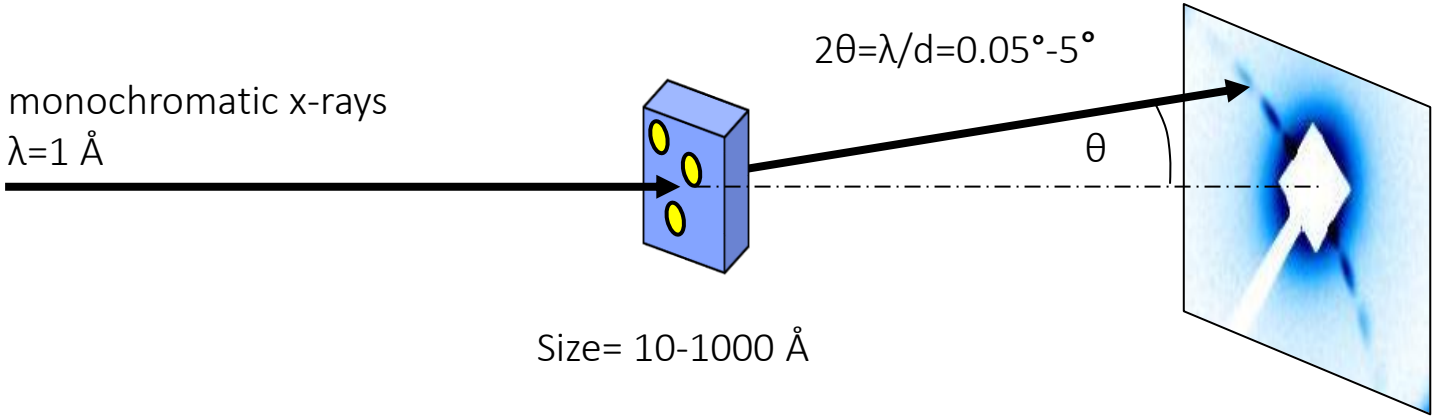


- Systematic characterization of the etching process is lacking and results vary significantly

↳ Pore characterisation is challenging → **small angle x-ray scattering**

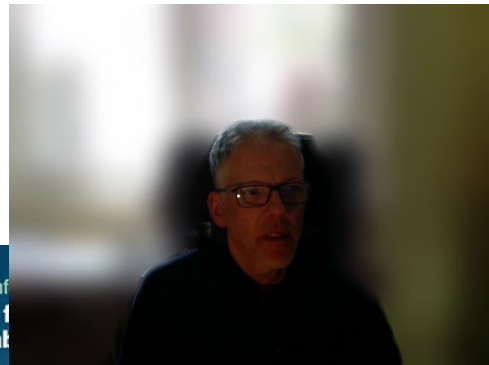


Small angle x-ray scattering (SAXS)

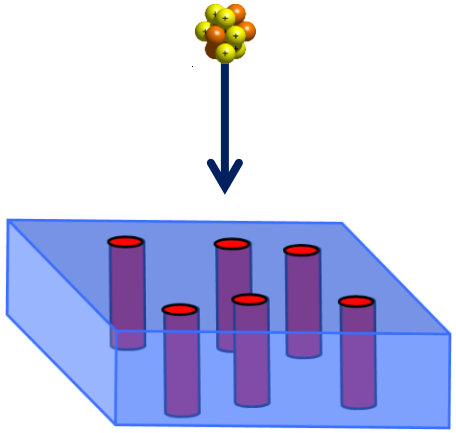


measures density fluctuations → **size, shape** and **spatial correlation** of **nm-objects**

- bulk technique → *can measure large sample volumes*
- non-destructive → *no sample preparation required*
- suitable for amorphous materials → *only small density contrast required*
- good statistics (10^5 tracks/pores) → *high accuracy*
- Flexible sample environments → *suitable for in situ measurements*
- short acquisition times → *good time resolution*



Track etched nanopores and SAXS

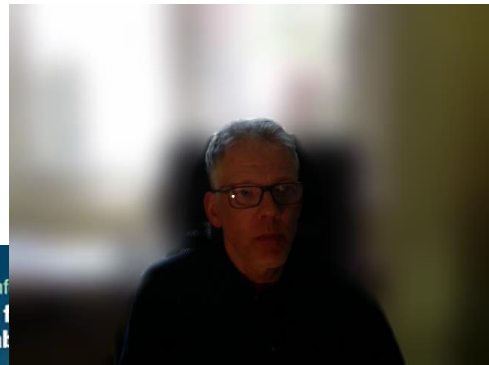


Ion tracks and track etched nanopores:

- “identical objects” nm-sized (narrow size distribution)
- ‘large’ volume (µm length)
- well aligned
- random “uncorrelated” distribution
- number of scatterers controlled by fluence

ion tracks/nanopores are great scattering objects

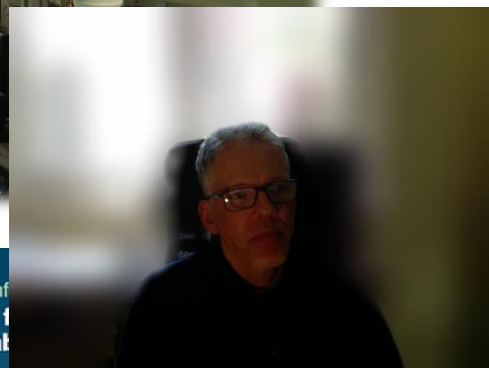
information about the ‘individual’ track/pore structure



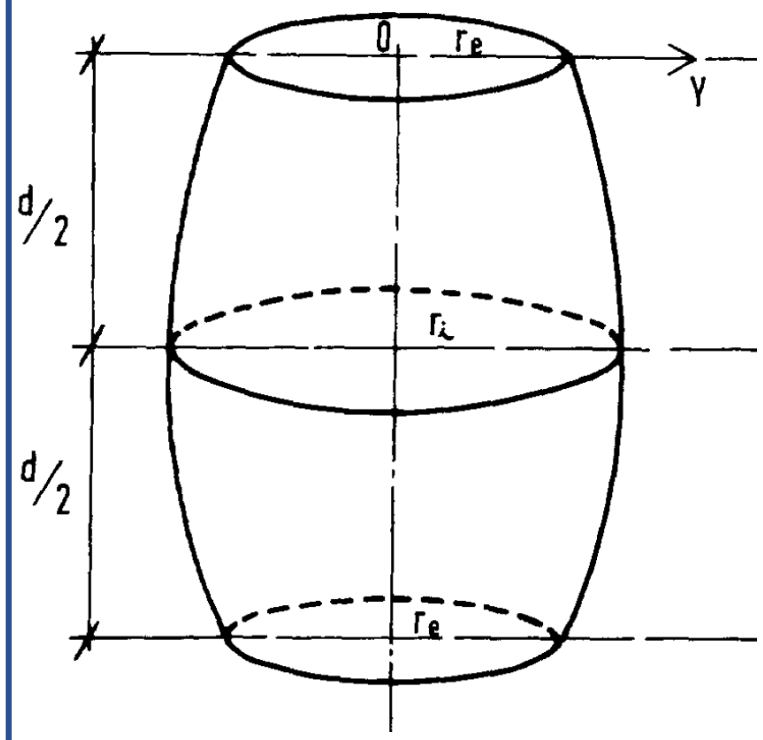
Australian Synchrotron

Melbourne, Australia

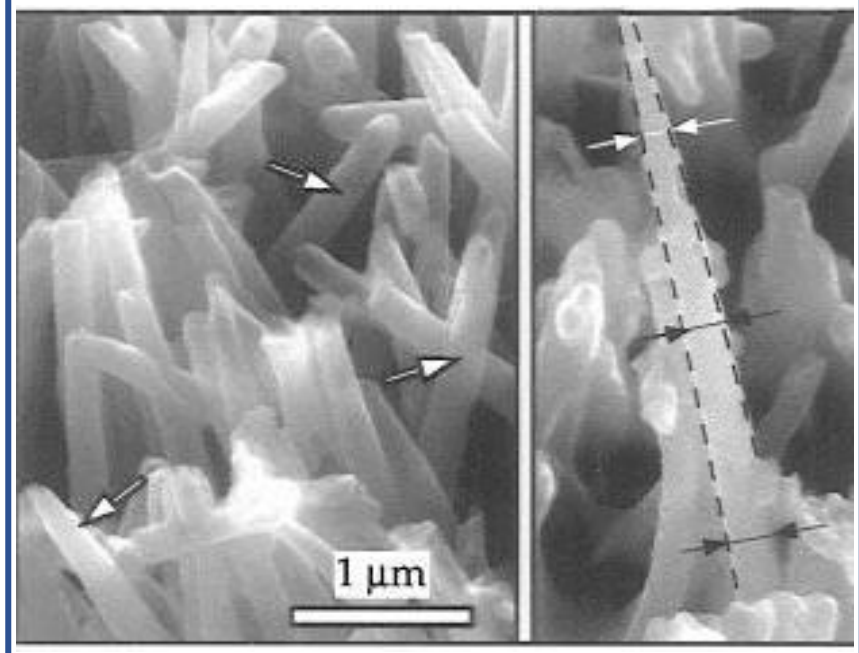
SAXS/WAXS beamline



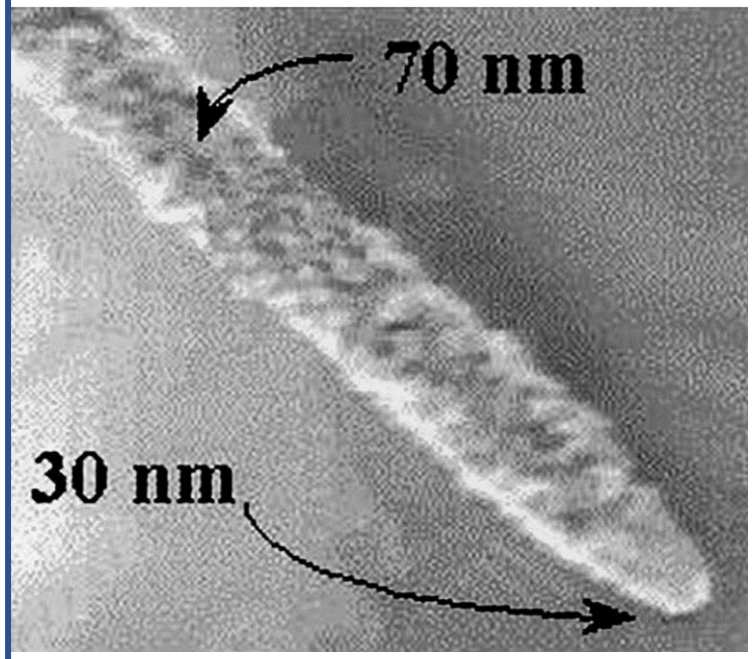
Polycarbonate nanopore membranes



A. Hernandez *et al Separation Science and Technology* (1986) 21, 665-677

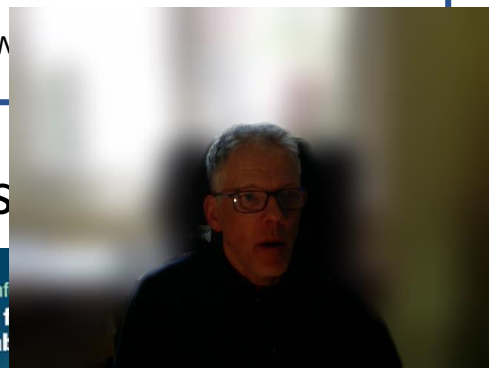


C. Schonenberger *et al J. Phys. Chem. B* (1997) 101, 5497-5505



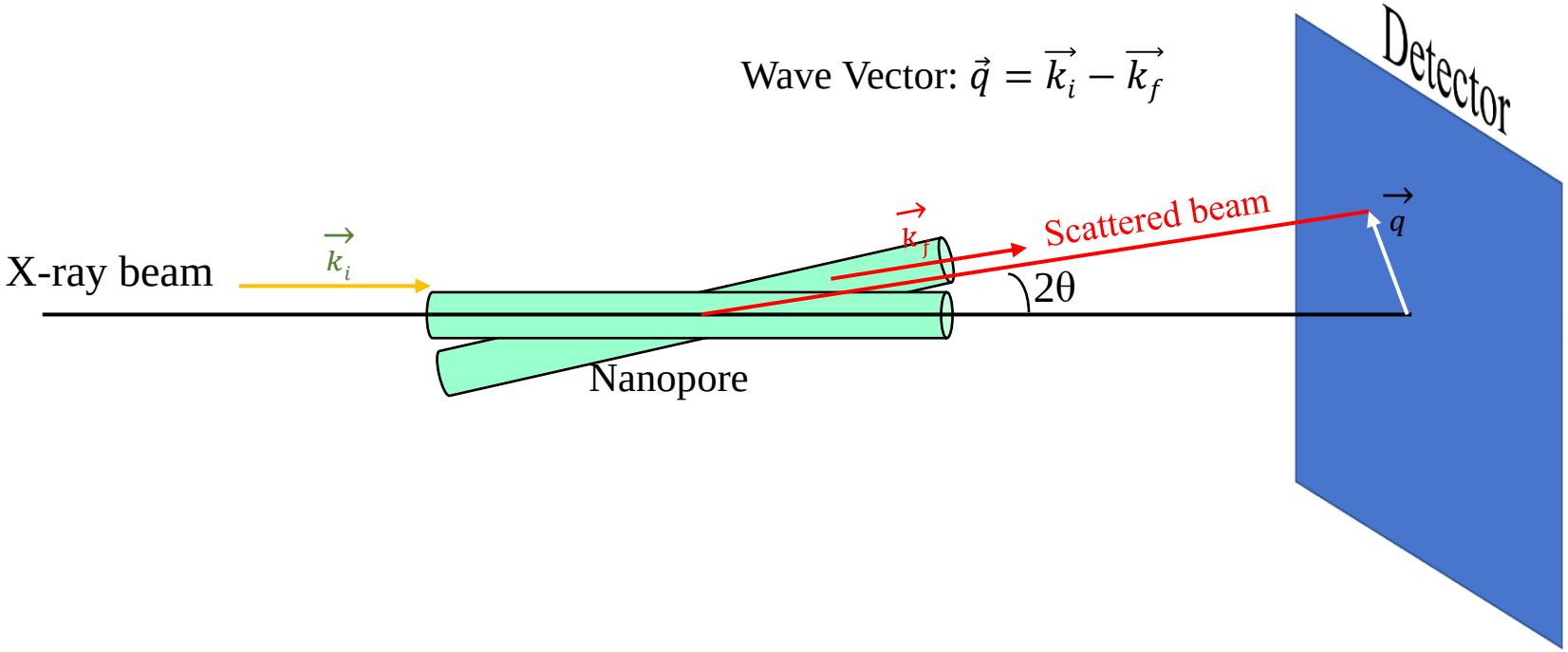
E. Ferain *et al N*

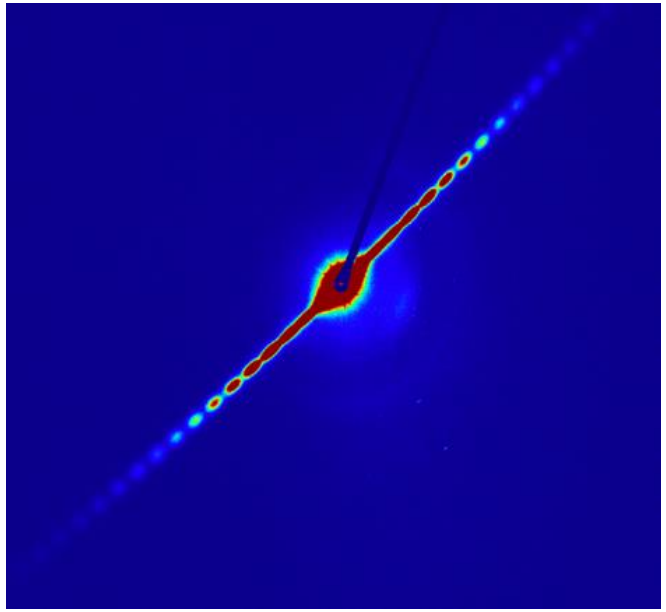
Are the nanopores cylindrical or have they got tapered sections towards the s



Polycarbonate nanopore membranes

20 μm PC, 2.3 GeV Pb





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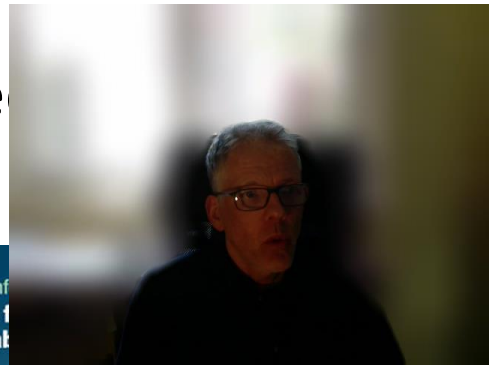
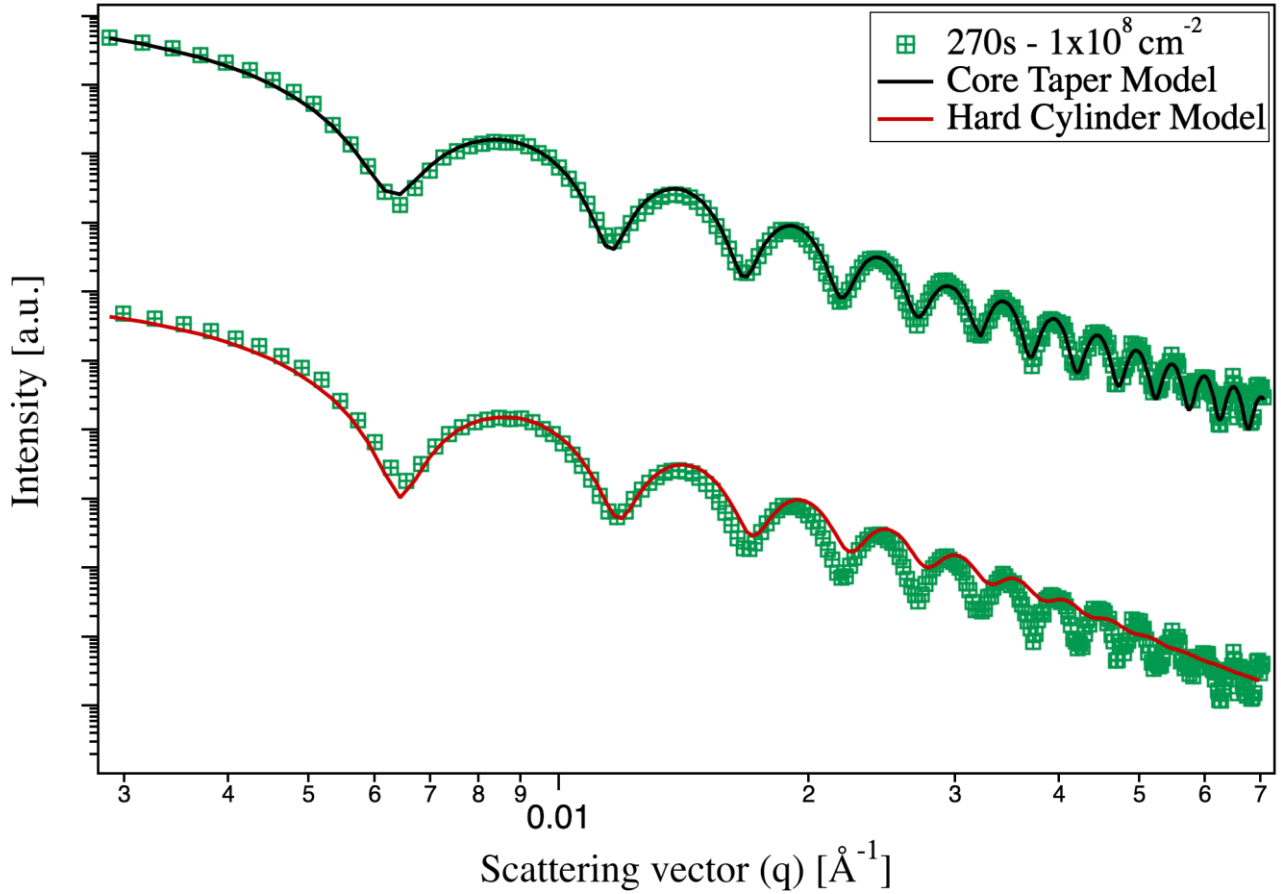
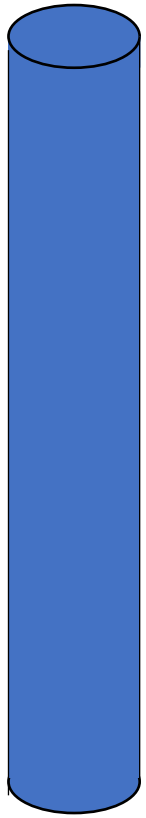


S. Dutt, P. Apel, N. Lizunov, C. Notthoff, Q. Wen, C. Trautmann, P. Mota-Santiago, N. Kirby, and P. Kluth, Journal of Membrane Science 639 (2021) 119681

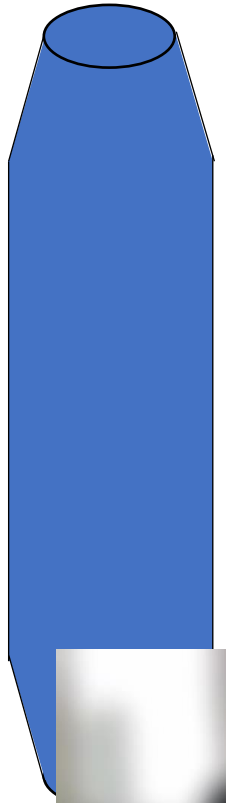
Polycarbonate nanopore membranes



Cylinder



Cylinder with tapered ends



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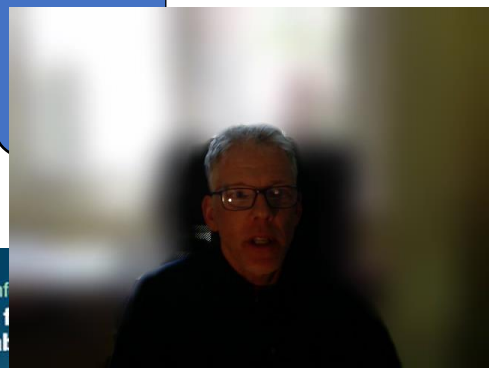
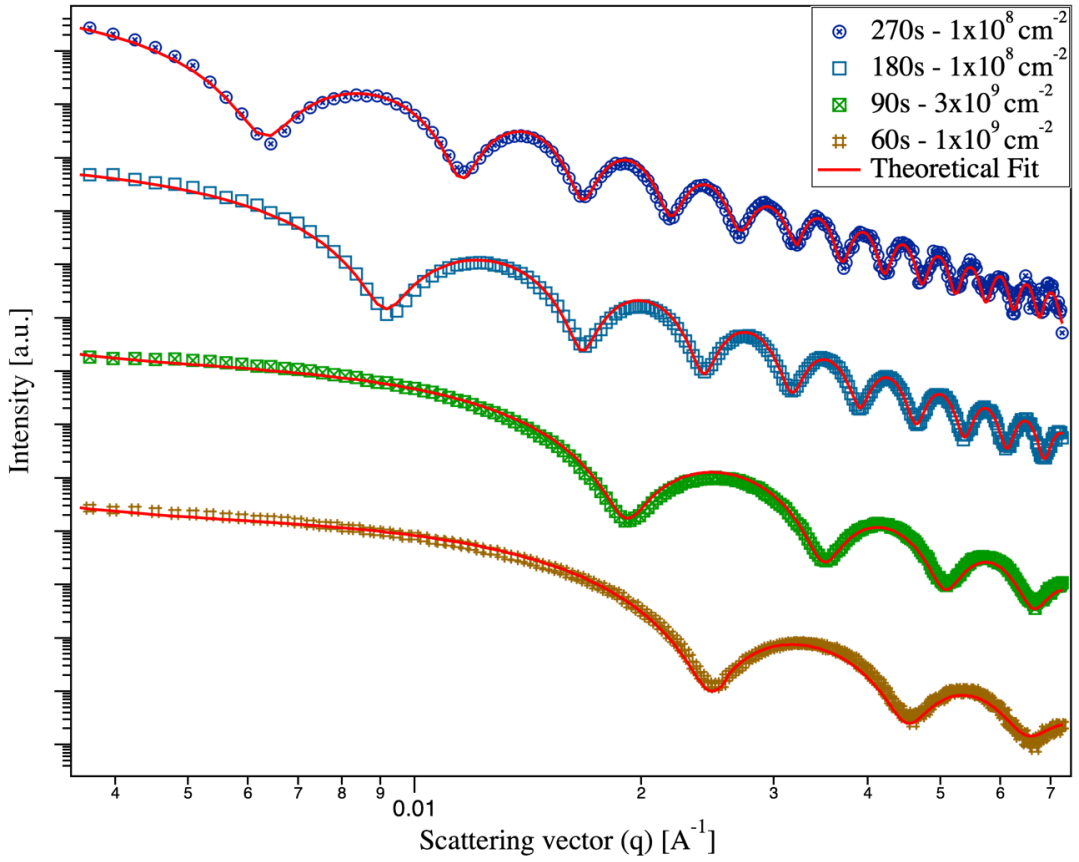
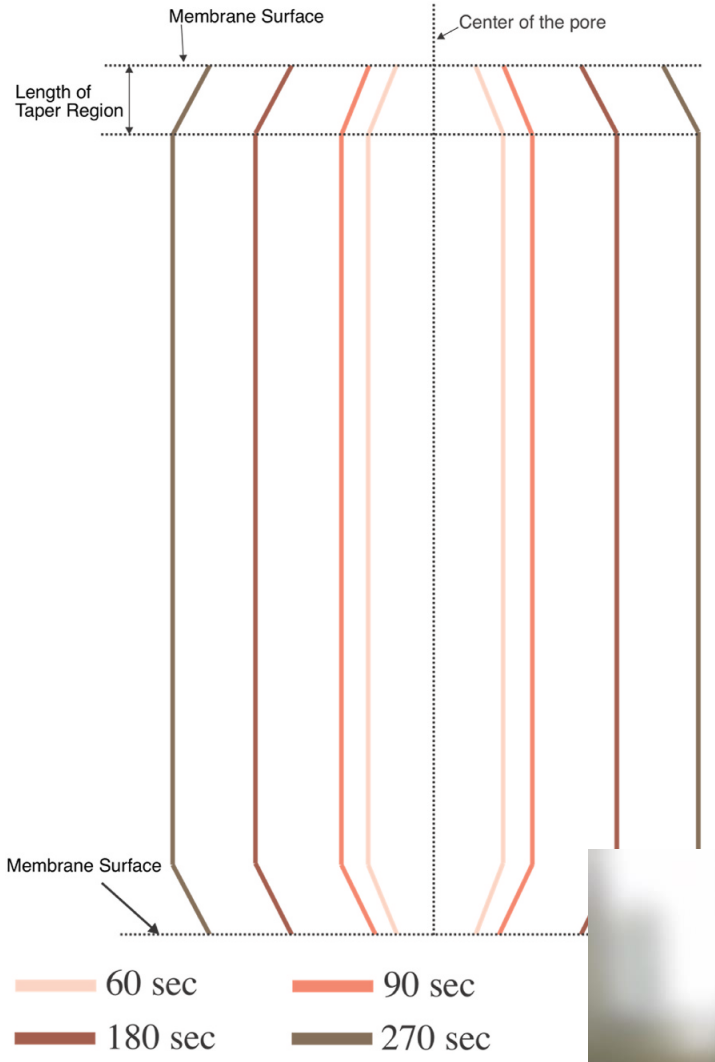


Polycarbonate nanopore membranes





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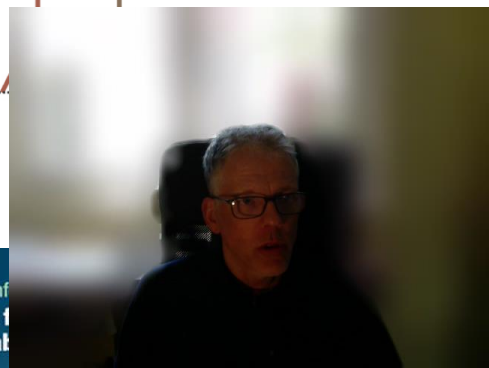
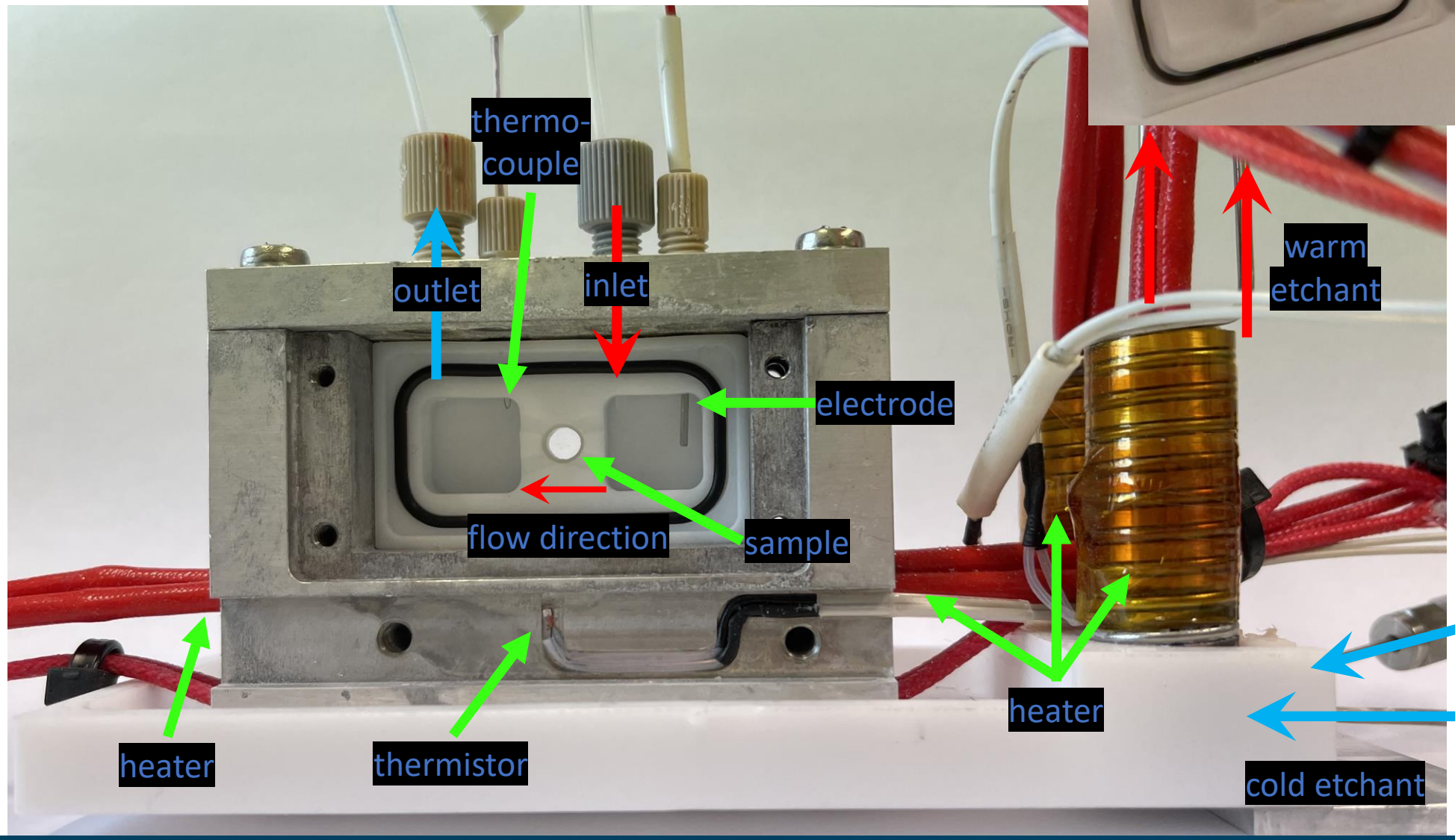
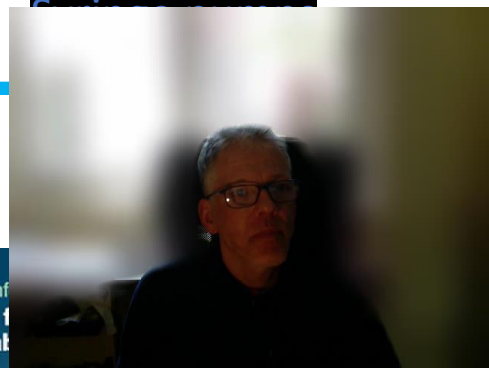


In situ SAXS experiment



***In situ* membrane cell**

- Temperature control
- Etchant flow control
- Separate injection on both sides
- Bias/membrane current
- ~1-10 s time resolution



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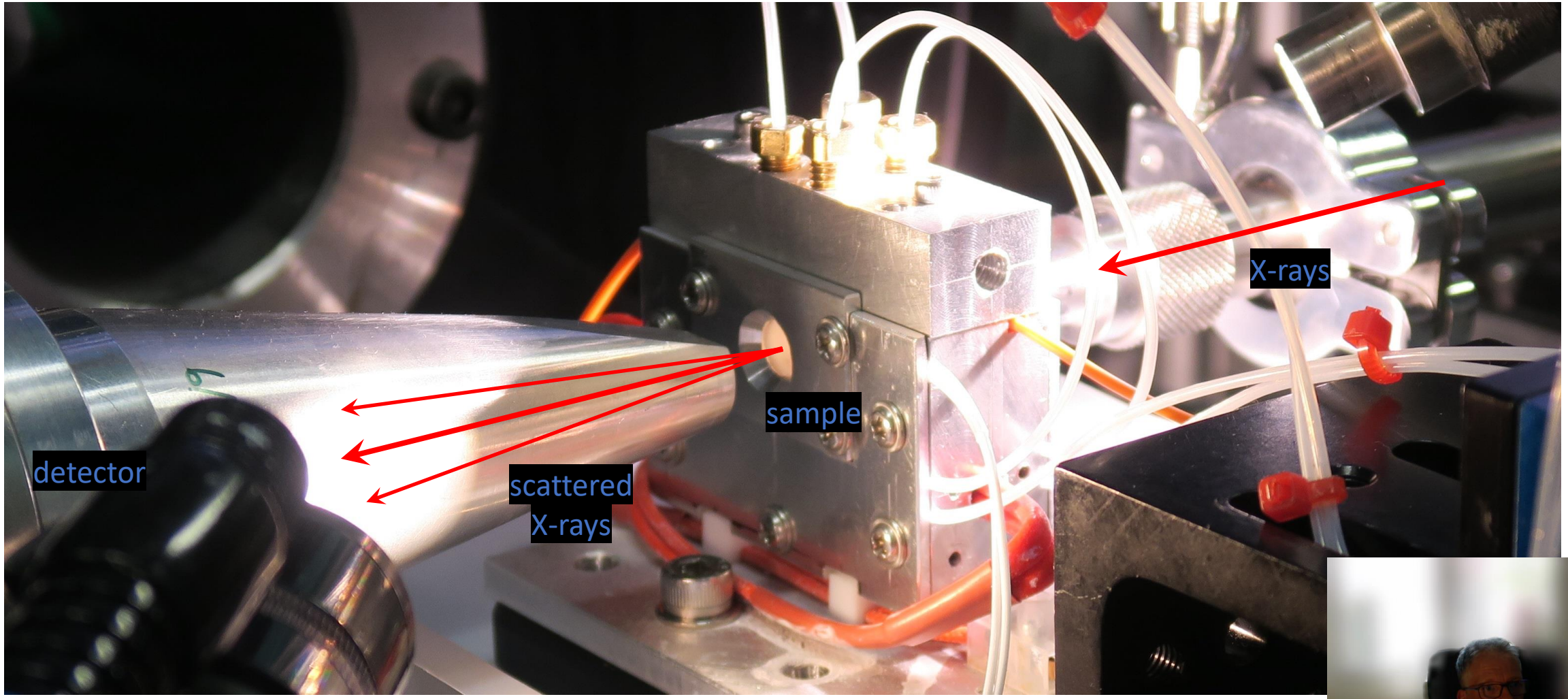
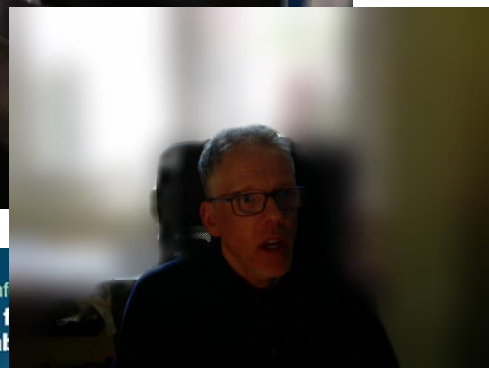
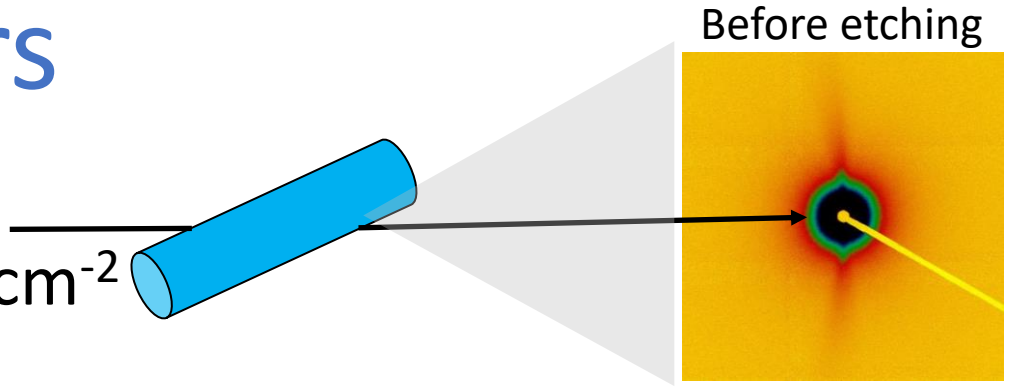
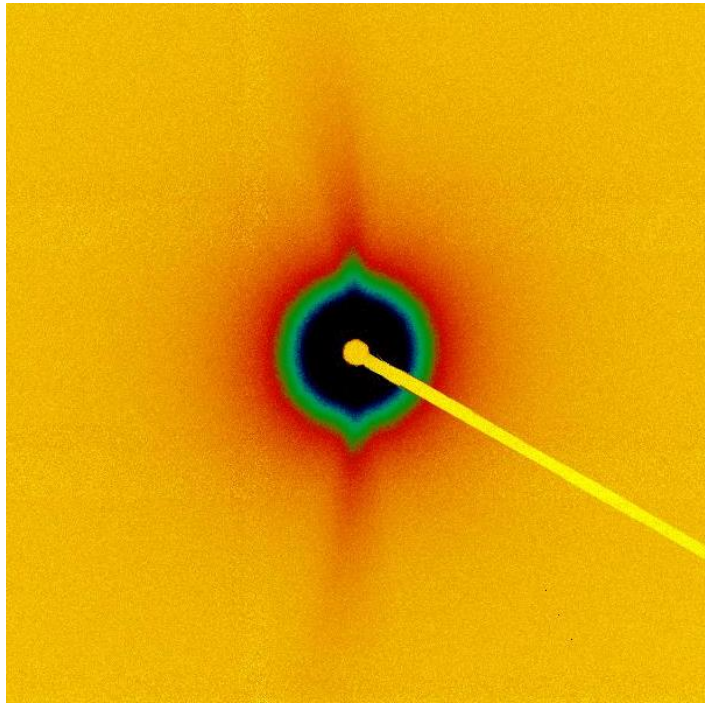


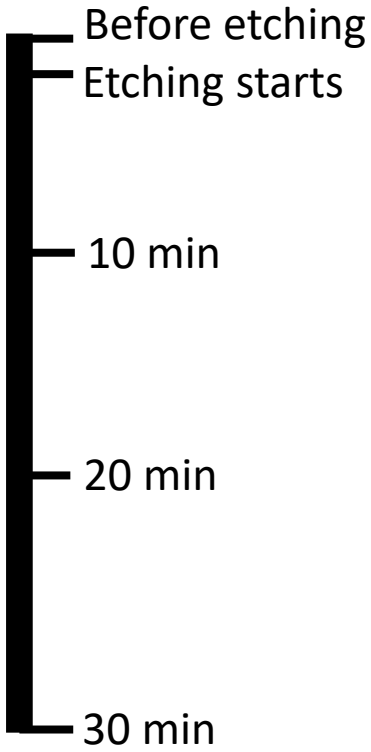


In situ etching in polymers

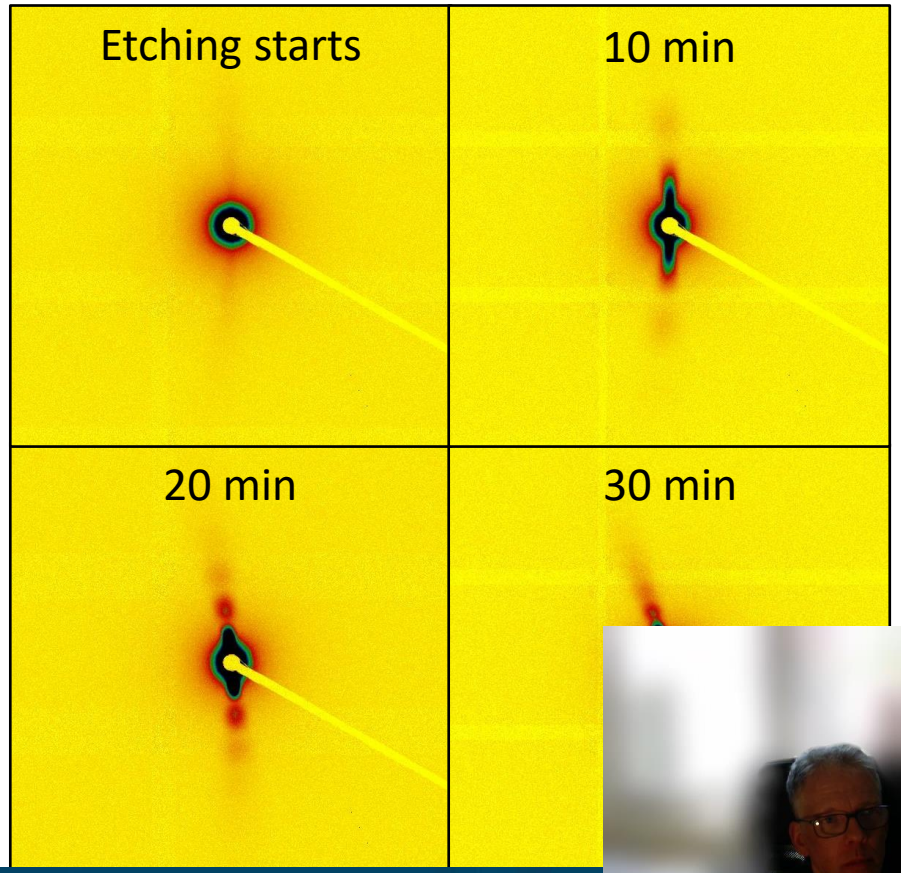
- Material: 30 µm polycarbonate
- Ion irradiation: 2.2 GeV Au ions, 10^9 ions cm^{-2}
- Etching conditions: 3 M NaOH at 50°C

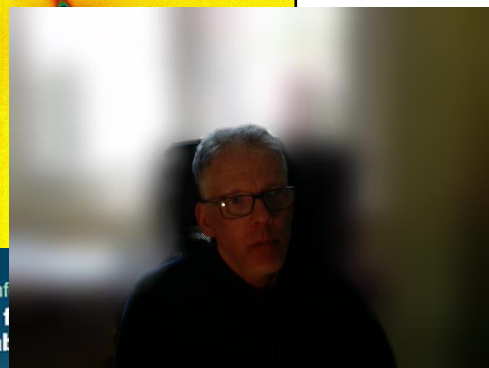






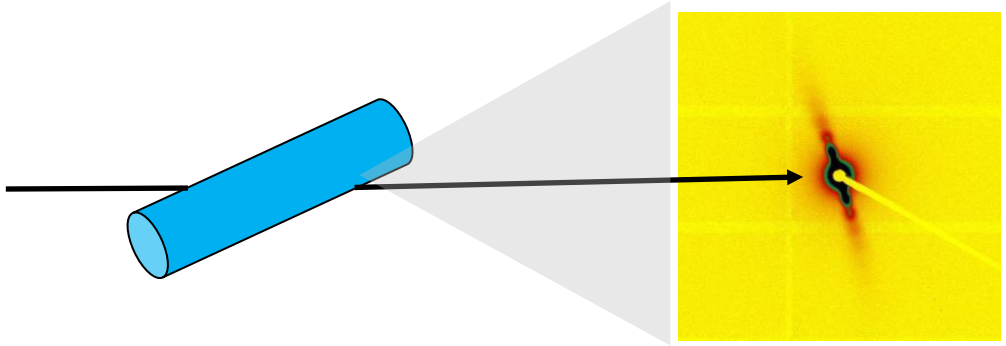
1 image ≙ 8 seconds

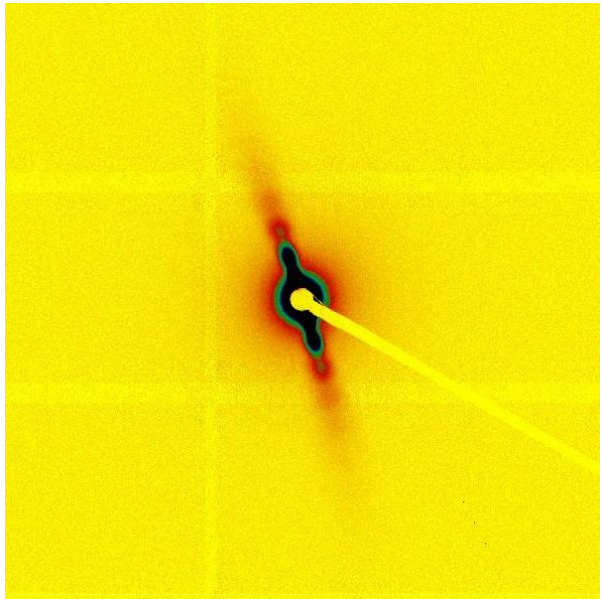


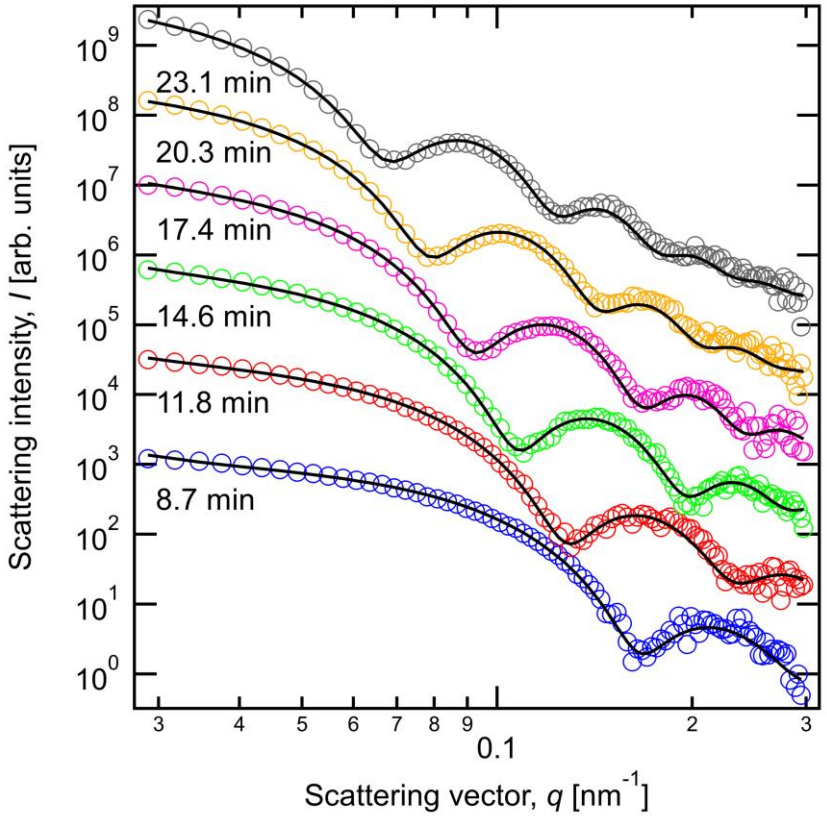


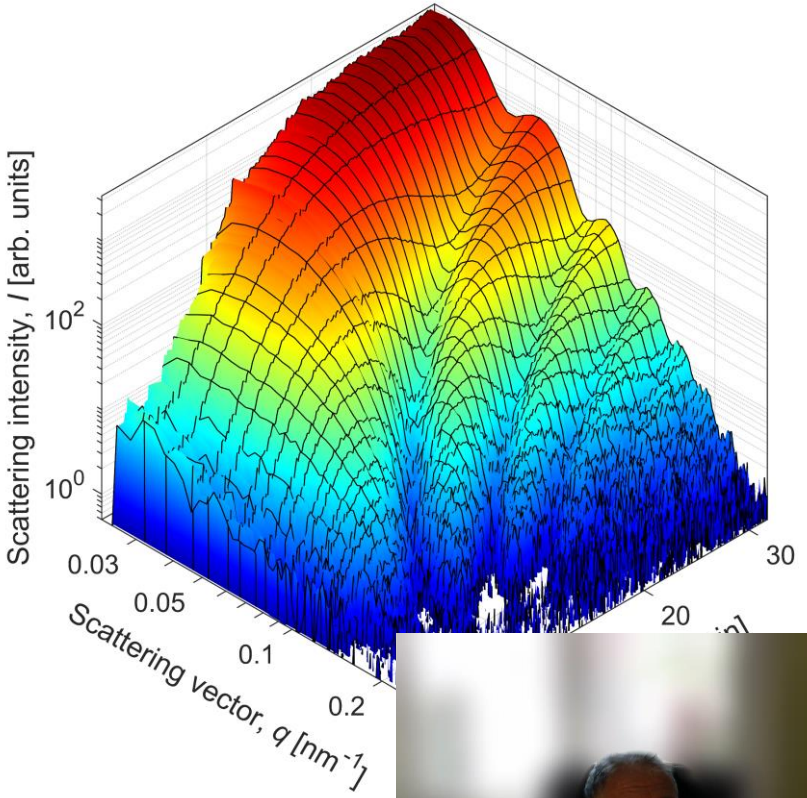
In situ data analysis

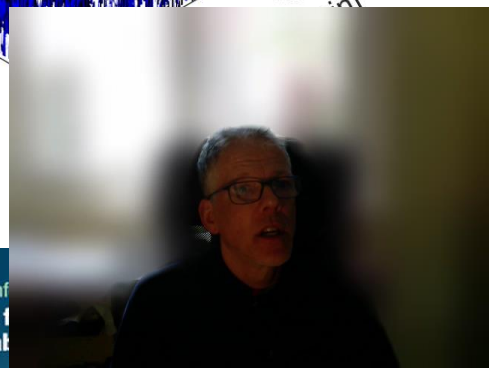
- Reducing the 2D scattering data to a 1D scattering intensity
- Fitting of the data using a hard cylinder model
  - **Pore radius**
  - **Radius distribution**







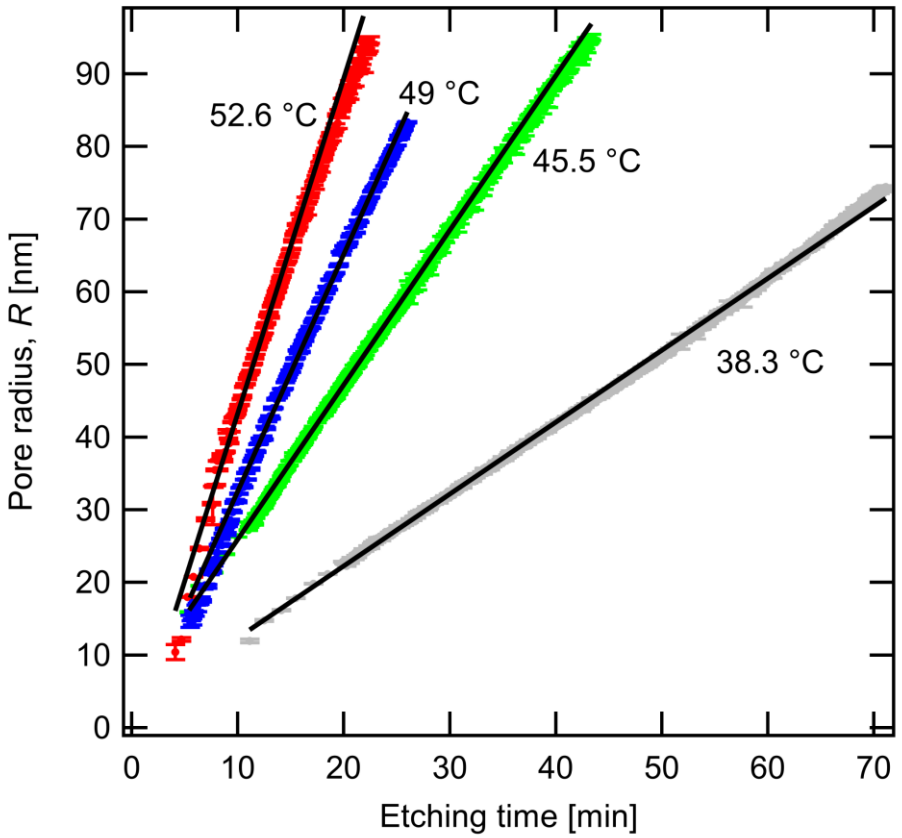


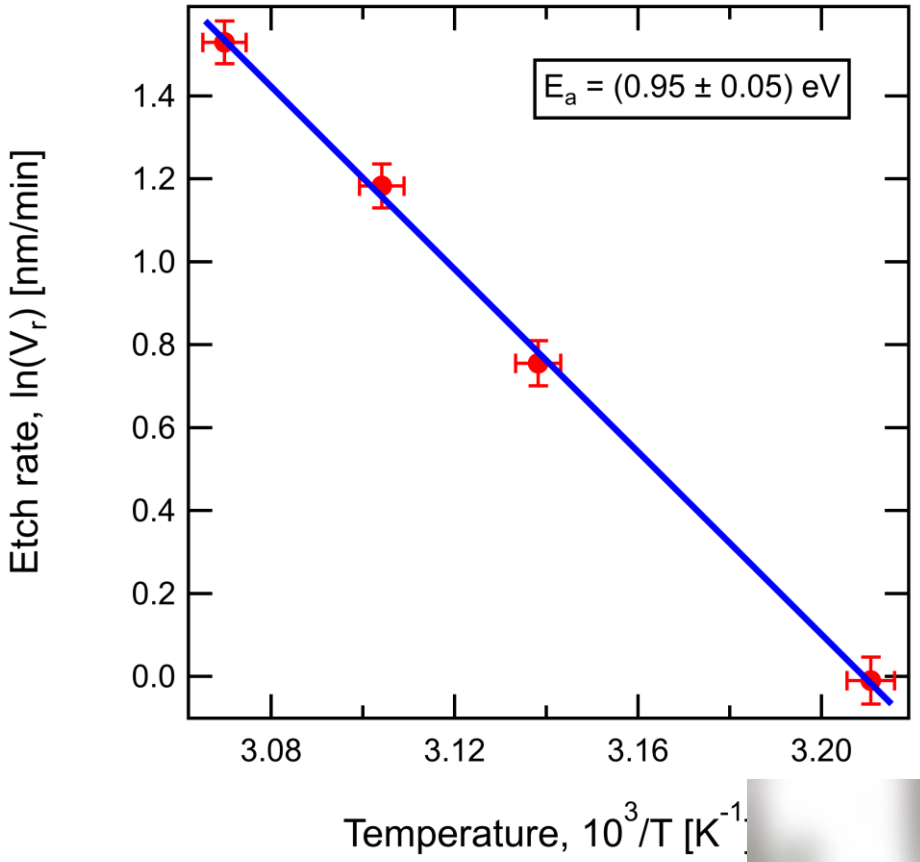


A. Kiy, C. Notthoff, S. Dutt, M. Grigg, A. Hadley, P. Mota-Santiago, N. Kirby, C. Trautmann, M. E. Toimil-Molares, and **P. Kluth**, *Physical Chemistry Chemical Physics* **23** (2021) 1423

•Radial etching

- 30 µm polycarbonate, 2.2 GeV Au ions, 10^9 ions cm^{-2}, 3 M NaOH





- Linear etching behaviour at all temperatures

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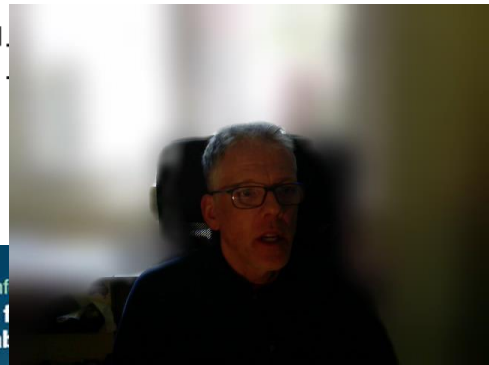
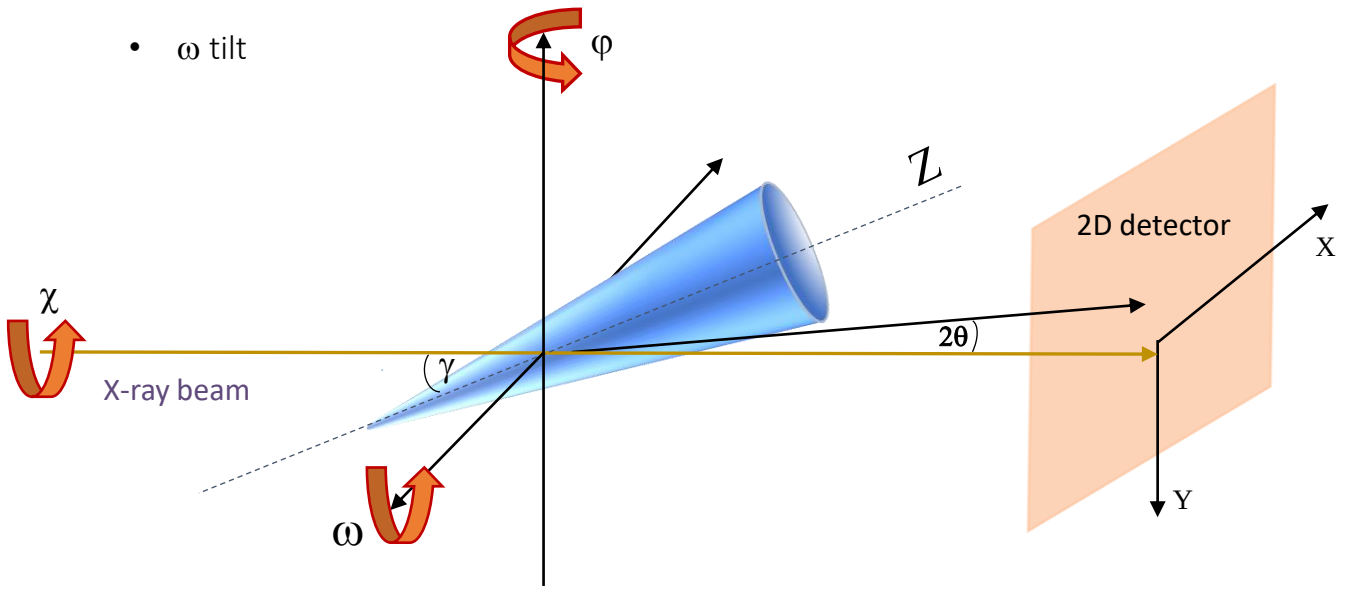
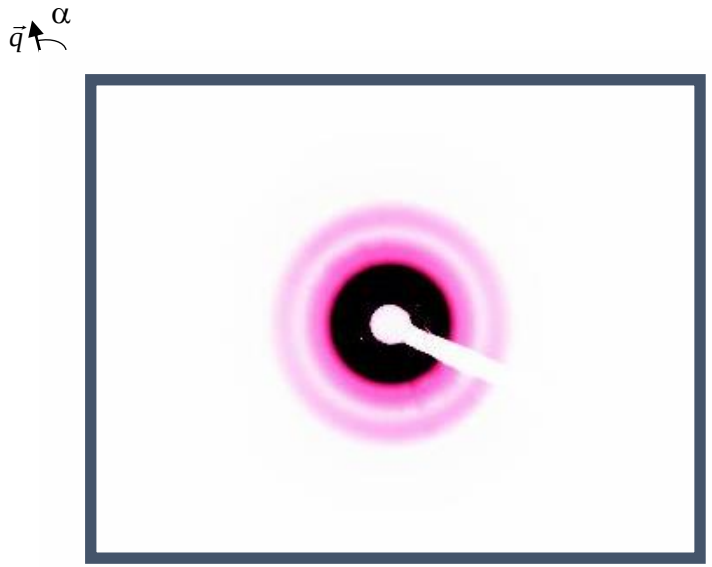


Conical nanopores in SiO_2





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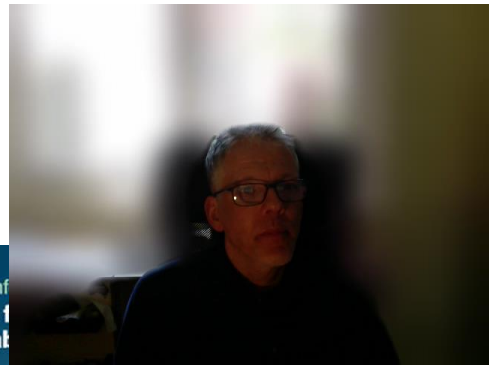
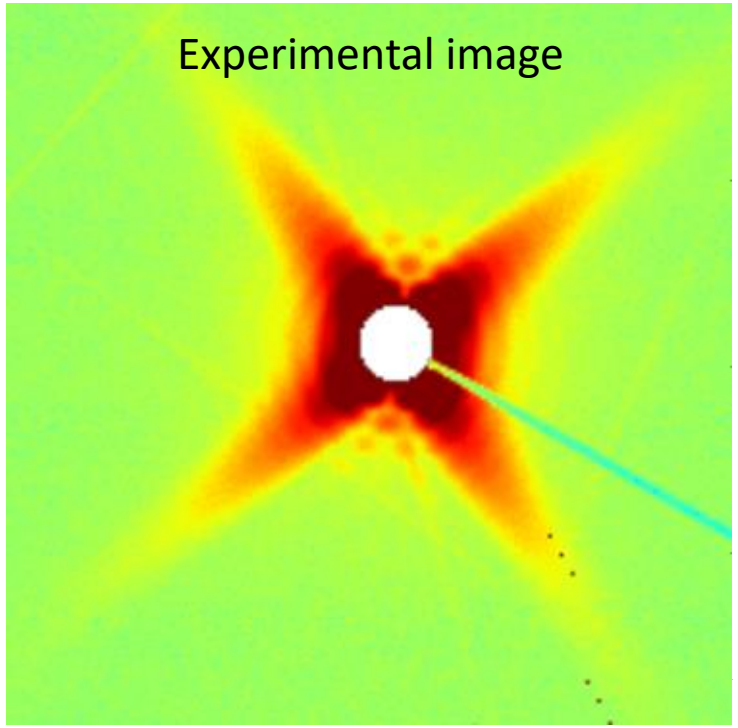
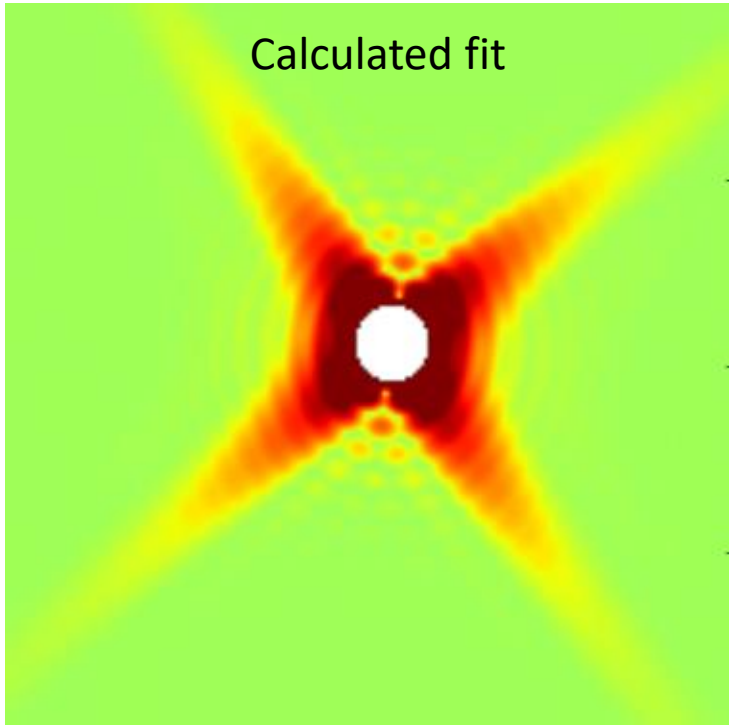


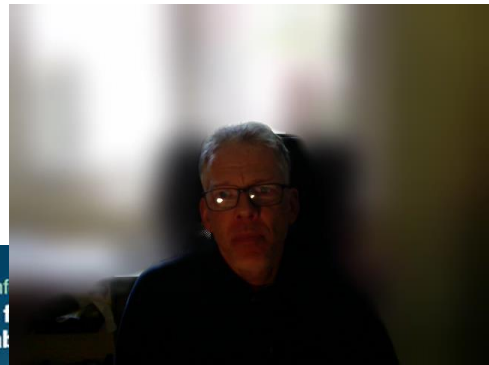
Conical nanopores in SiO_2

2mm SiO_2 irradiated with 1.1 GeV Au, Etched in 2.5%HF for 8 minutes

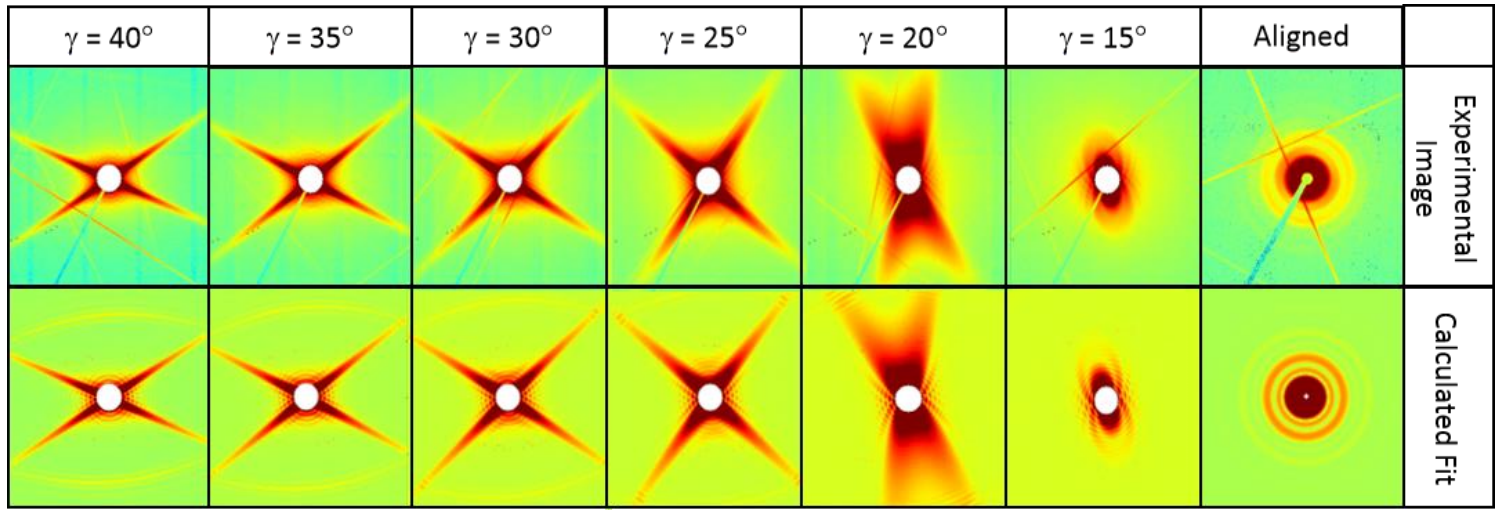




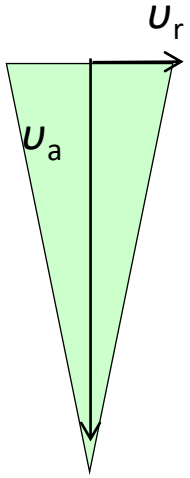
Cone height H = 267.3nm
Cone opening angle b = 16.2°
Outer radius R = 77.5 nm

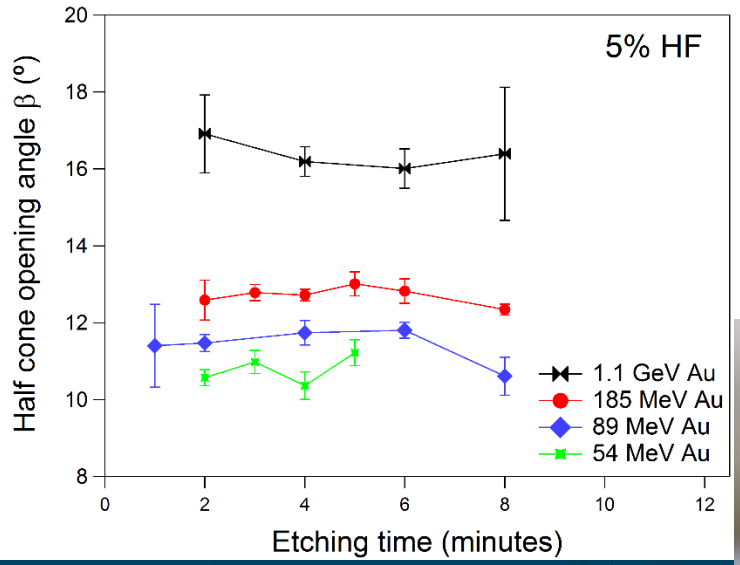


Conical nanopores in SiO_2



- Simultaneous multiple image fits





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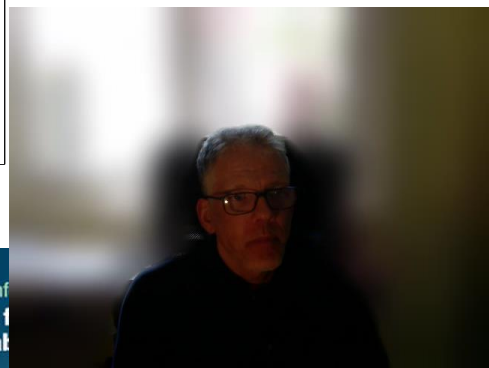
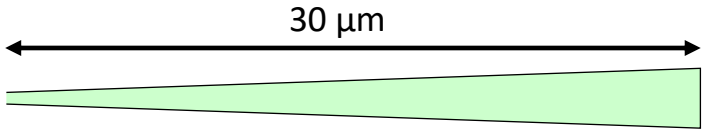
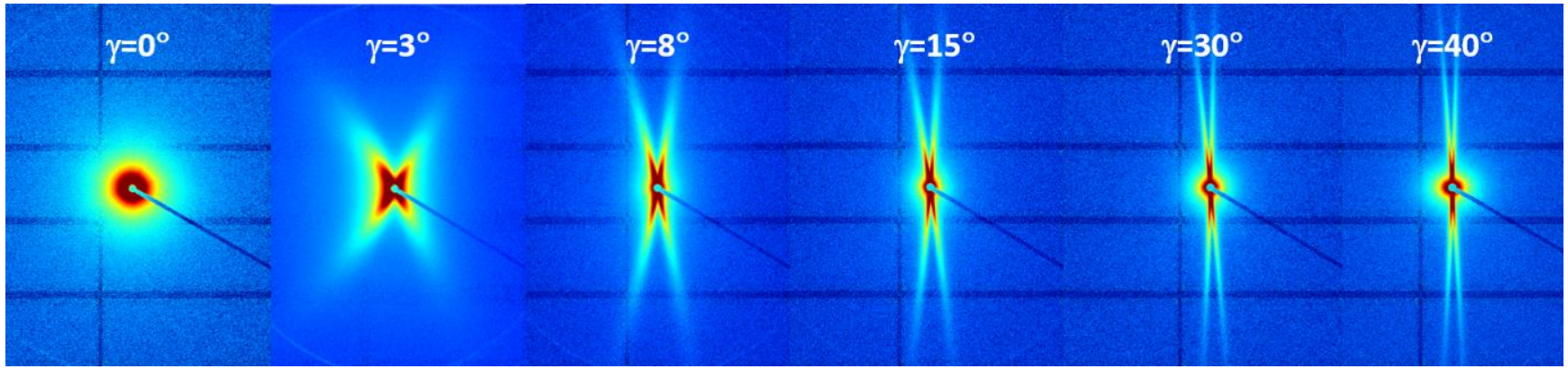


Conical nanopores in PC

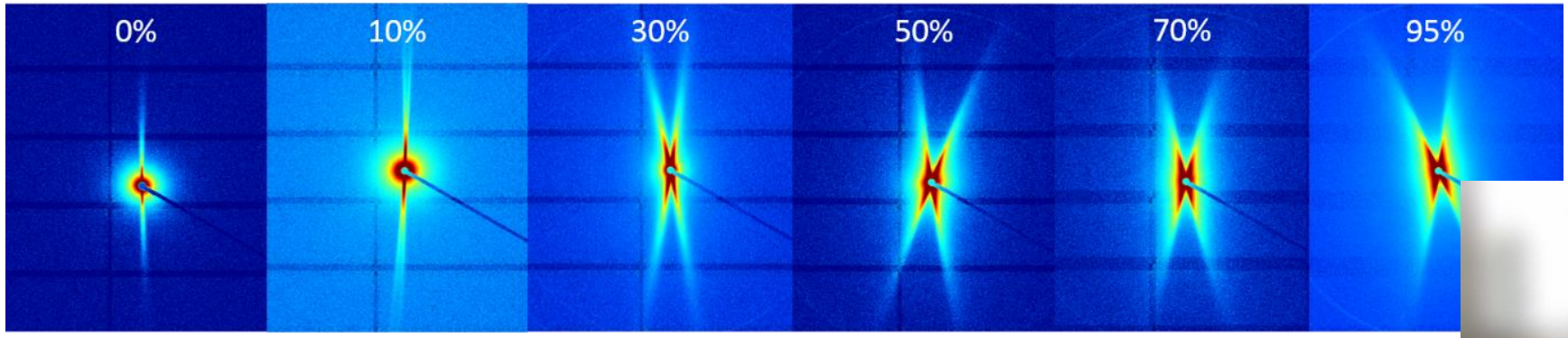
Methanol + NaOH leads to the formation of conical pores in PC



Tilt sequence @ 30% Methanol



Methanol concentration series @ 10° tilt



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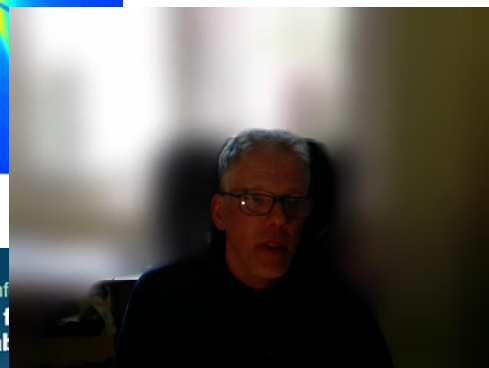
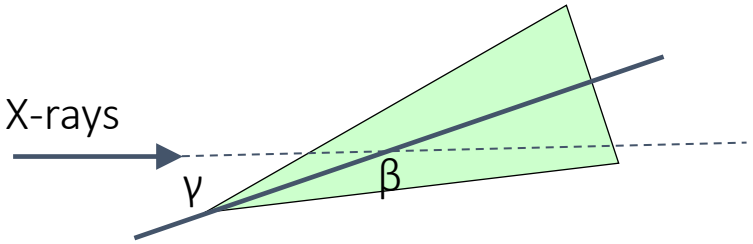
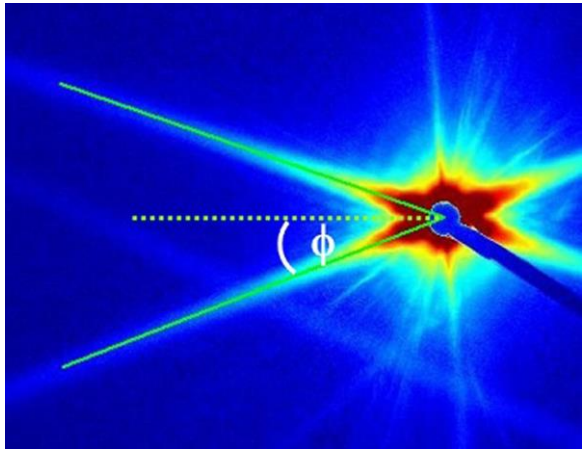
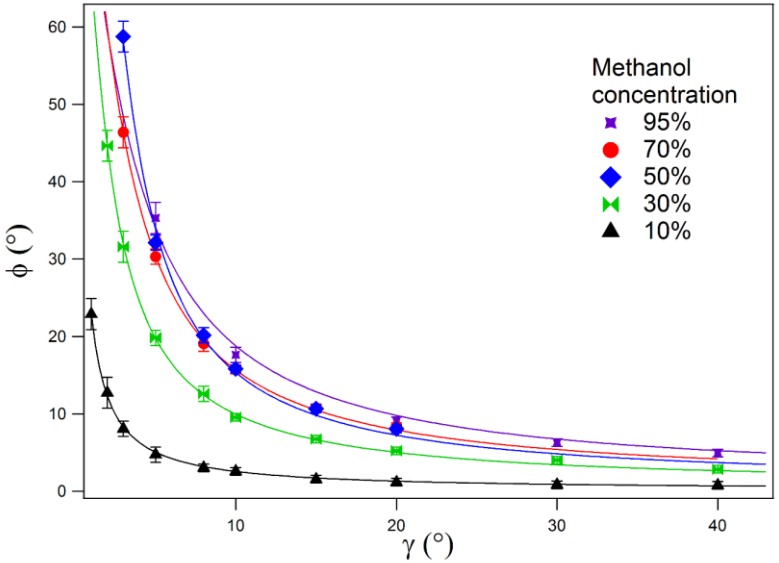


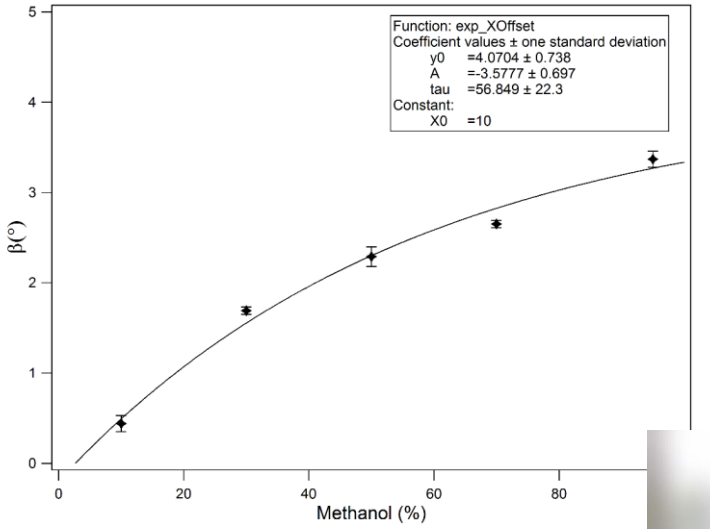
Conical nanopores in PC

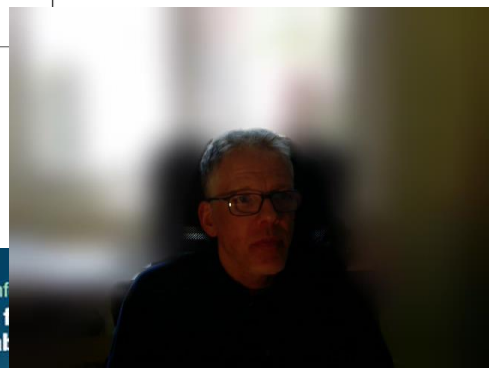
$$\tan \beta = \tan \phi \sin \gamma$$











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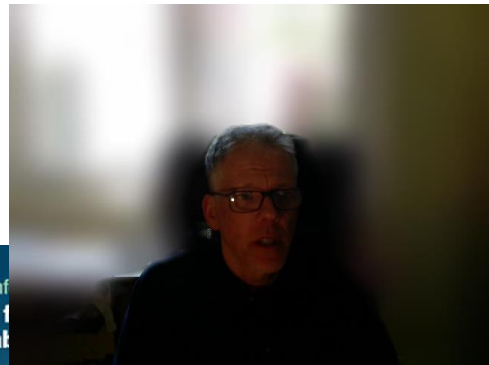
Summary

- Development of track etched nanopore in inorganic membranes
- SAXS provides a powerful tool to study track etched pore morphologies with high precision
- SAXS results of nanopores in PC to quantify cylindrical/tapered structure
- *In situ* SAXS measurements track etching in polymer membranes
- SAXS characterisation of conical pores in SiO_2

Australian Synchrotron

Australian Government
Australian Research Council



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