Micro-mechanics and Polarized Raman Spectroscopy on Irradiated Nuclear Graphite

Dr. Dong Liu

EPSRC Postdoctoral Research Fellow
1851 Exhibition Brunel Research Fellow
Junior Research Fellow, Mansfield College
Department of Materials, University of Oxford, U.K.

Research Affiliate
Lawrence Berkeley National Laboratory, U.S.A.

Outline

Background

Micro-mechanical testing

- Nano-indentation
- *In situ* micro-cantilever testing
  - ✓ Glassy carbon
  - ✓ Filter graphite
  - ✓ Gilsocarbon graphite
  - ✓ PGA graphite (unirradiated and irradiated)
  - ✓ HOPG graphite (unirradiated and irradiated)
  - ○ Scale up to larger size

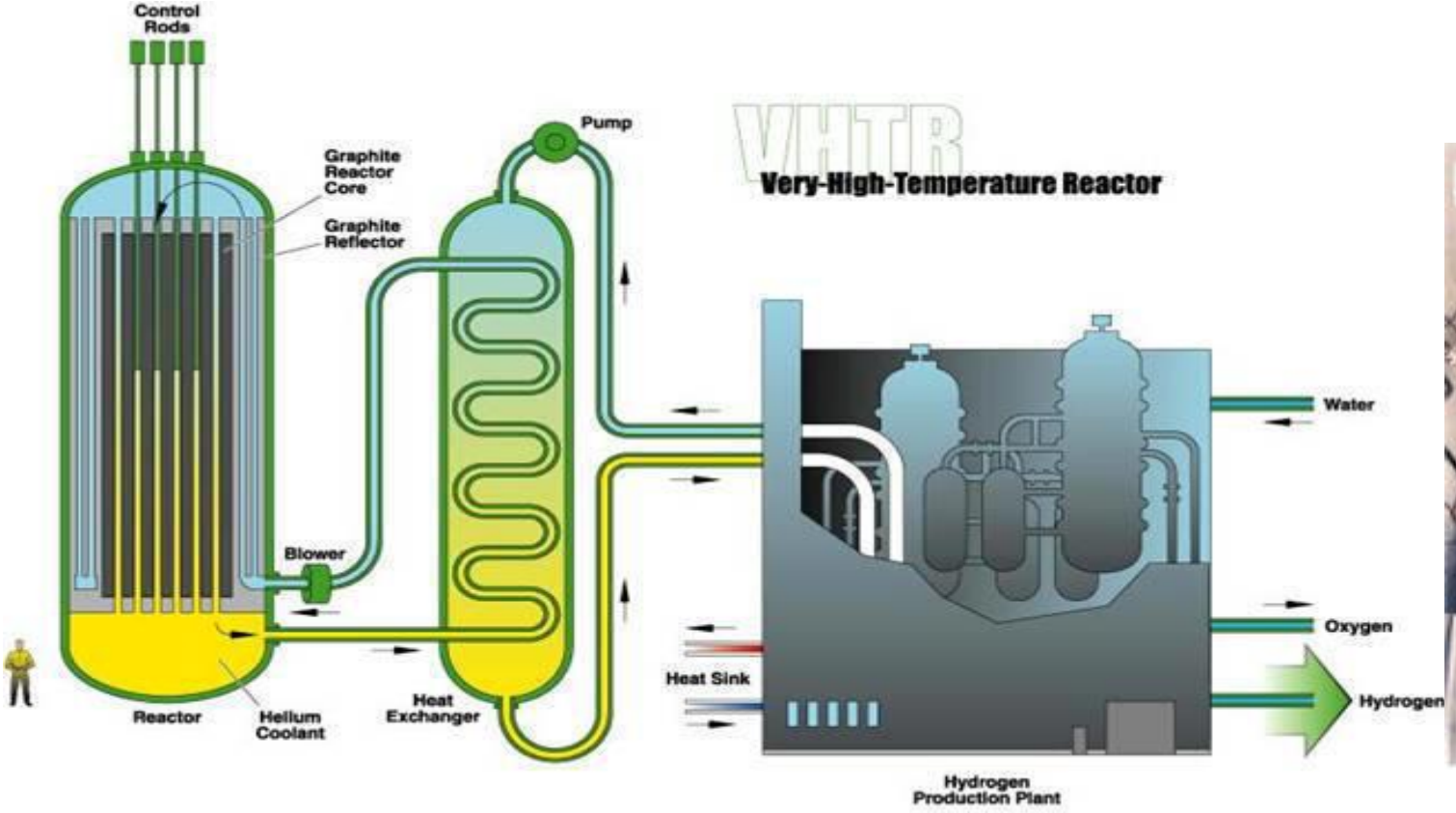
Raman spectroscopy: Applications

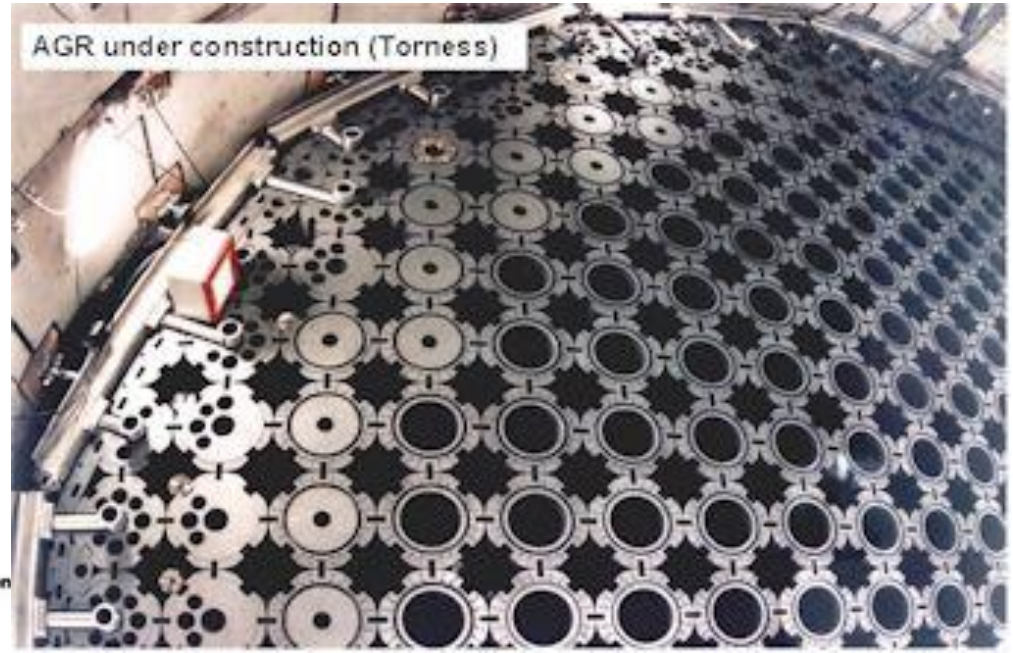
- ✓ Micro-Raman for residual stress
- ✓ Polarized-Raman for preferred orientation measurements

Key messages

Nuclear Graphite

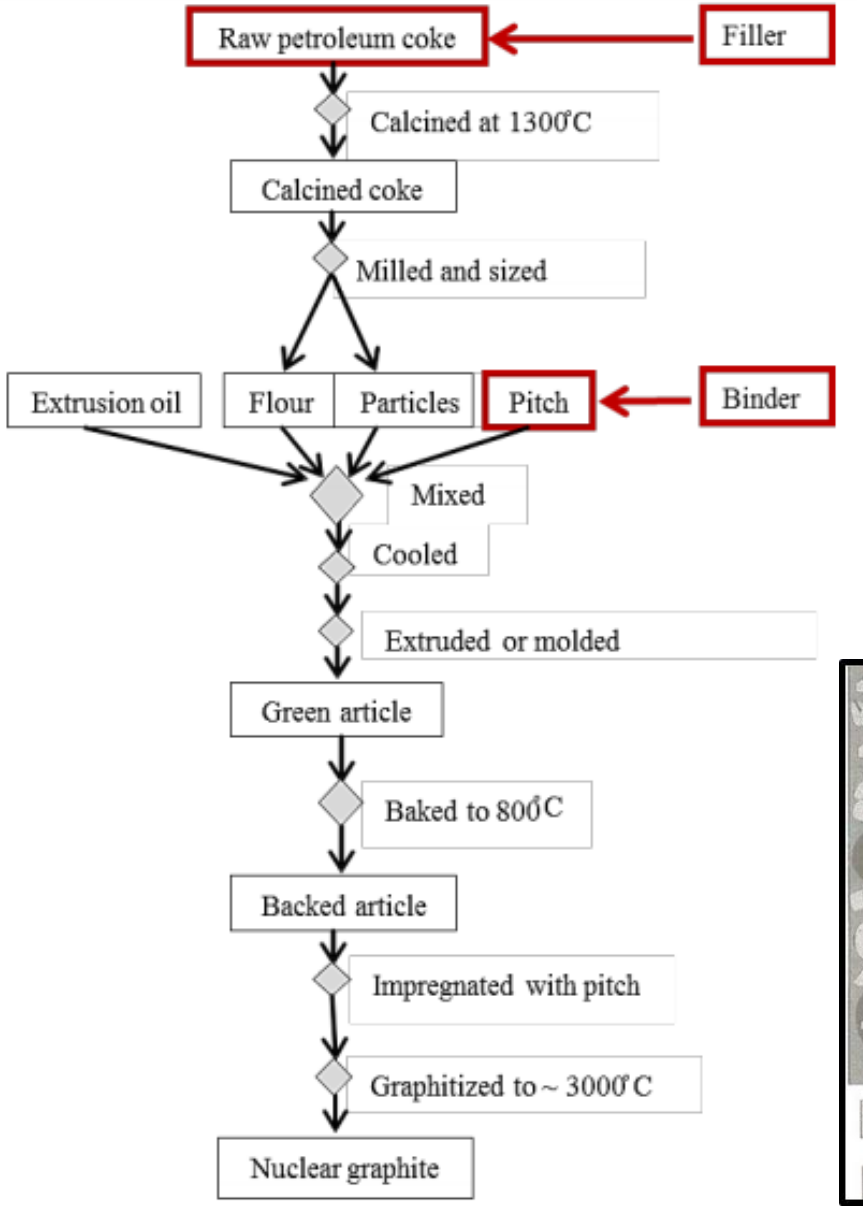
- Used as moderators and structural components in operating Advanced Gas-cooled Reactors (AGRs) in the UK
- Life-limiting as it is not replaceable; porous, multi-phase (filler and binder), heterogeneous
- Laboratory tests / inspections are limited by the size of the sample that trepanned from irradiated bricks
- Candidate material for some Gen IV designs





UNIVERSITY OF OXFORD

OxfordMaterials

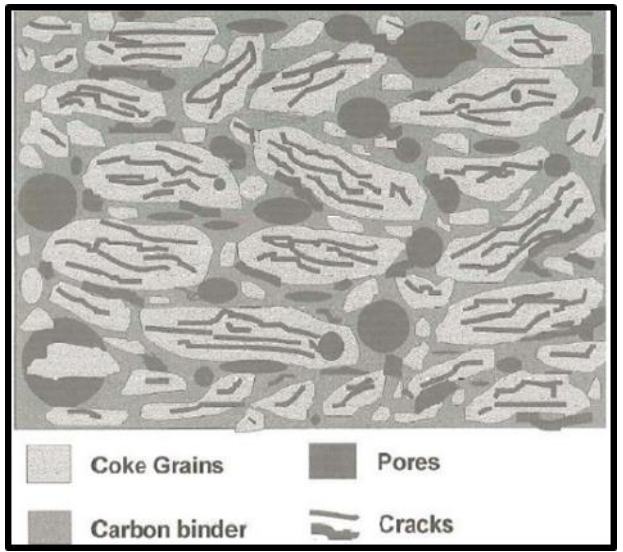


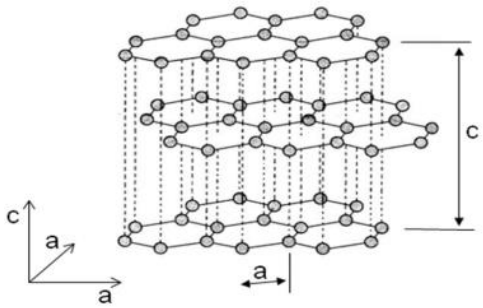
Desired properties in nuclear-grade graphite:

- High purity; High density; High thermal conductivity; Low CTE
- High irradiation stability (pitch, coke and manufacture process);
- High strength (flexural: 20-30MPa);
- Low anisotropy, (less than 1.1, defined by CTE in orthogonal directions)
- Low elastic modulus (~11 GPa for Gilsocarbon)

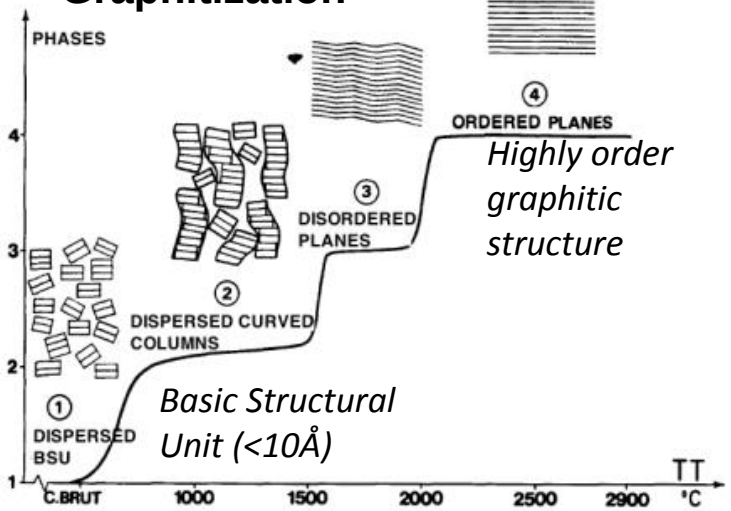
Facts:

- Damage and fracture
- Microstructure, porosity
- Residual stresses





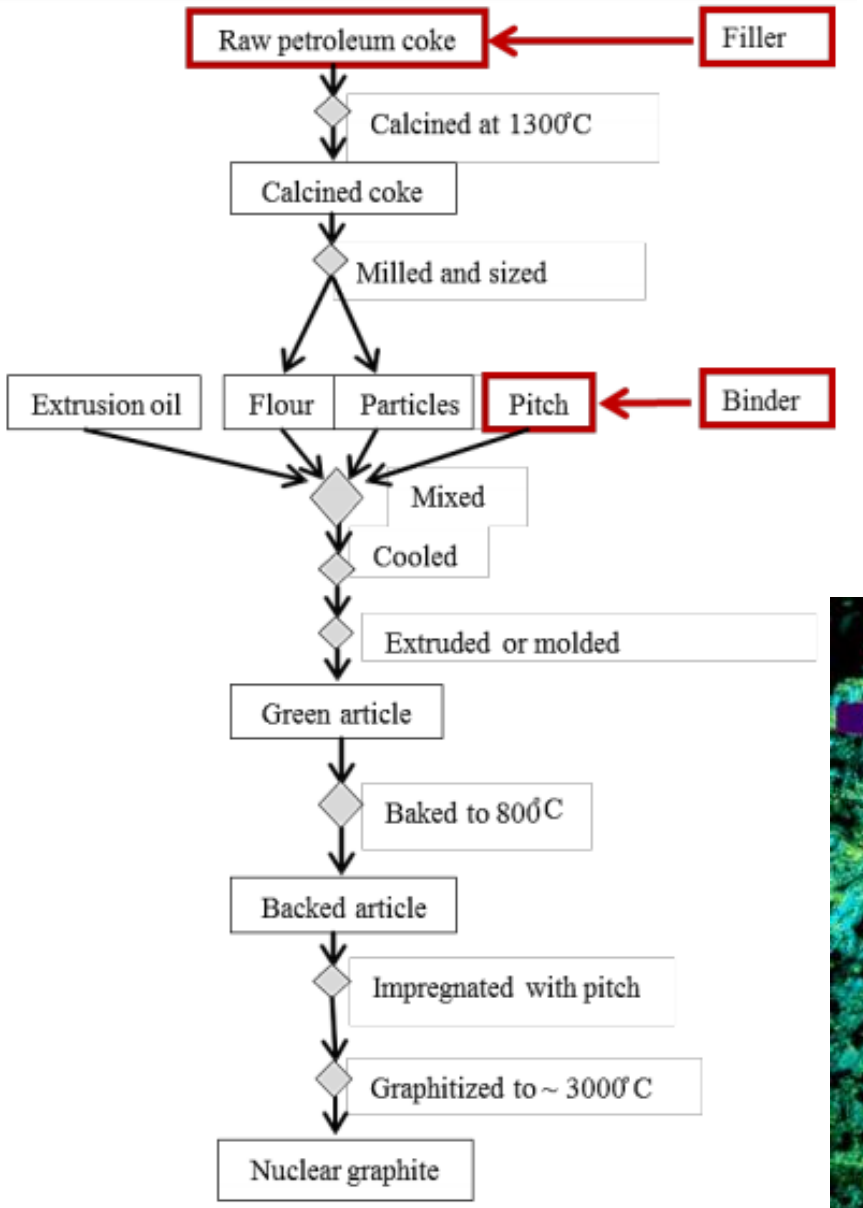
Graphitization



Oberlin A. Carbon N Y 1984;22:521-41

UNIVERSITY OF OXFORD

OxfordMaterials

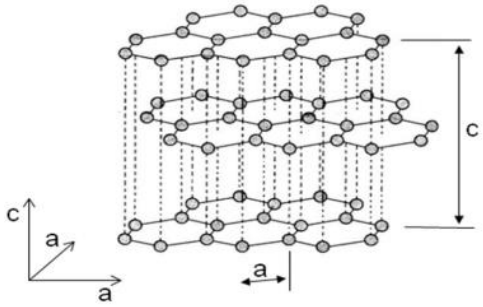


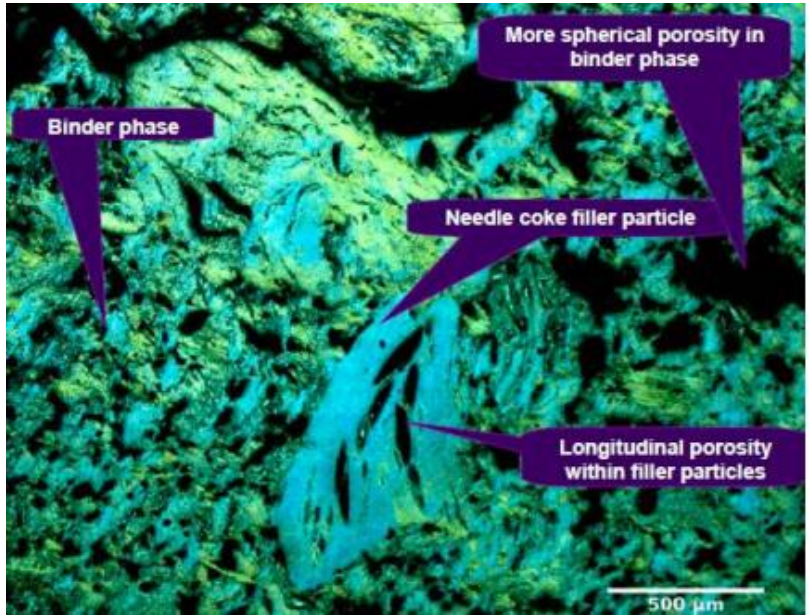
Desired properties in nuclear-grade graphite:

- High purity; High density; High thermal conductivity; Low CTE
- High irradiation stability (pitch, coke and manufacture process);
- High strength (flexural: 20-30MPa);
- Low anisotropy, (less than 1.1, defined by CTE in orthogonal directions)
- Low elastic modulus (~11 GPa for Gilsocarbon)

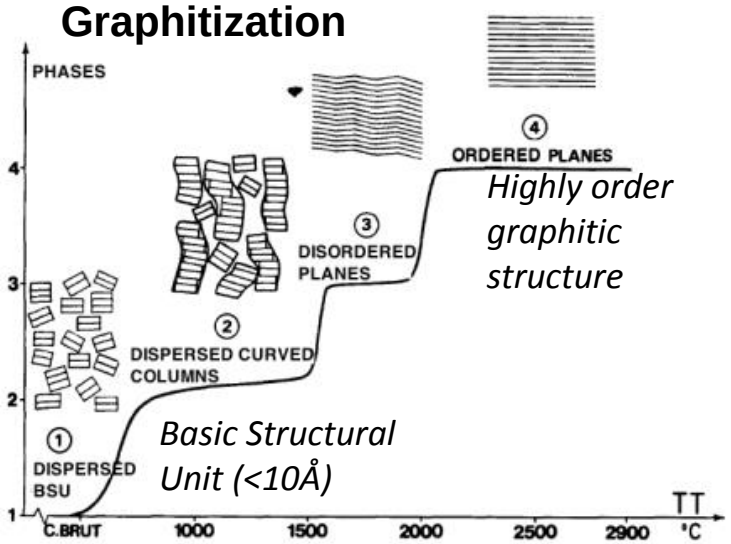
Facts:

- Damage and fracture
- Microstructure, porosity
- Residual stresses





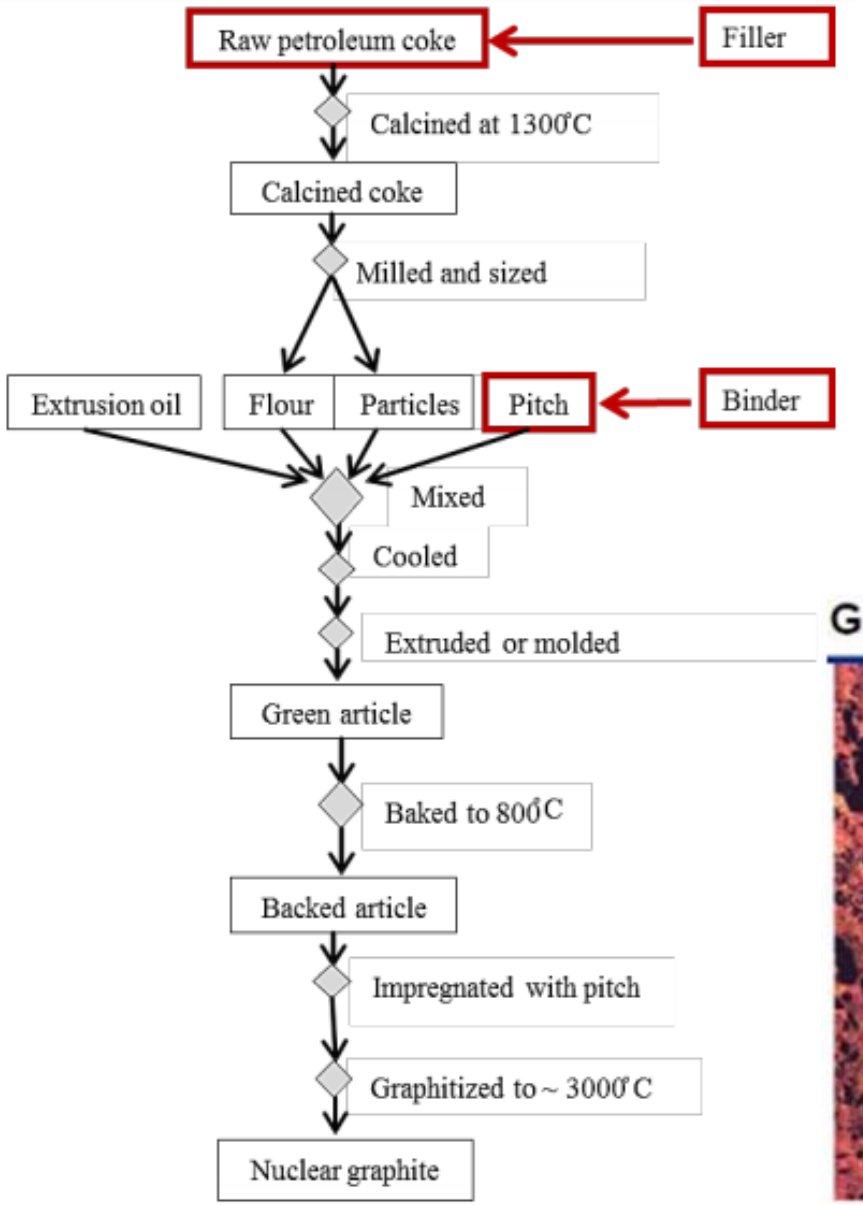
Graphitization



Oberlin A. Carbon N Y 1984;22:521-41

UNIVERSITY OF OXFORD

OxfordMaterials

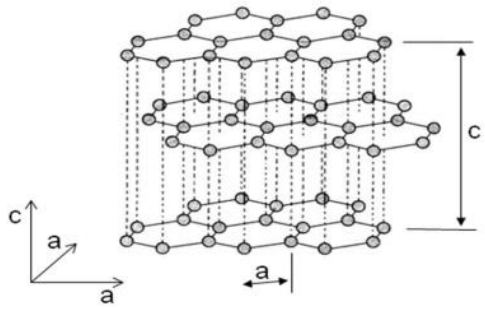


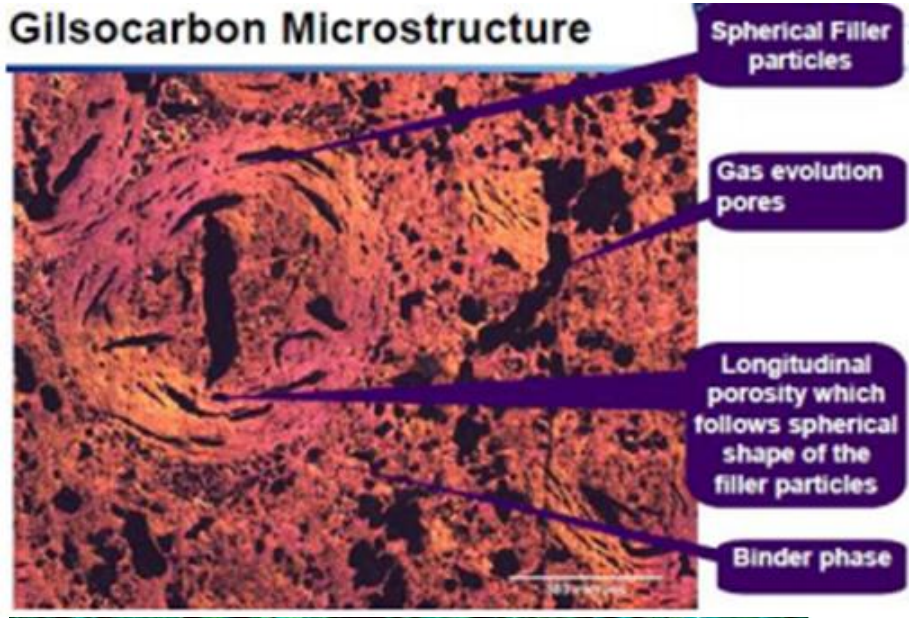
Desired properties in nuclear-grade graphite:

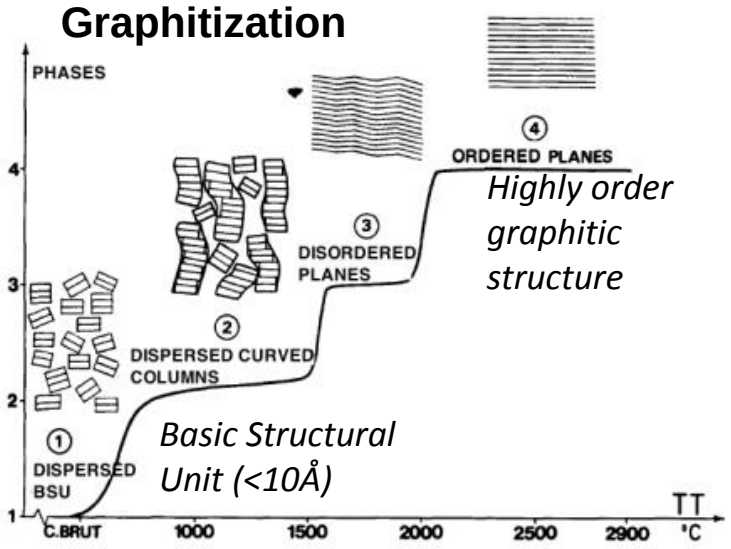
- High purity; High density; High thermal conductivity; Low CTE
- High irradiation stability (pitch, coke and manufacture process);
- High strength (flexural: 20-30MPa);
- Low anisotropy, (less than 1.1, defined by CTE in orthogonal directions)
- Low elastic modulus (~11 GPa for Gilsocarbon)

Facts:

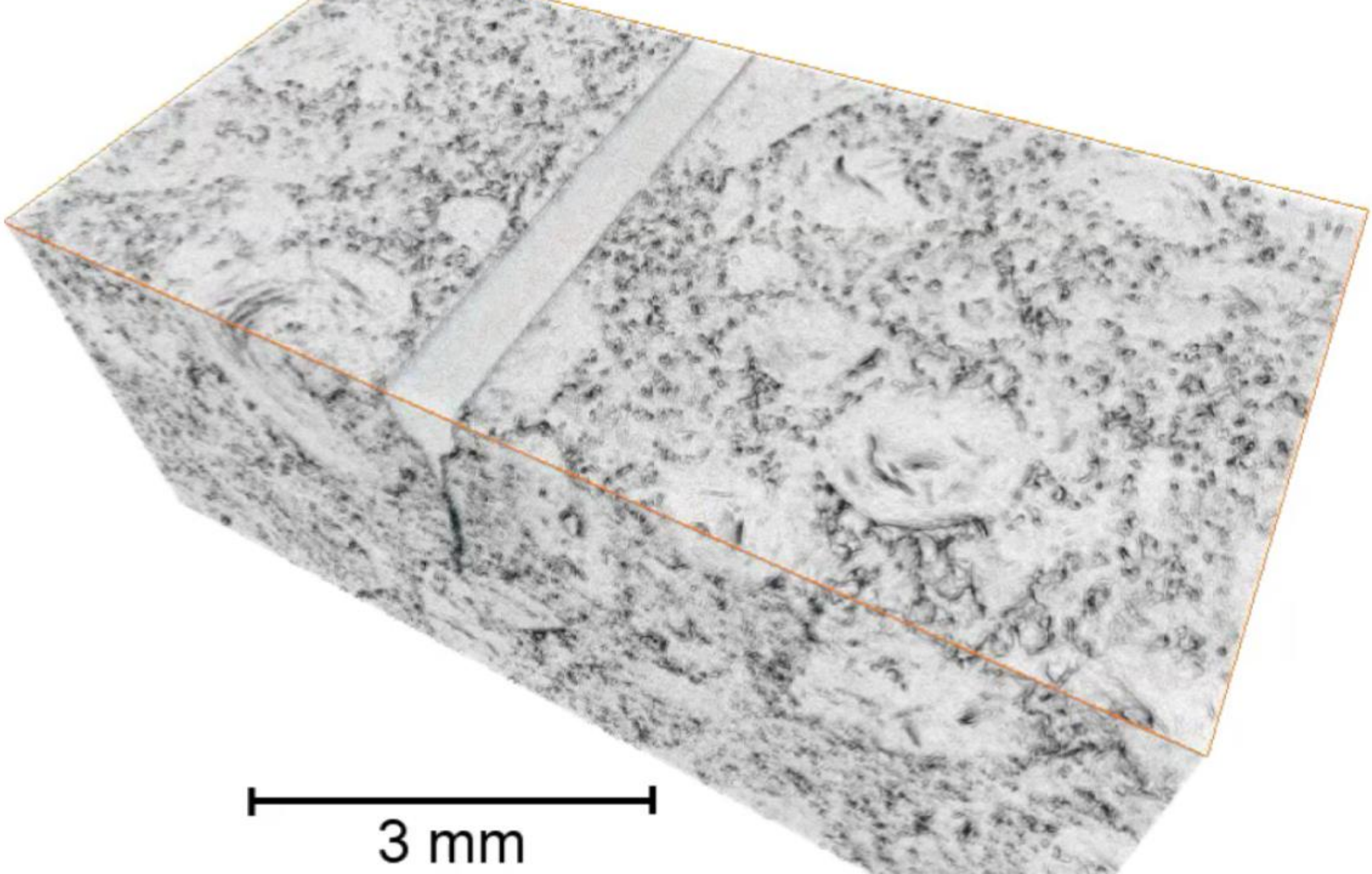
- Damage and fracture
- Microstructure, porosity
- Residual stresses

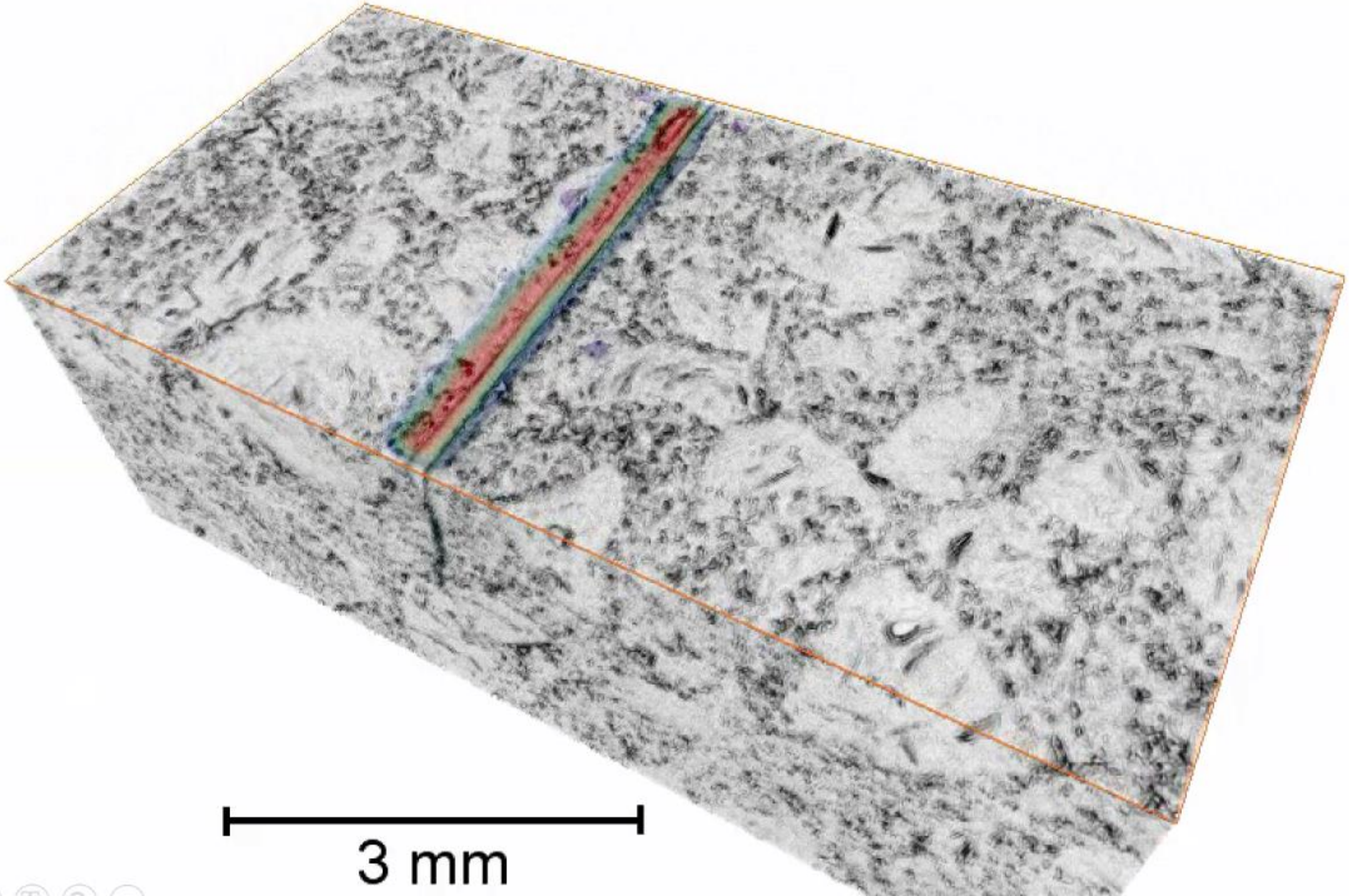


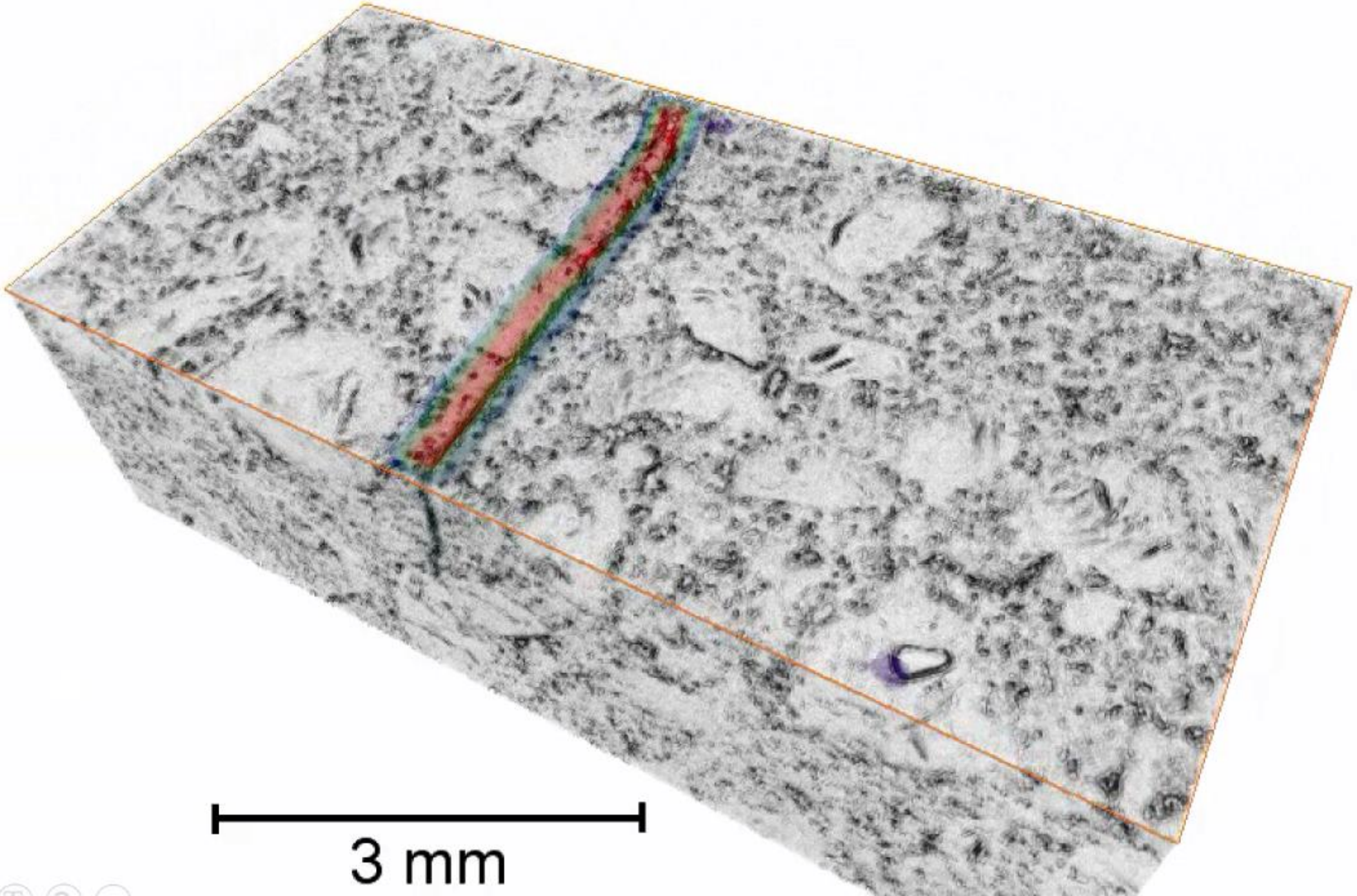


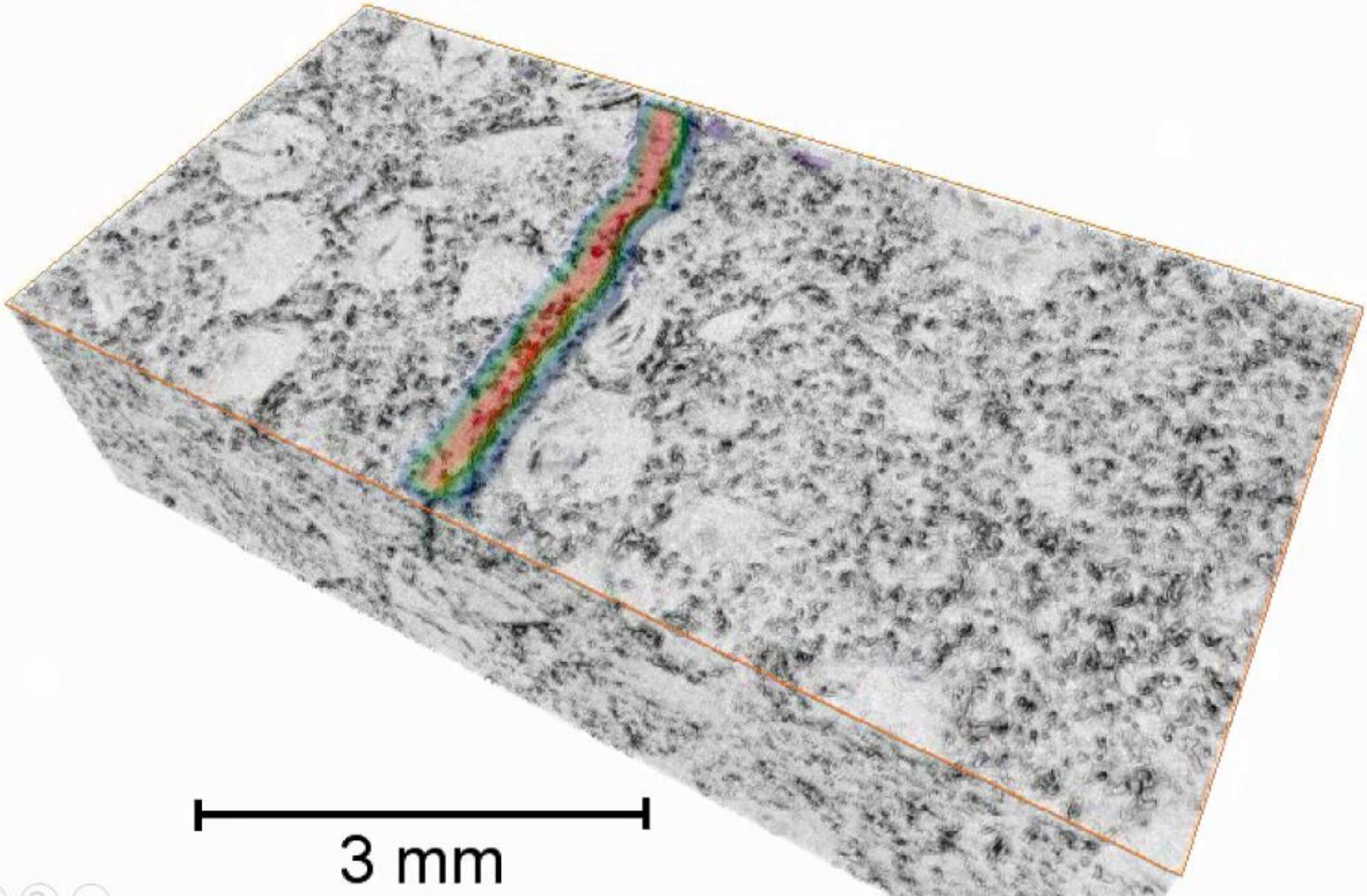


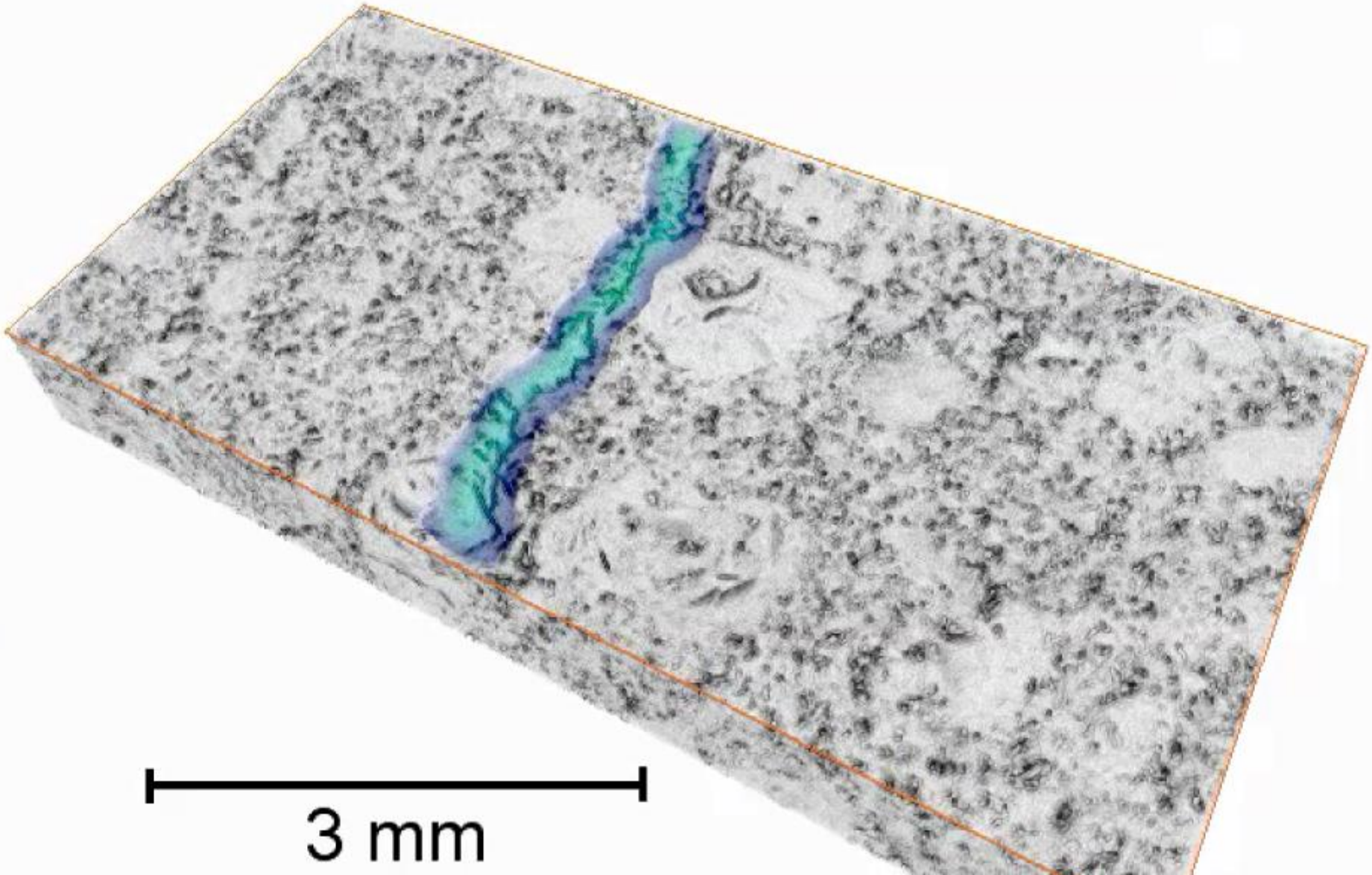
Oberlin A. Carbon N Y 1984;22:521-41


3 mm

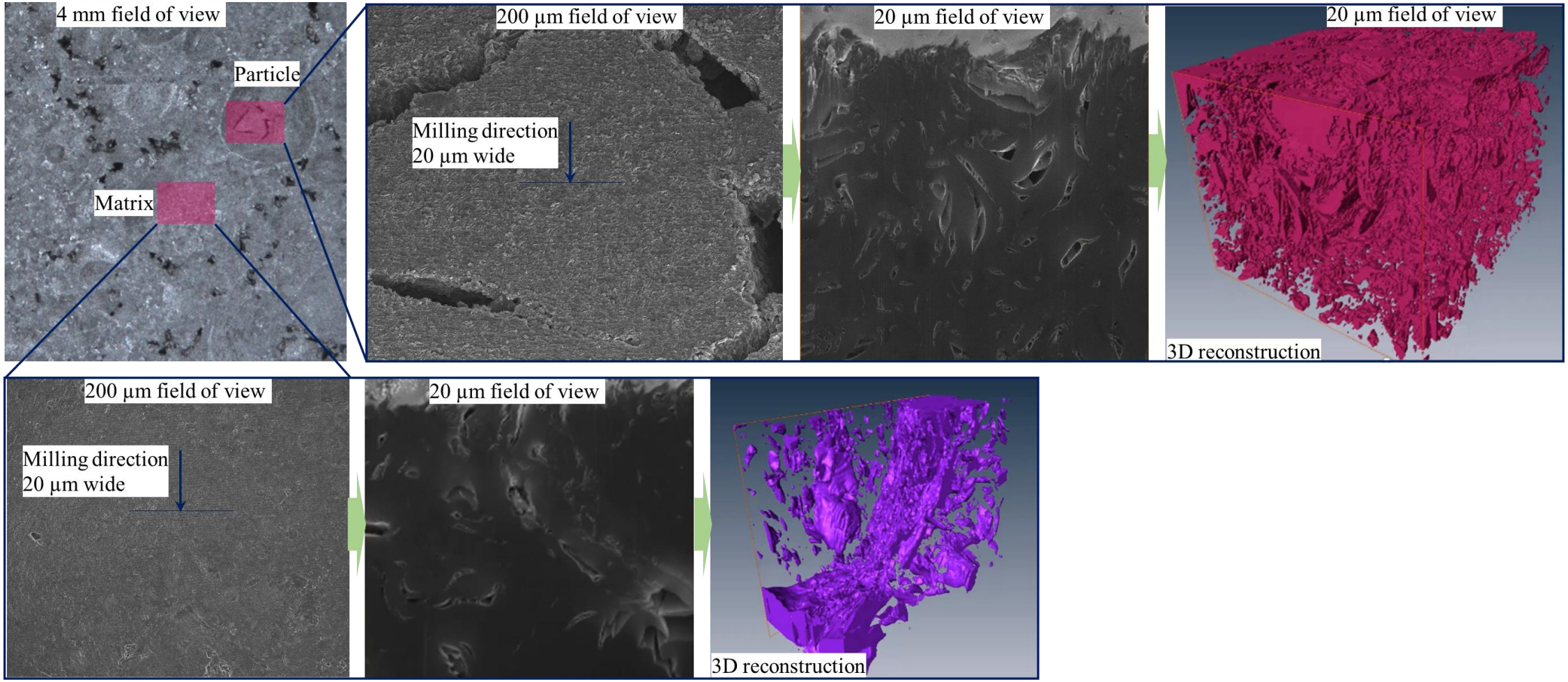

3 mm


3 mm


3 mm

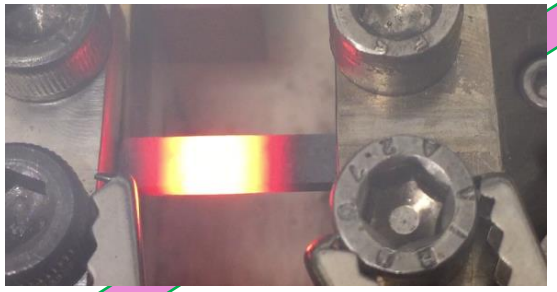

3 mm

Gilsocarbon graphite: Multi-scale Microstructure

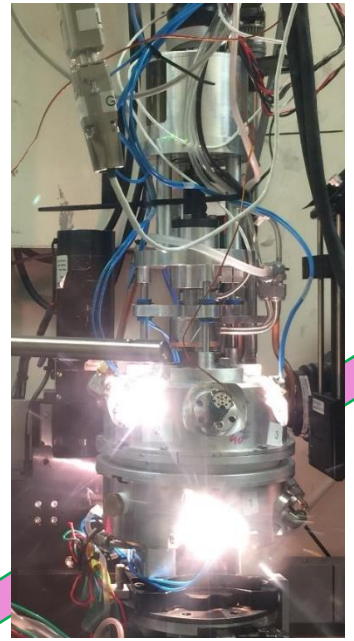


Nuclear Graphite: Multi-scale Characterisation

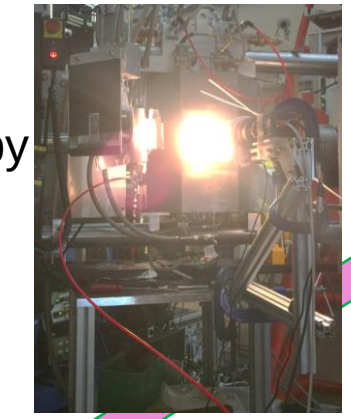
Macro-scale deformation



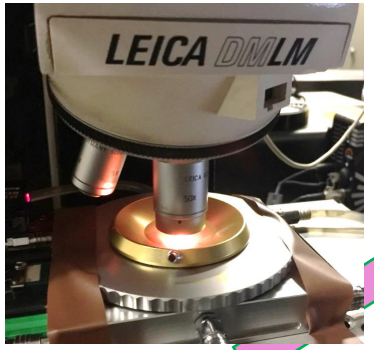
X-ray tomography
Micro-scale deformation



Neutron diffraction
Lattice strain

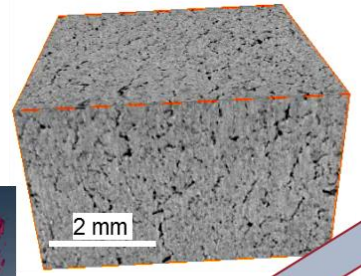


Raman spectroscopy
Crystal bonding

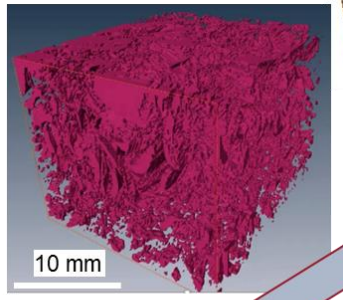


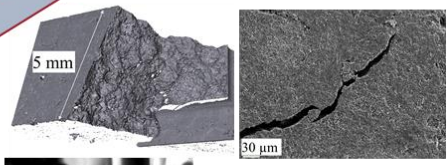
Component size

Macro

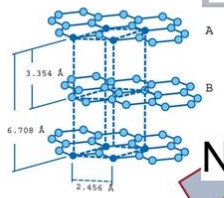


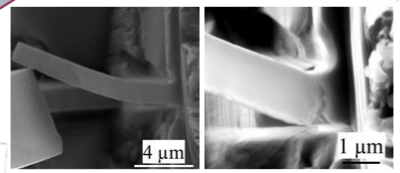
Micro

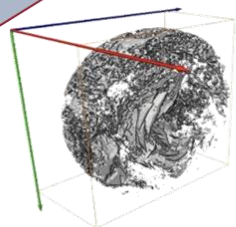




Nano







Elevated temperature

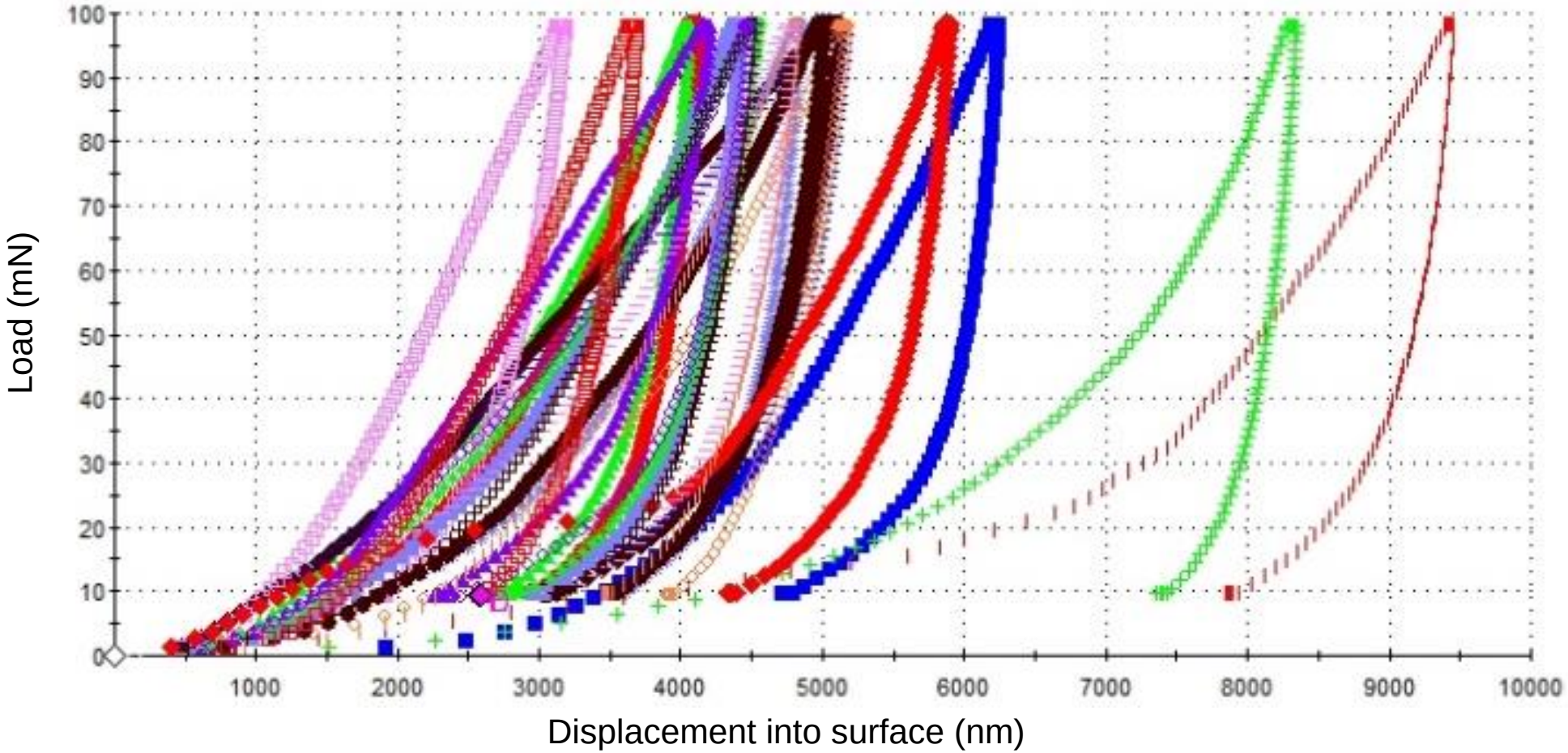
Room temperature

Micro-mechanical testing

Nano-indentation

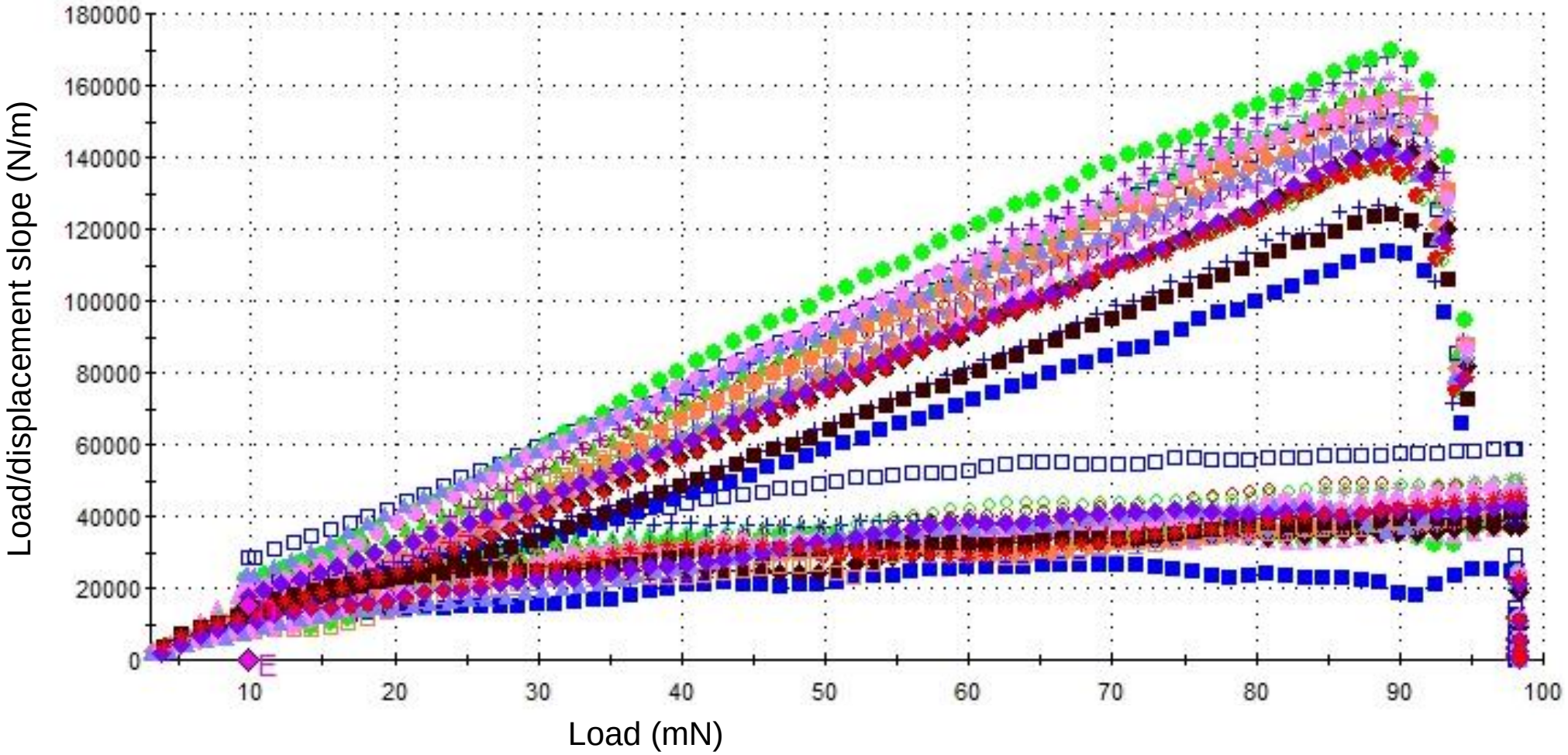
Nano-indentation (*Ex situ*)

- Measurements at different locations on the same sample

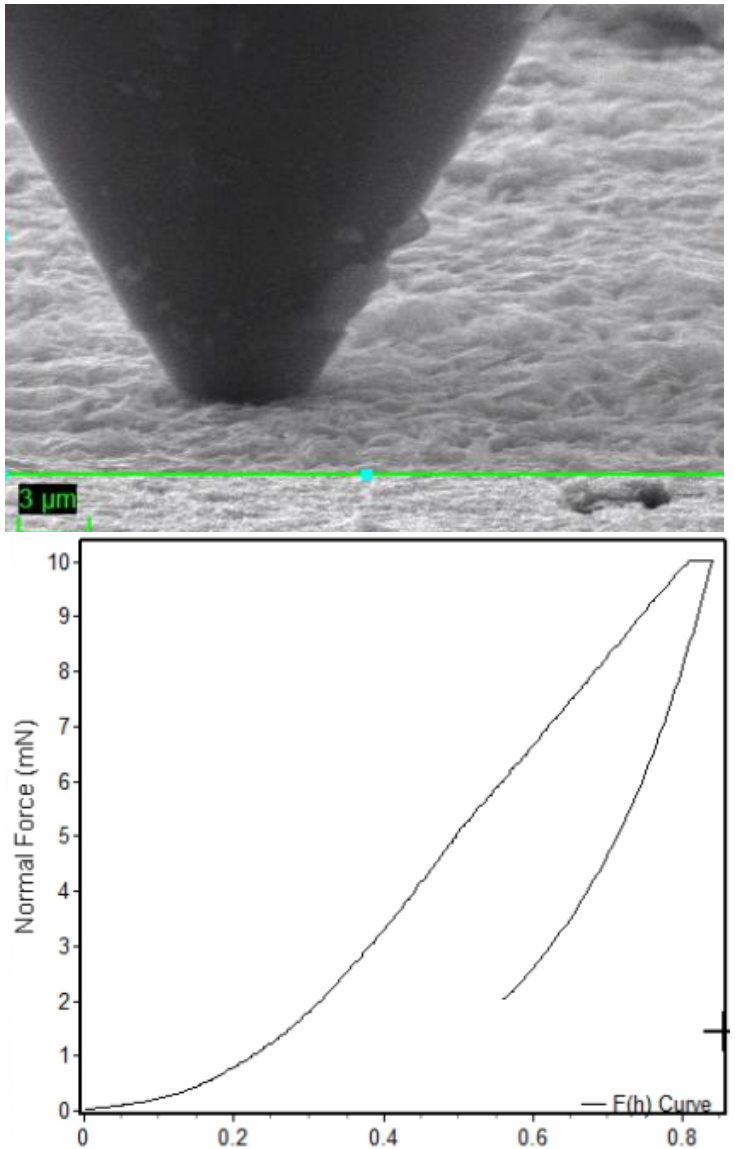


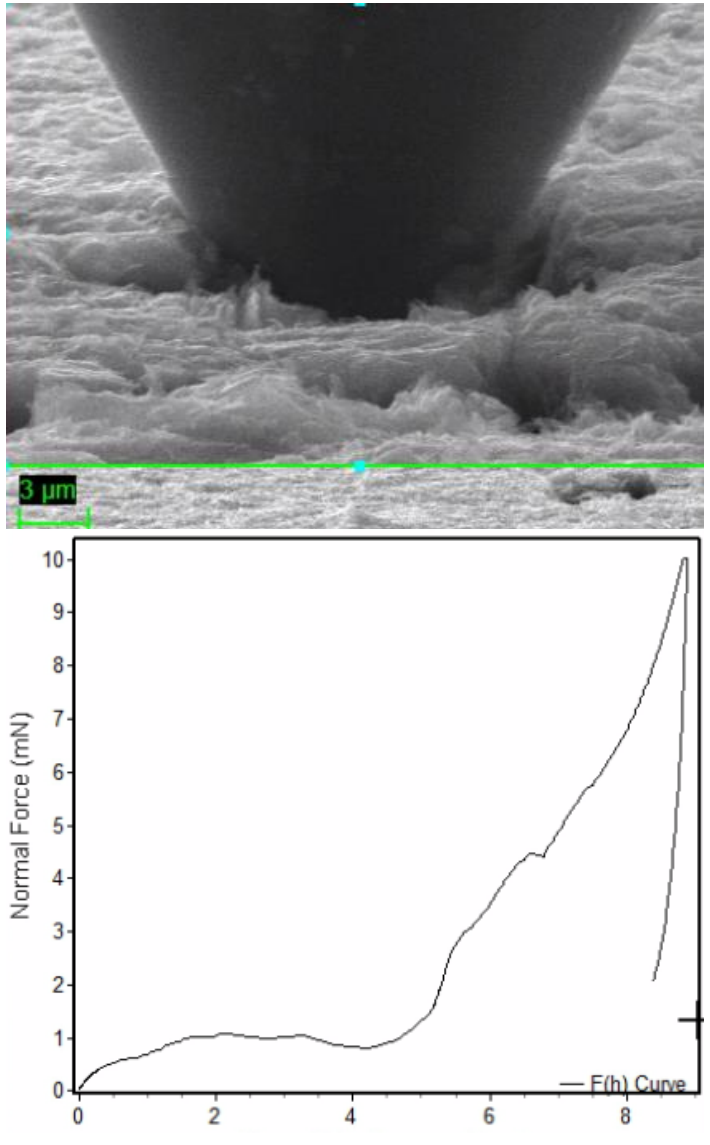
Nano-indentation (*Ex situ*)

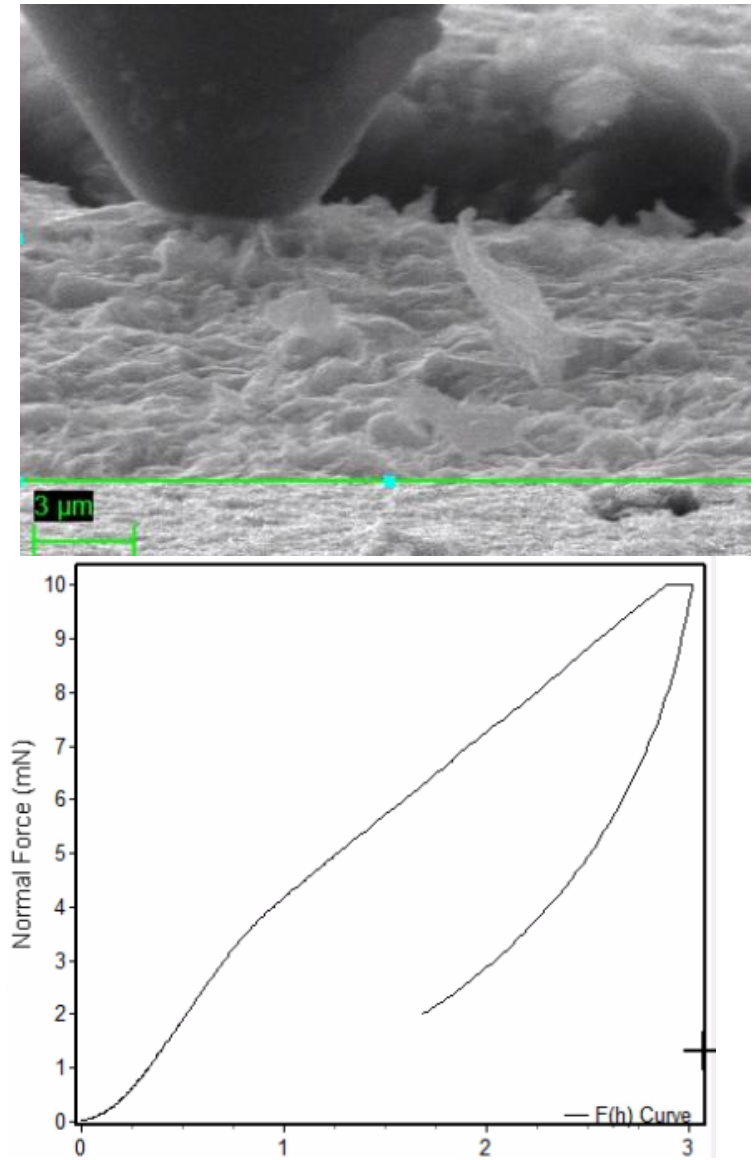
- Measurements at different locations on the same sample



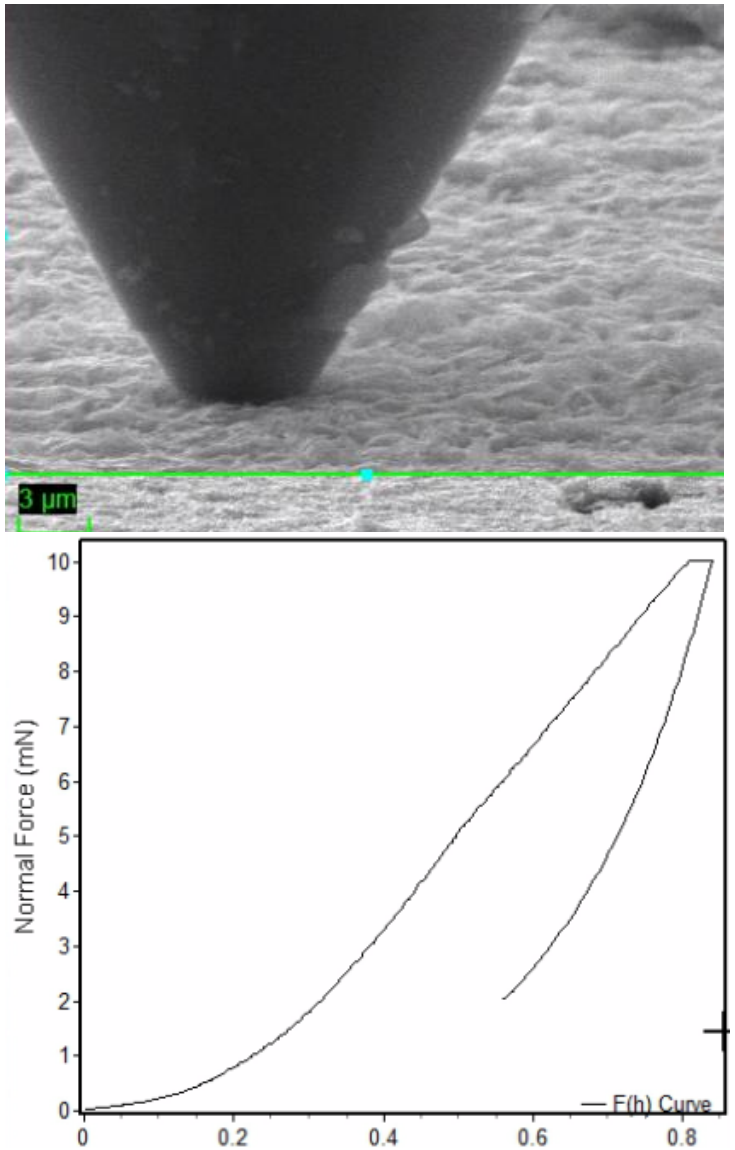
Nano-indentation (*In situ*)

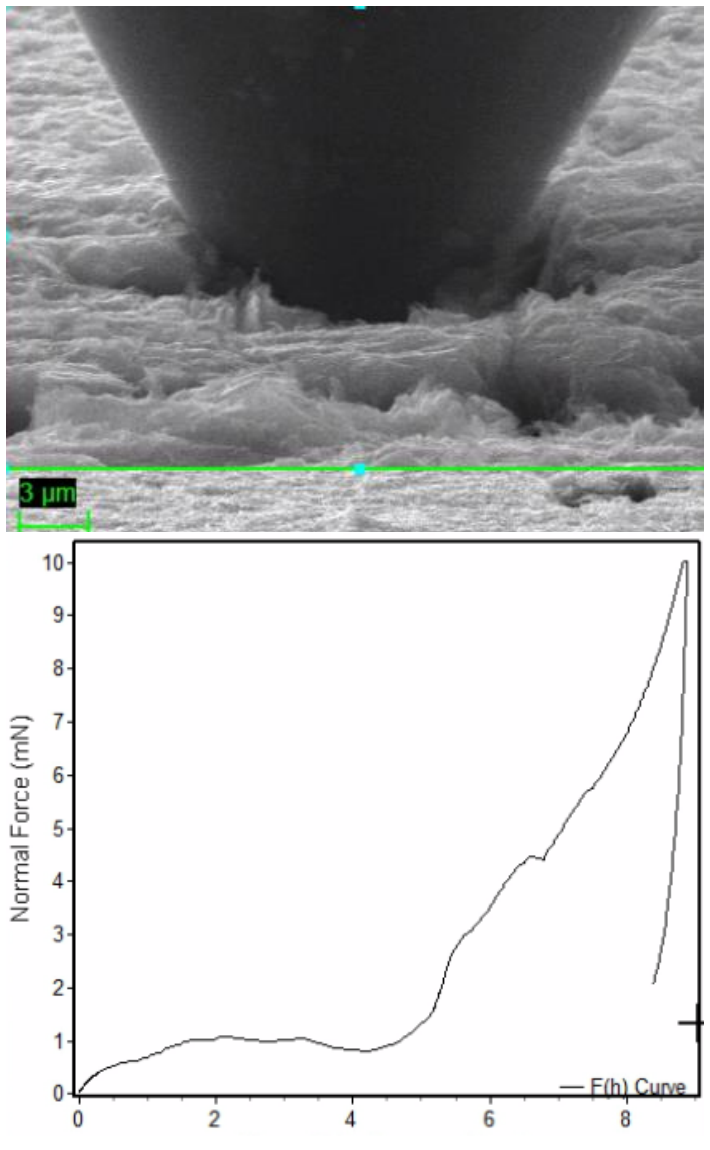


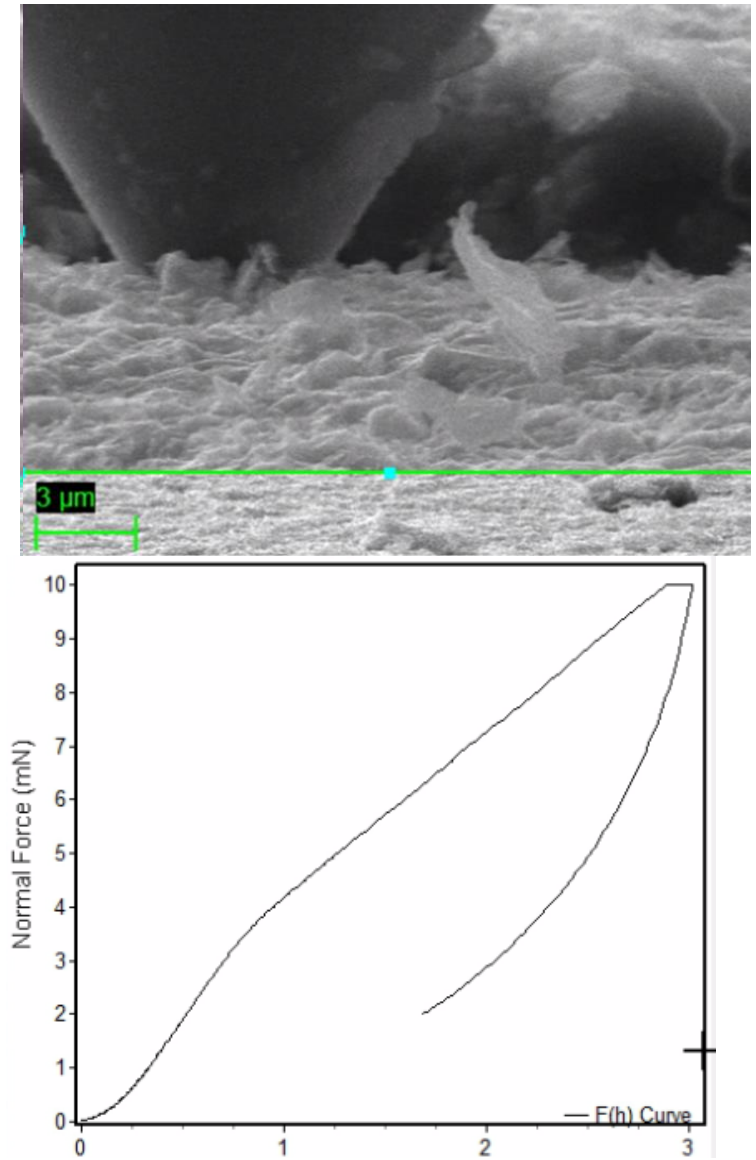




Nano-indentation (*In situ*)





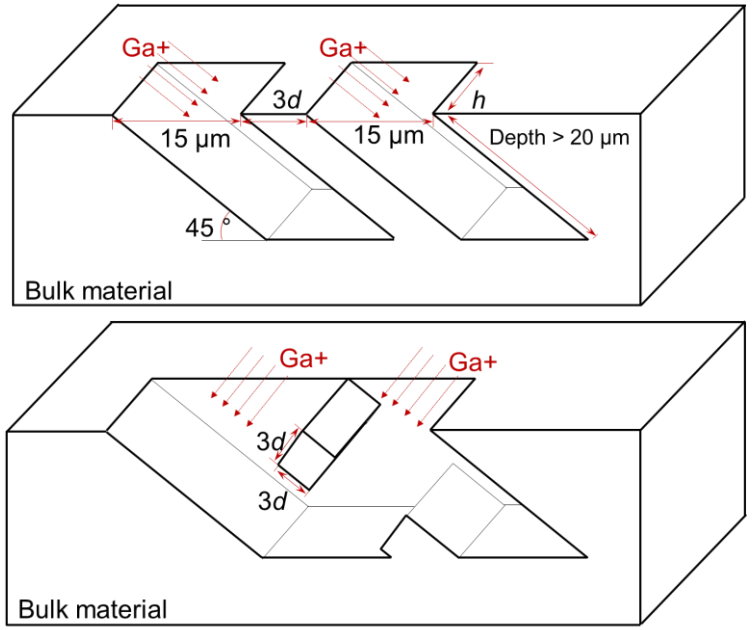


Micro-mechanical testing

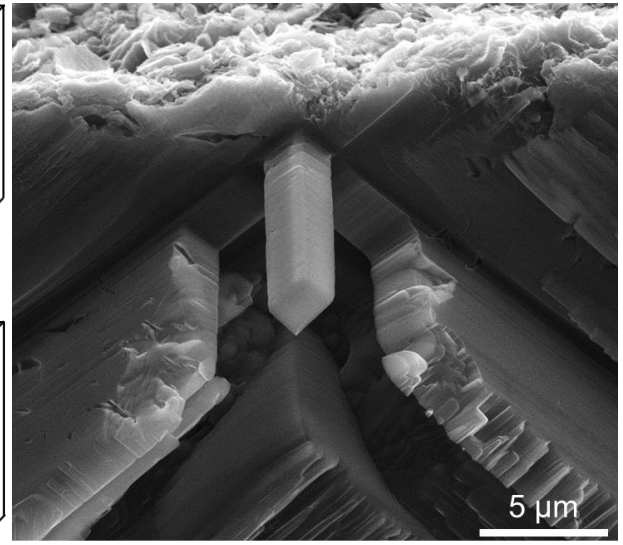
In situ micro-cantilever bending

In situ micro-cantilever bending

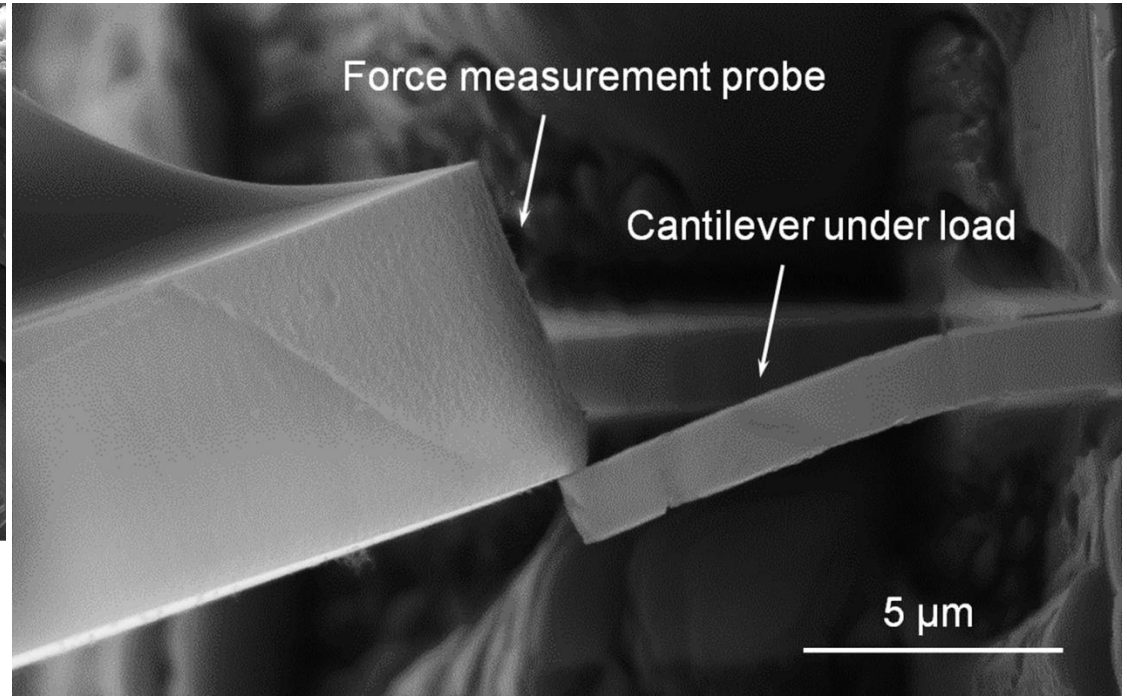
- Step I



- Step II



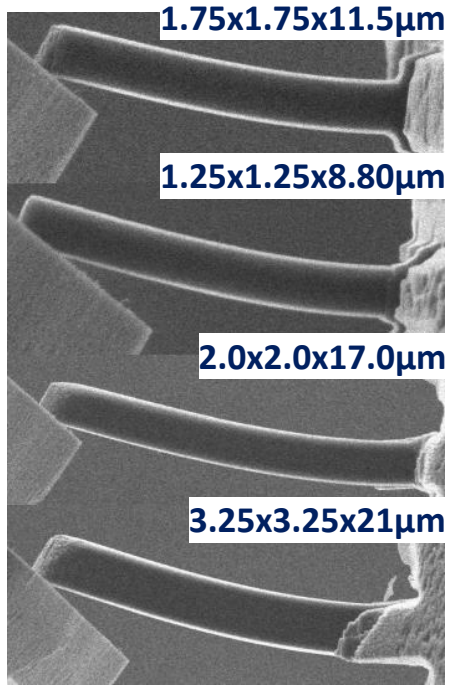
- Step III



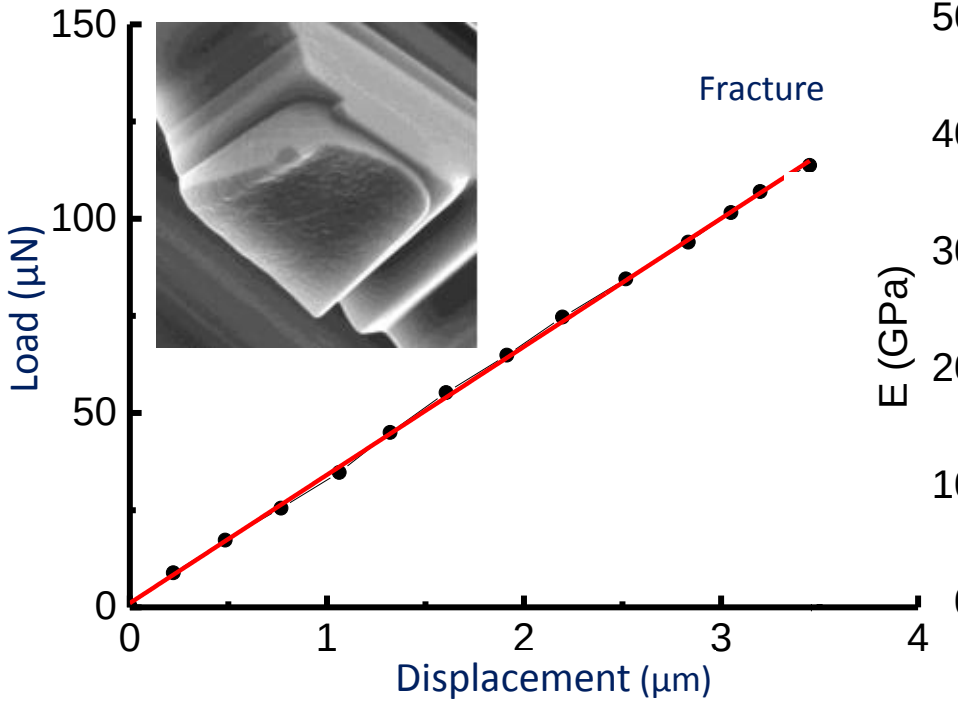
- Dualbeam workstation (FEI Helios NanoLab 600i Workstation)
- Force measurement system (FMS) (Kleindiek Nanotechnik)
- Workstation stage monitored and debris collected

Calibration: Glassy carbon

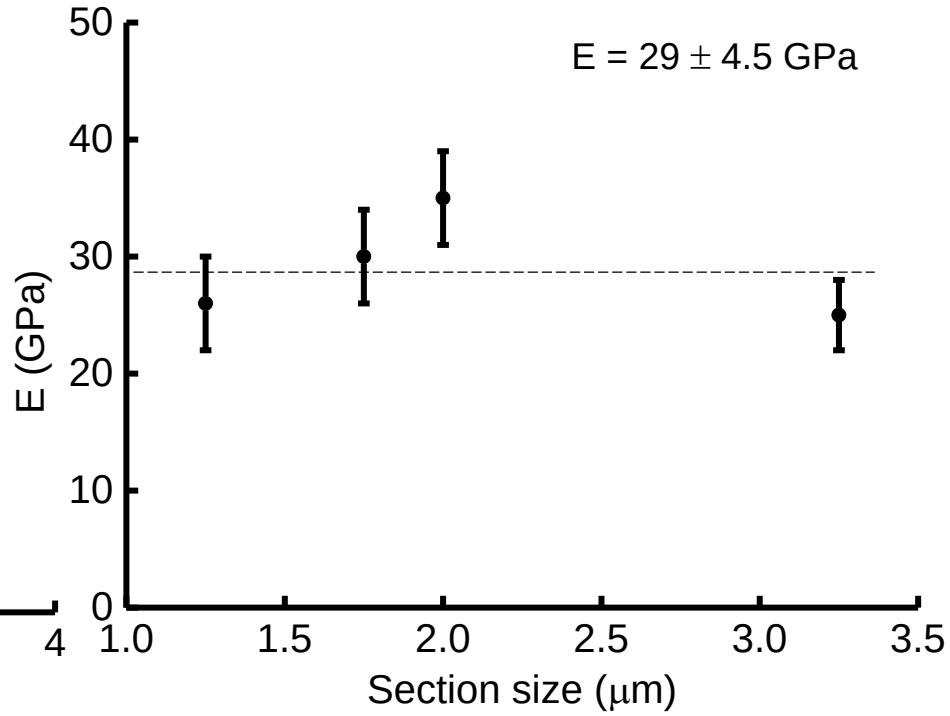
- Specimens prior to failure



- Linear load-displacement relation



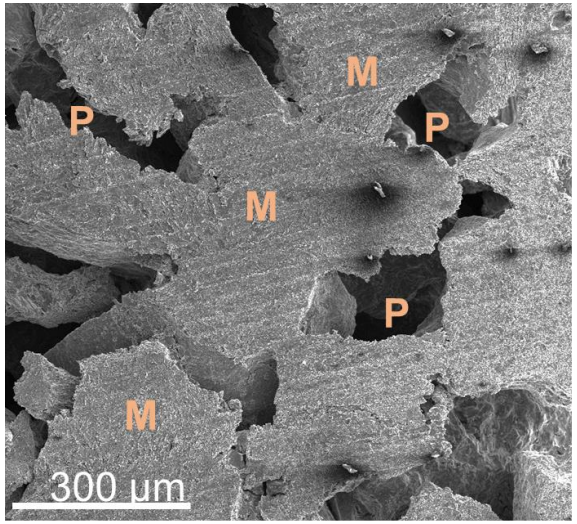
- Small variation in E with sample size



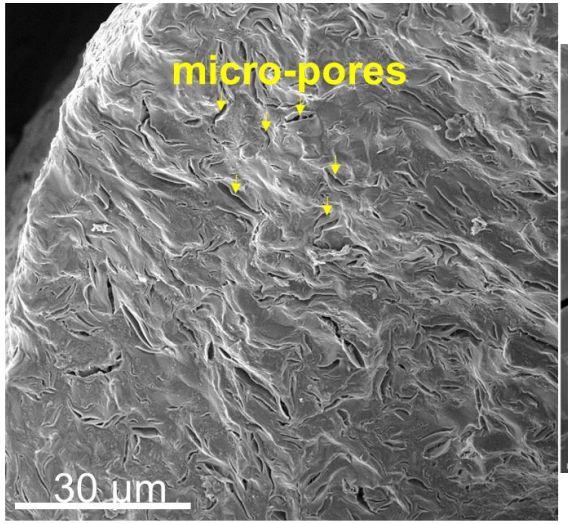
- Repeatable modulus and flexural strength as measured at macro-scale
- Similar brittle fracture modes observed at micro-scale as in macro-size samples

Filter graphite

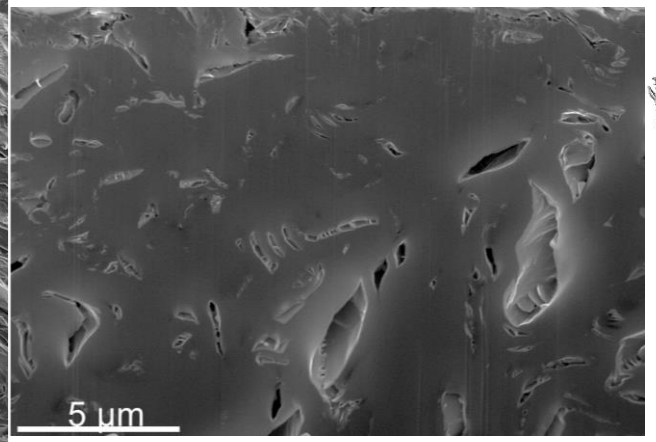
Large pores



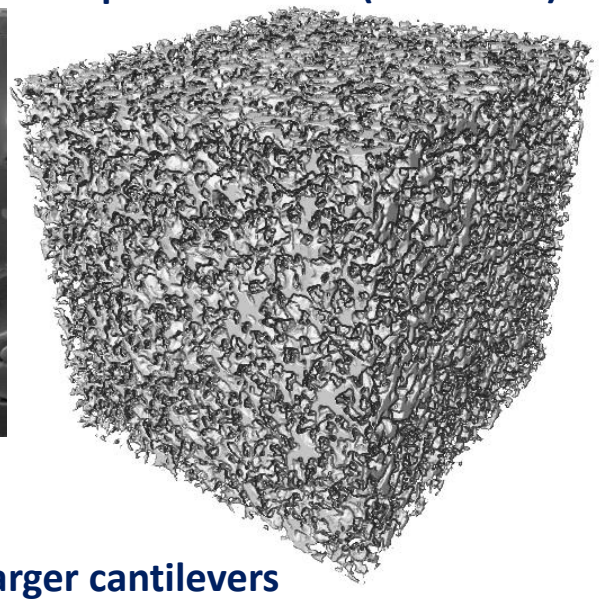
Surface micro-pores



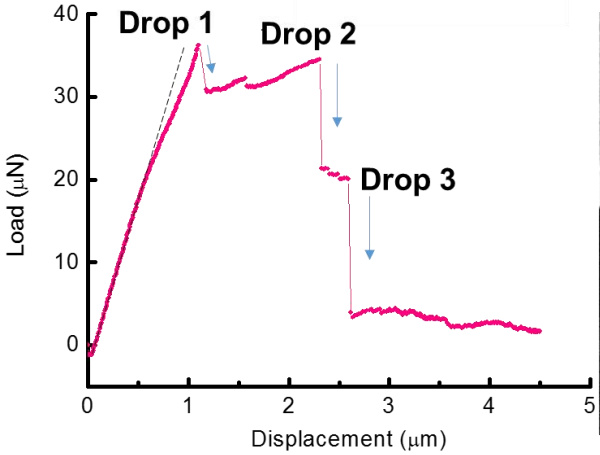
Embedded micro-pores

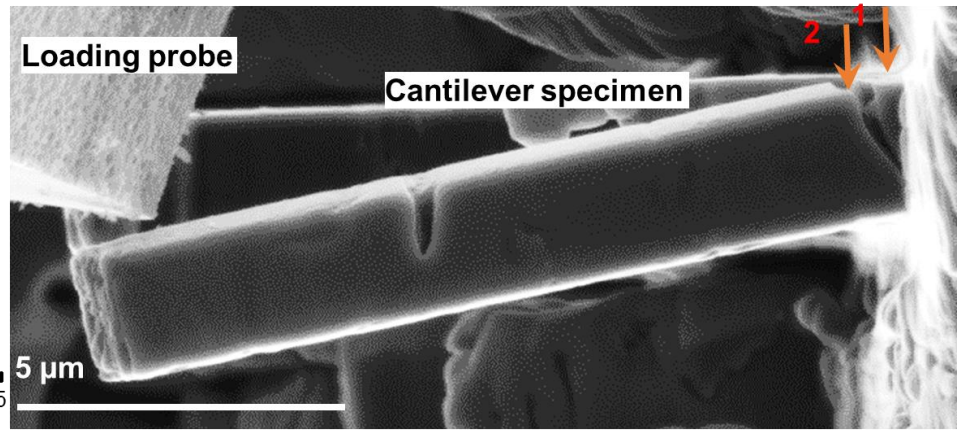


X-ray tomography scan of pores 16 µm^3 voxel size (5x5x5mm)

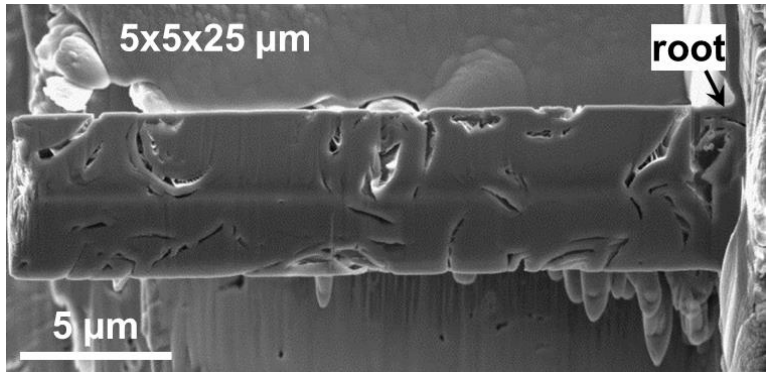


In situ observation of fracture as cantilever being deformed



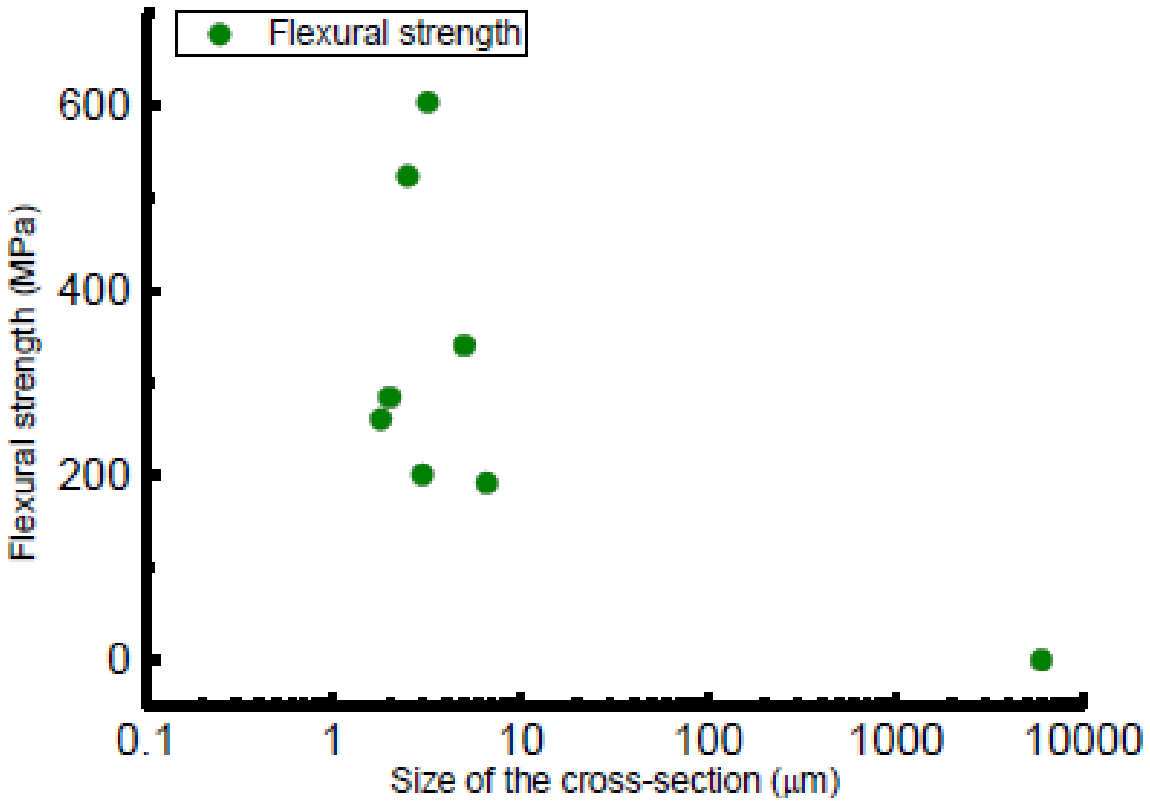


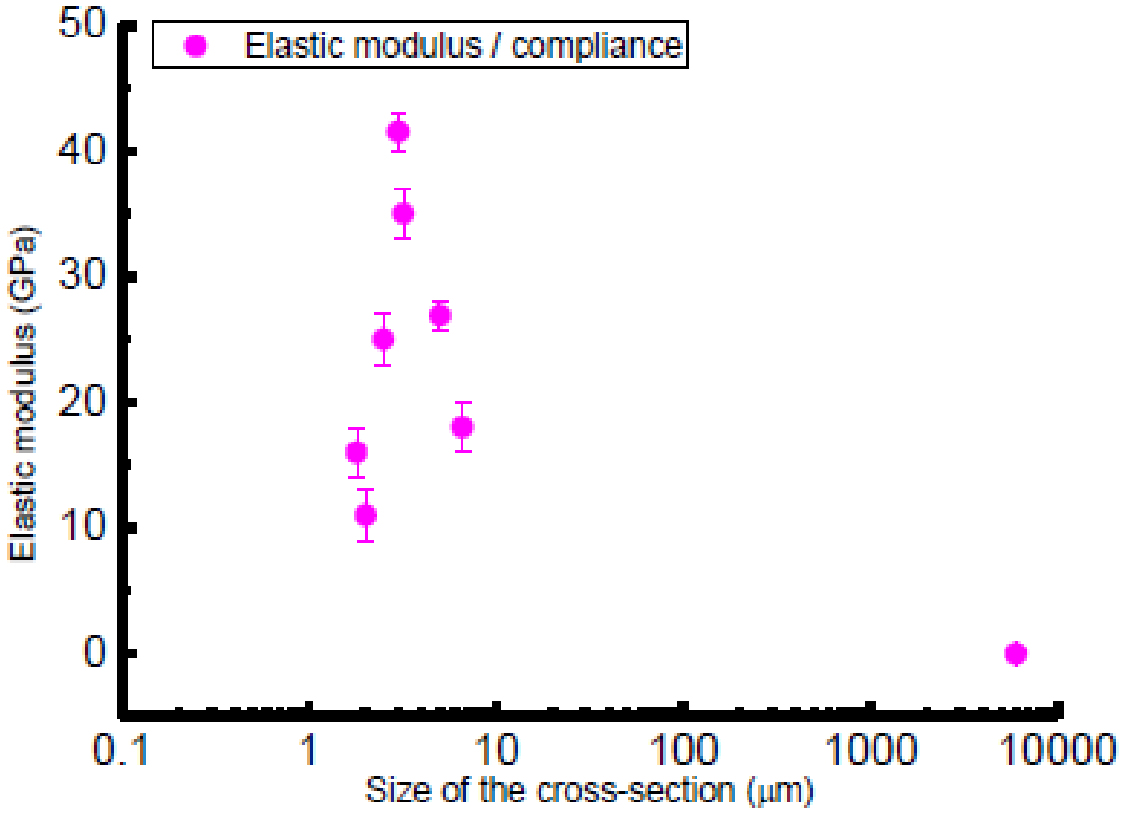
Pores in larger cantilevers



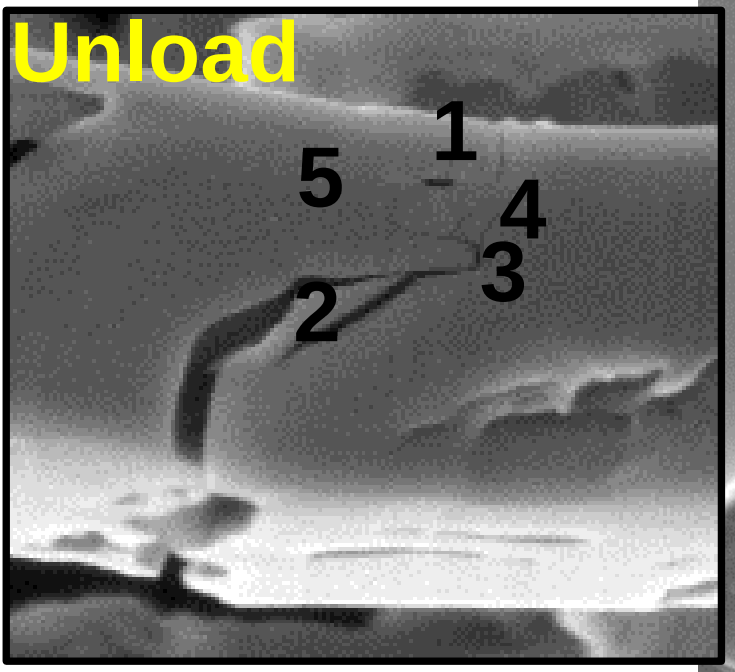
Filter graphite

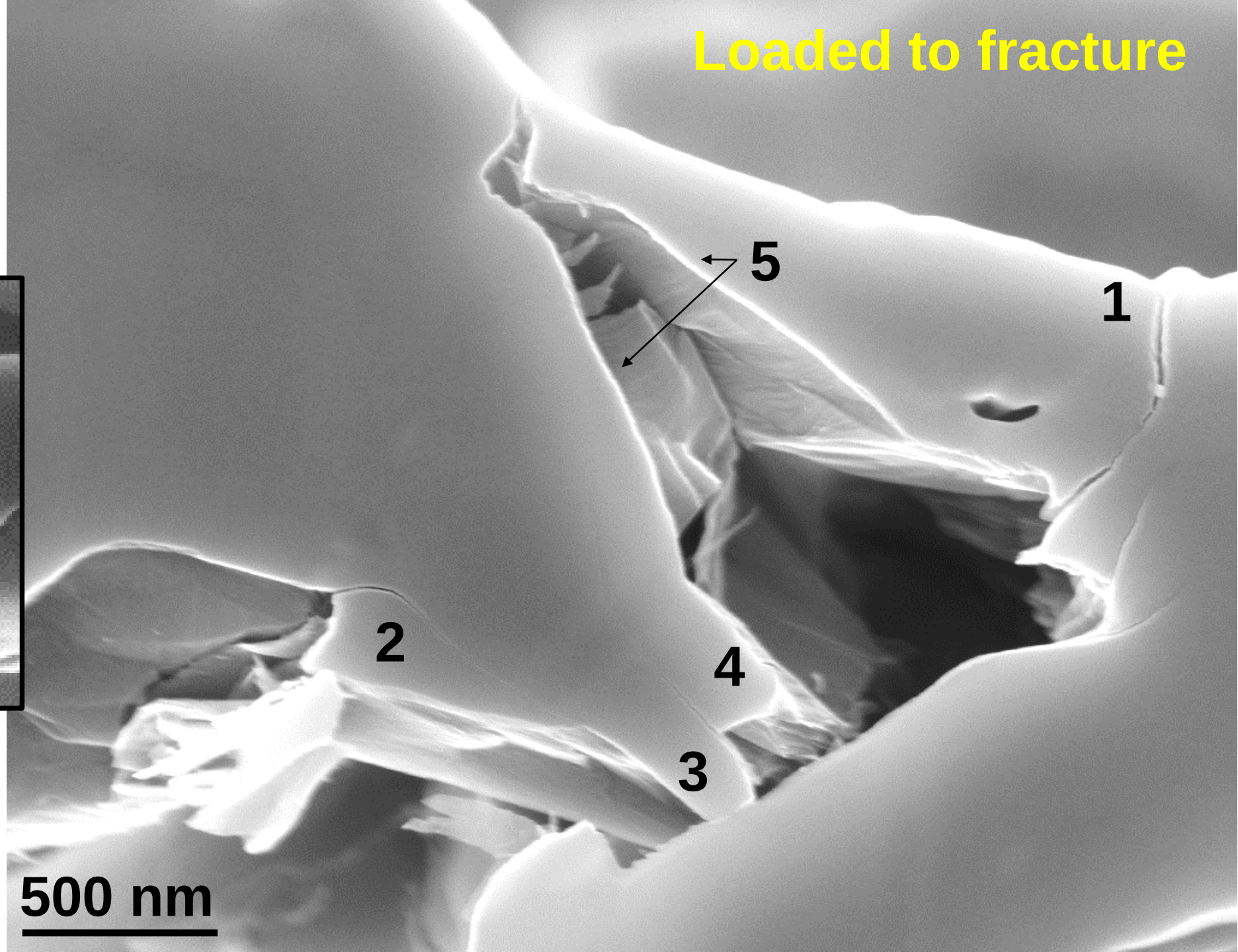
- Cross-section size varies from 1.8 µm x 1.8 µm to 6.6 µm x 6.6 µm
- Flexural strength changes from ~200 to ~600 MPa
- Elastic modulus varies from 10 GPa to about 40 GPa



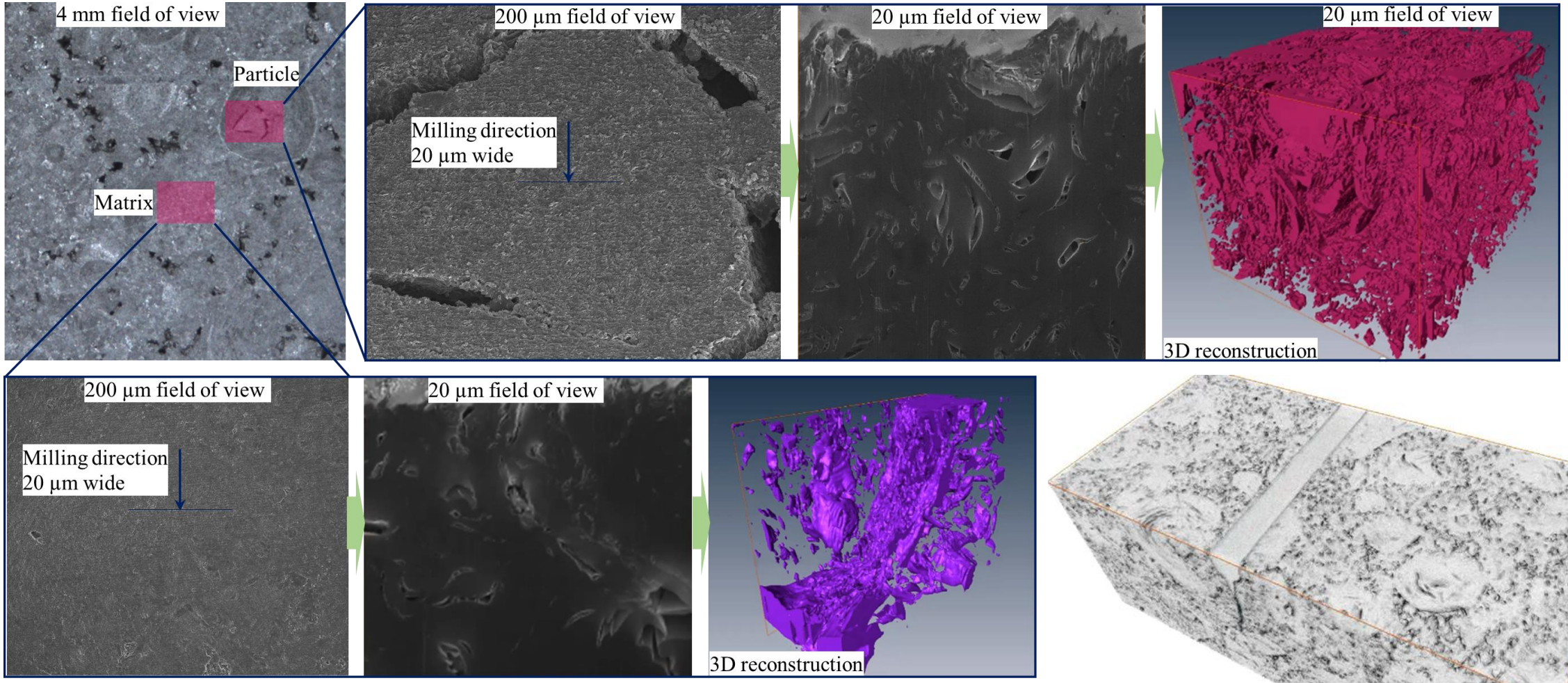


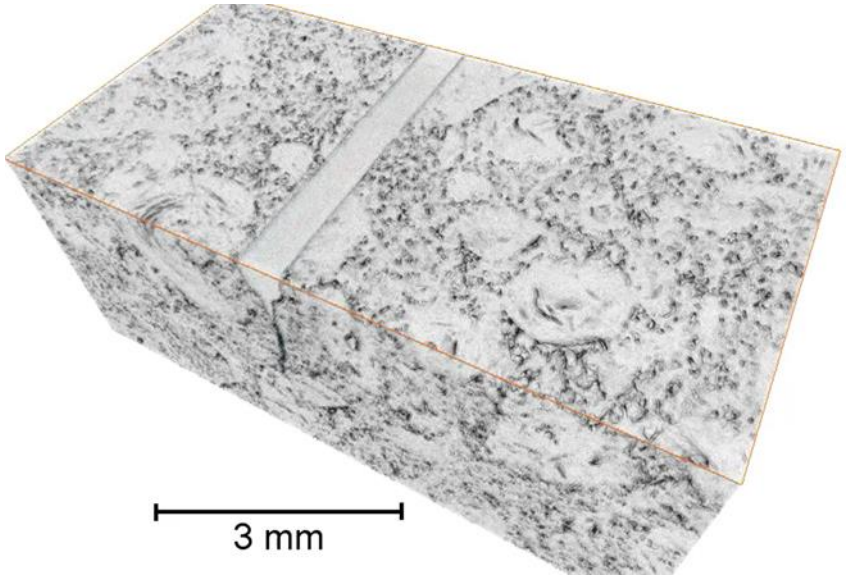
UNIVERSITY OF OXFORD



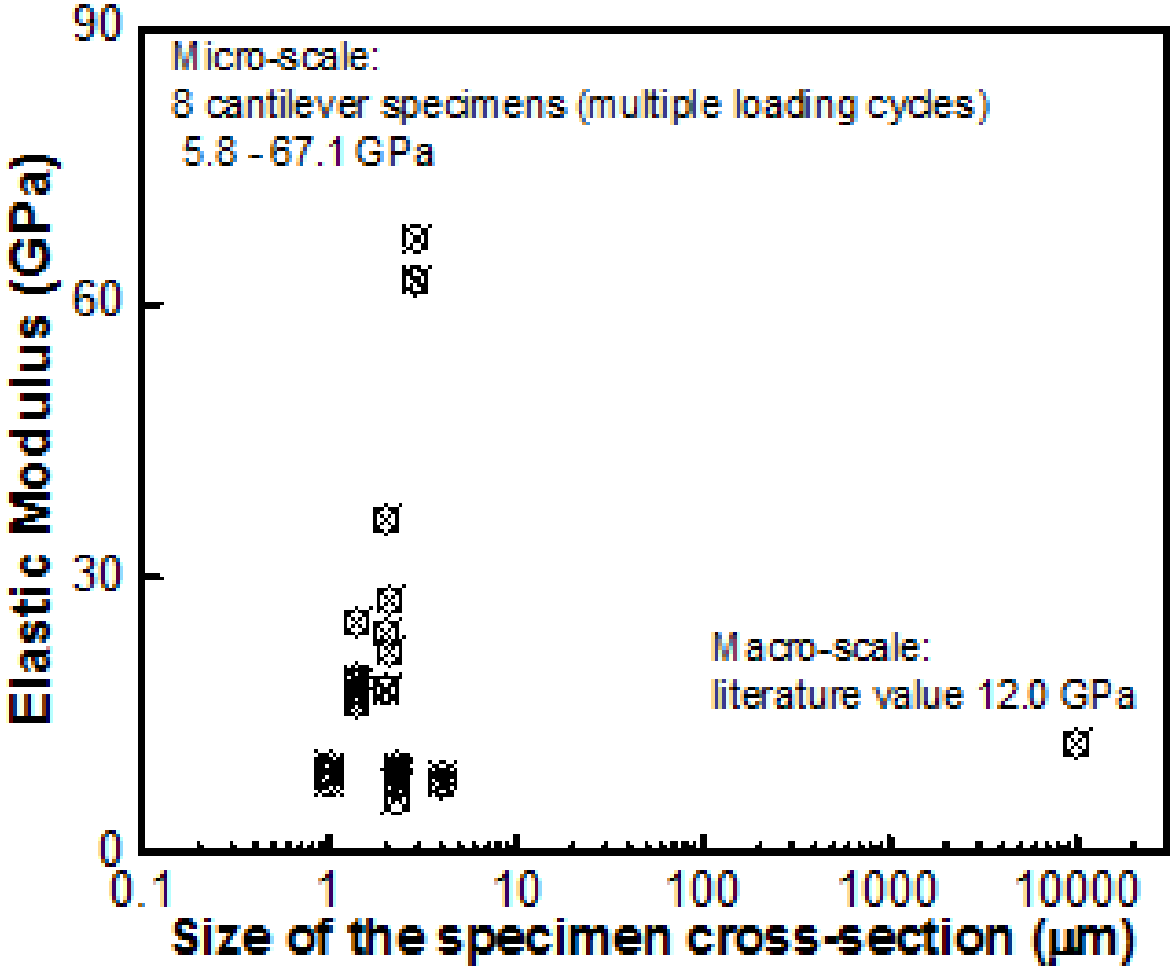


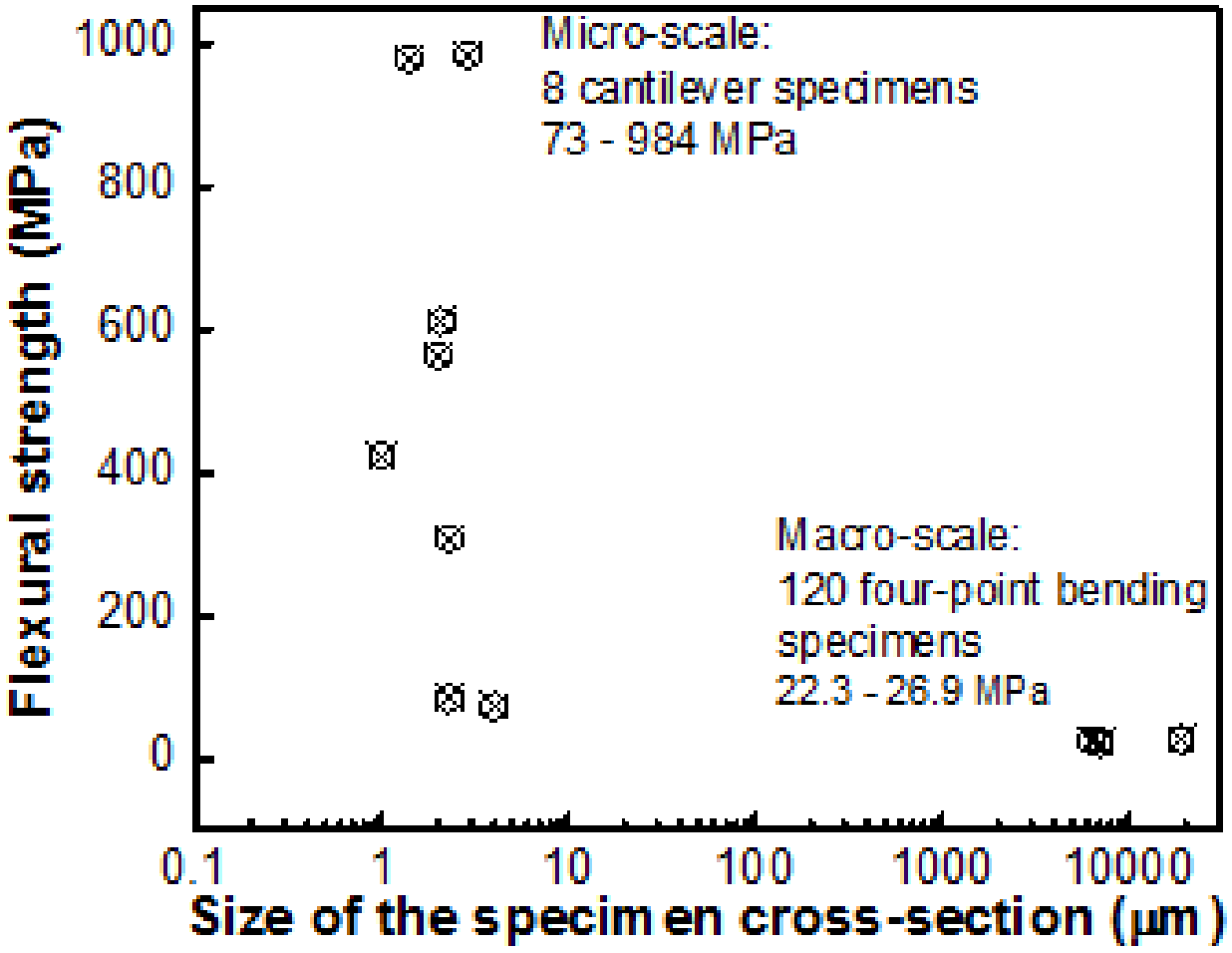
Gilsocarbon graphite





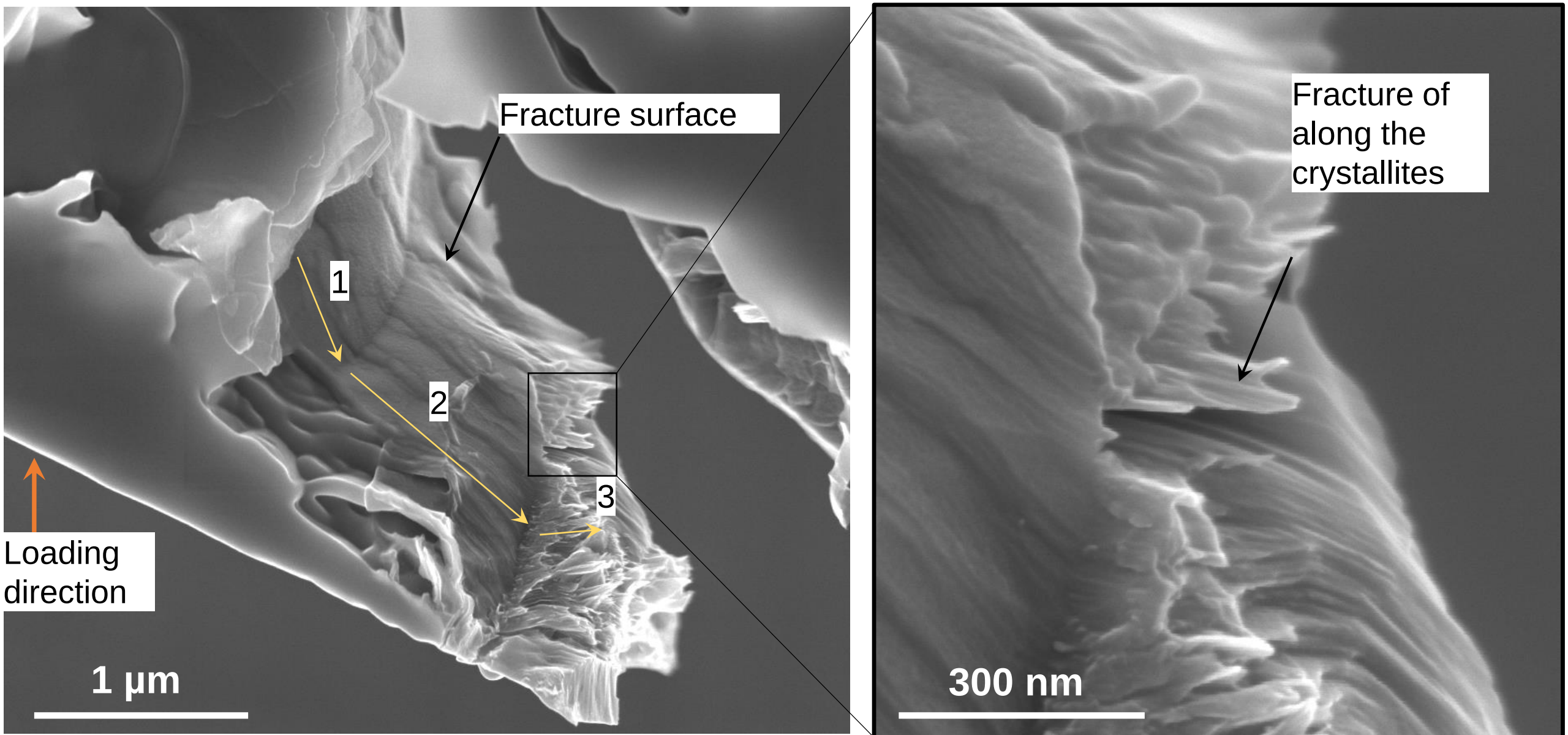
Gilsocarbon graphite



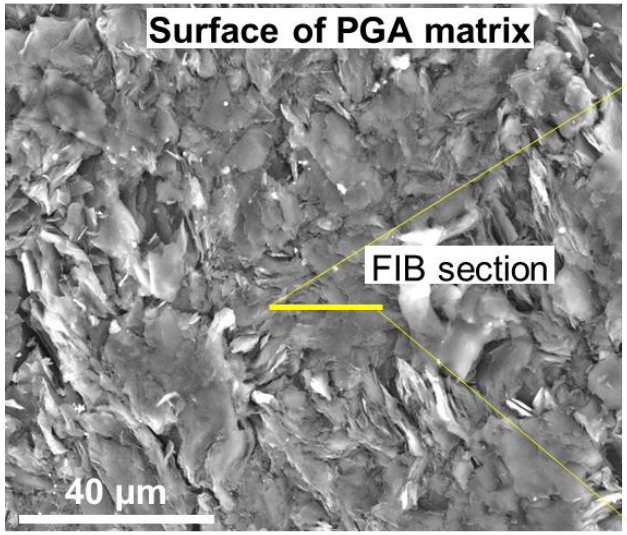


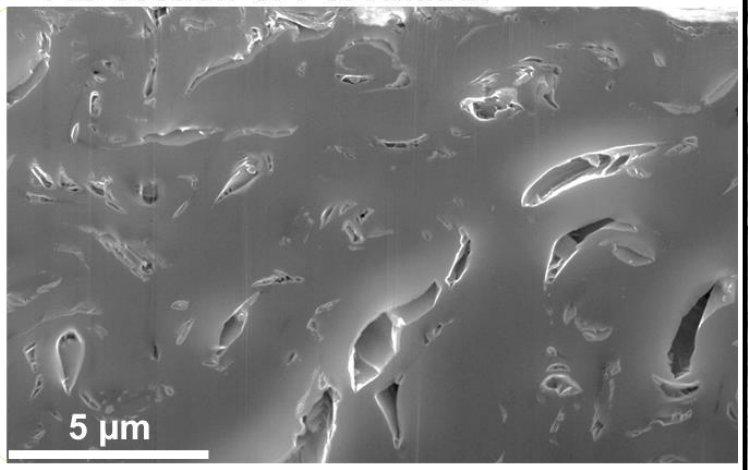
UNIVERSITY OF OXFORD

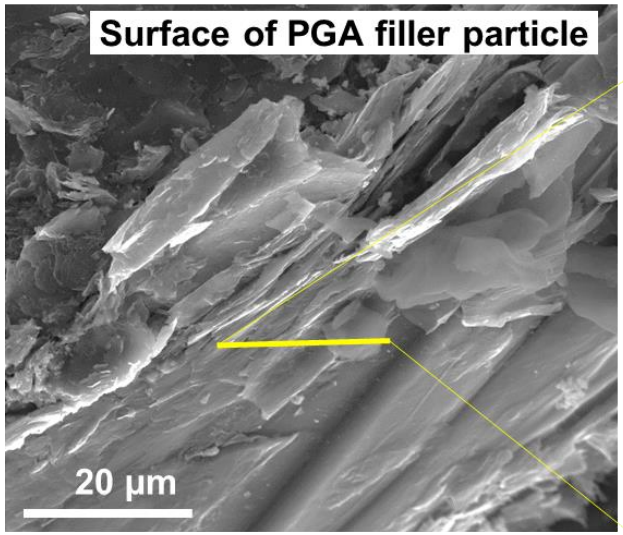
OxfordMaterials

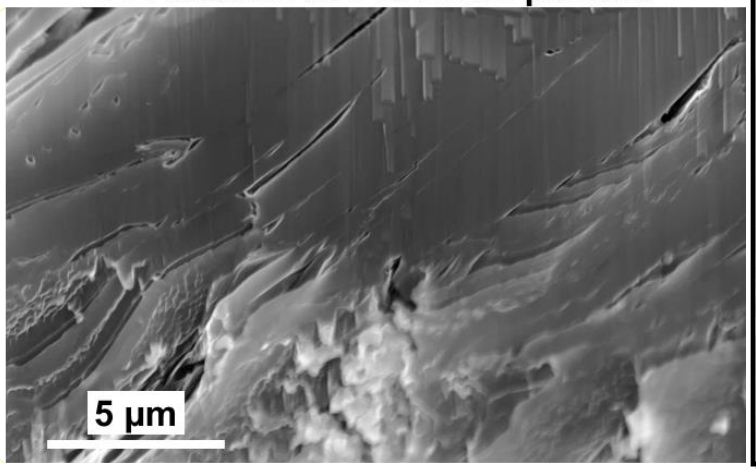


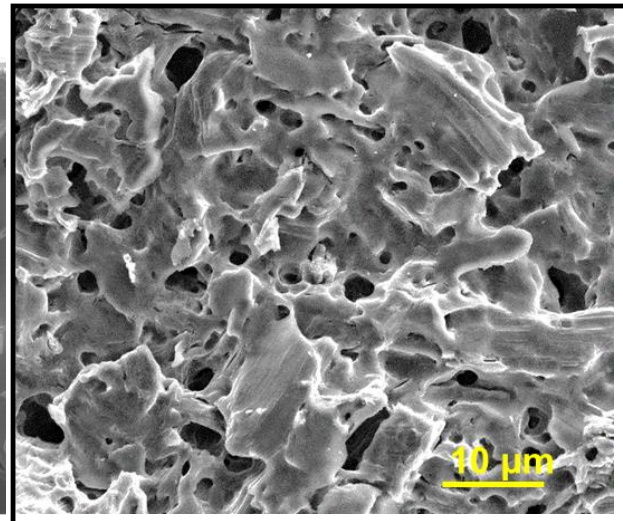
PGA graphite (unirradiated and neutron irradiated)







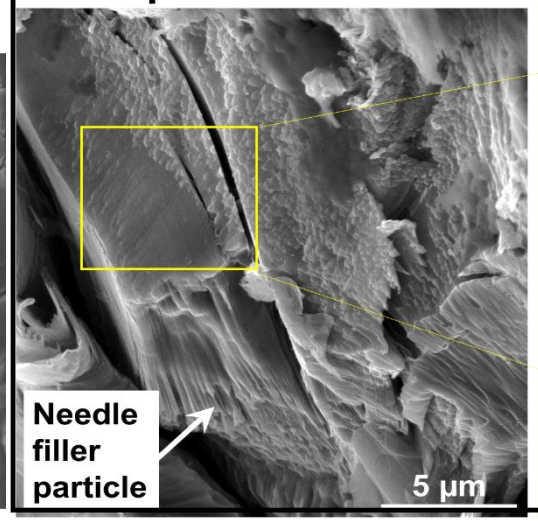


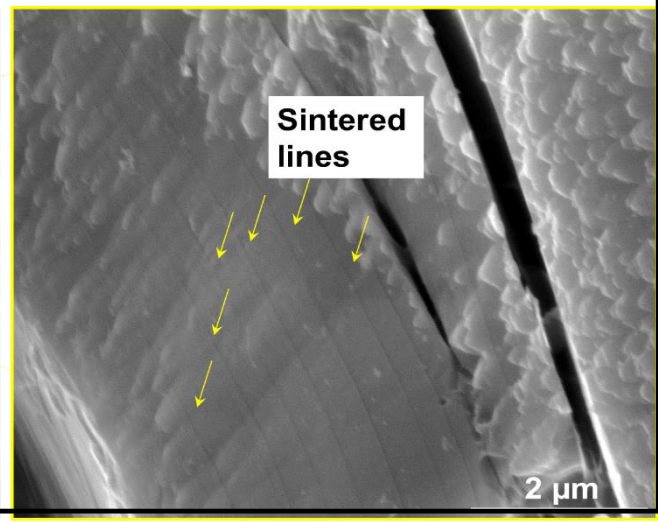


Matrix

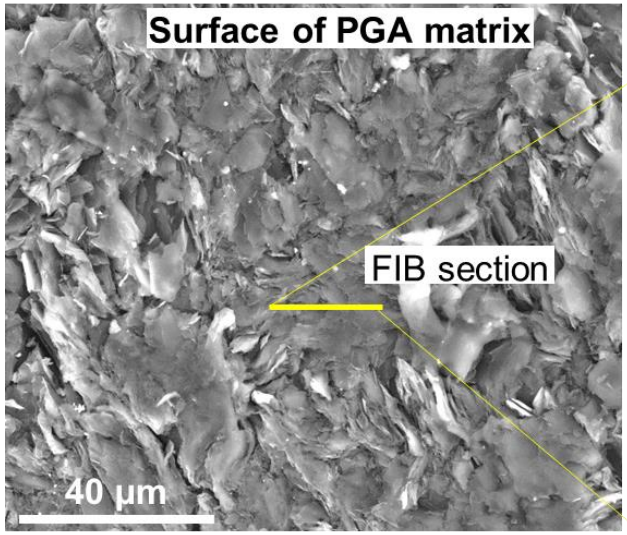
- Radiolytically-oxidised (CO_2 environment) PGA graphite samples from a Magnox reactor supplied by Magnox Ltd.
- 15% weight loss
- 33.2×10^{20} DIDO equiv. (n/cm^2)
- Temp: 287°C

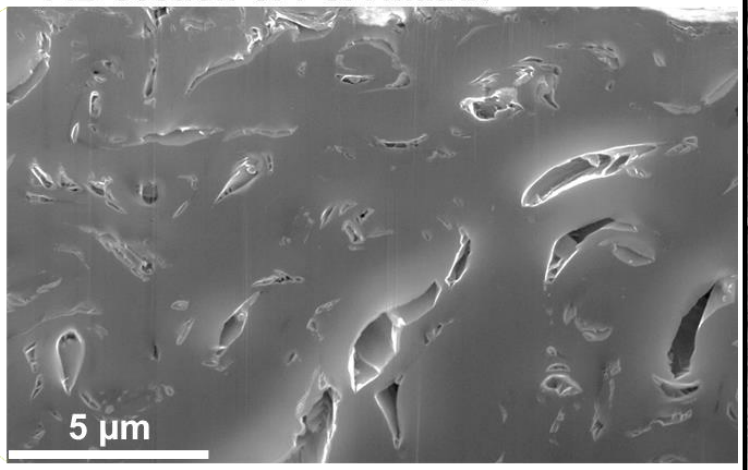
Filler particles

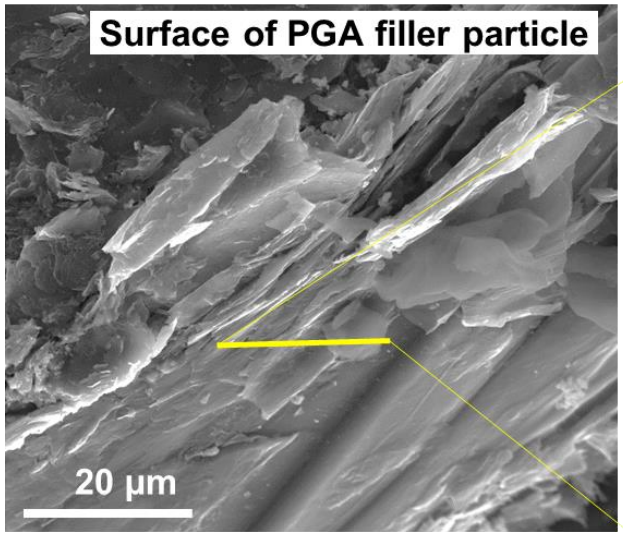


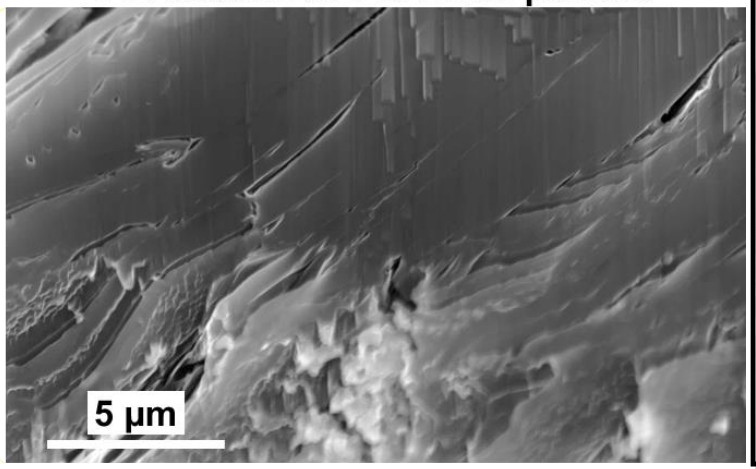


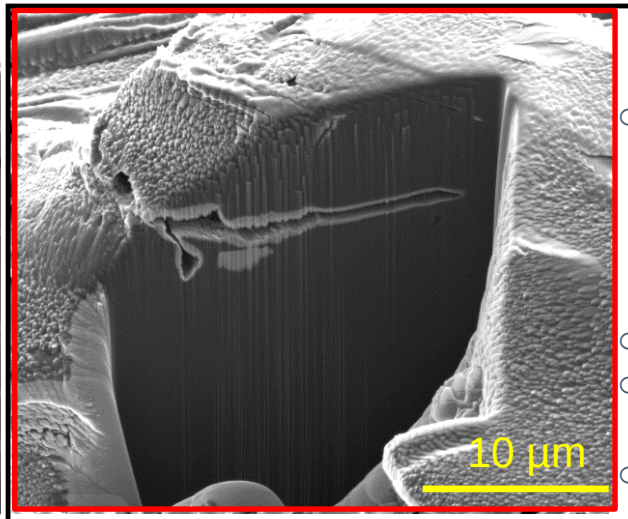
PGA graphite (unirradiated and neutron irradiated)







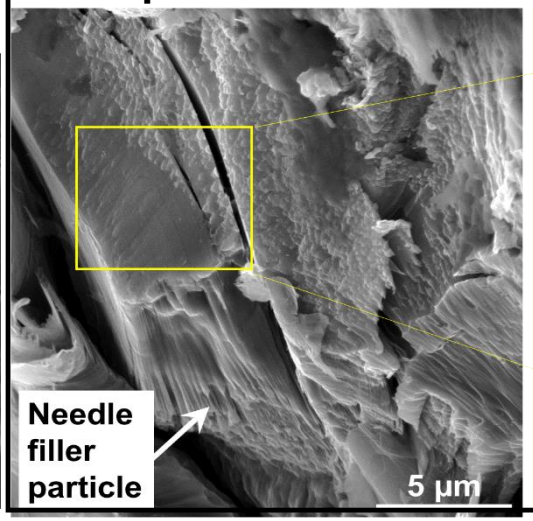


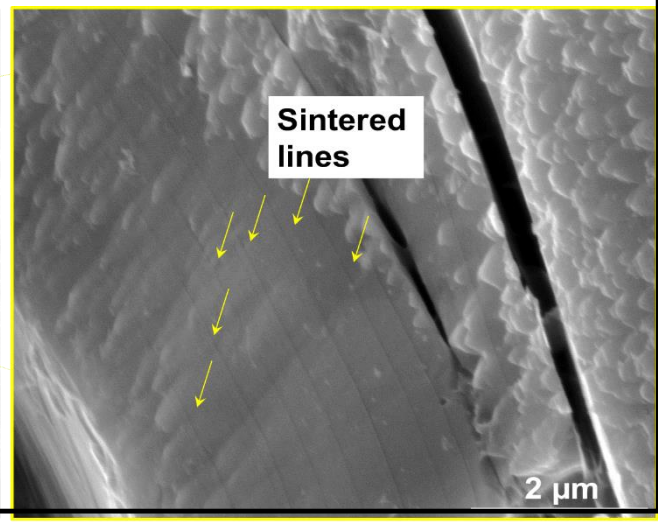


Matrix

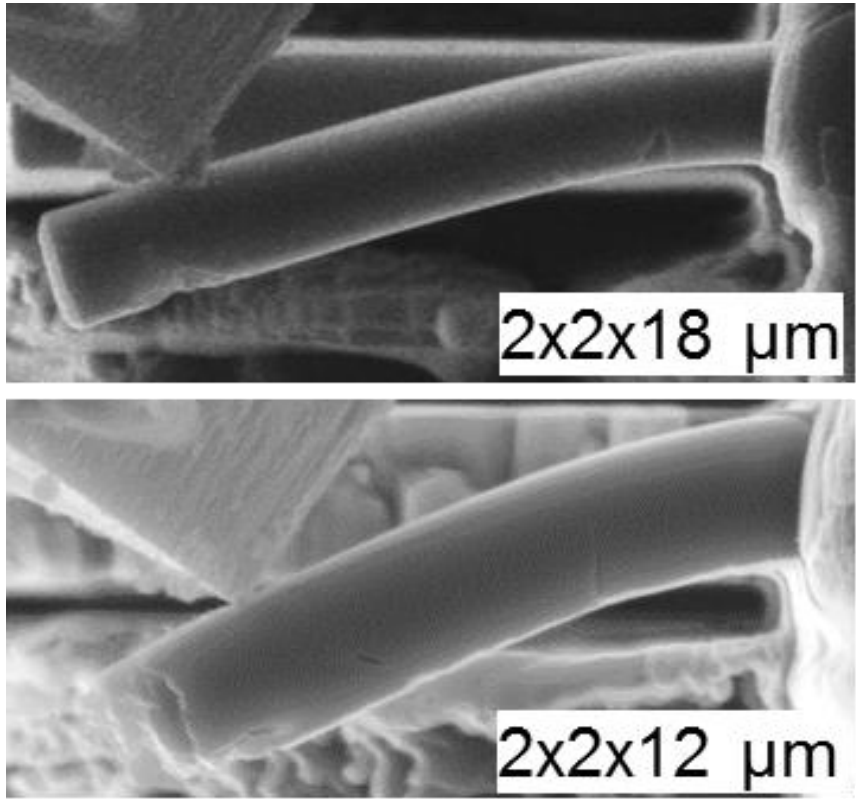
- Radiolytically-oxidised (CO_2 environment) PGA graphite samples from a Magnox reactor supplied by Magnox Ltd.
- 15% weight loss
- 33.2×10^{20} DIDO equiv. (n/cm^2)
- Temp: 287°C

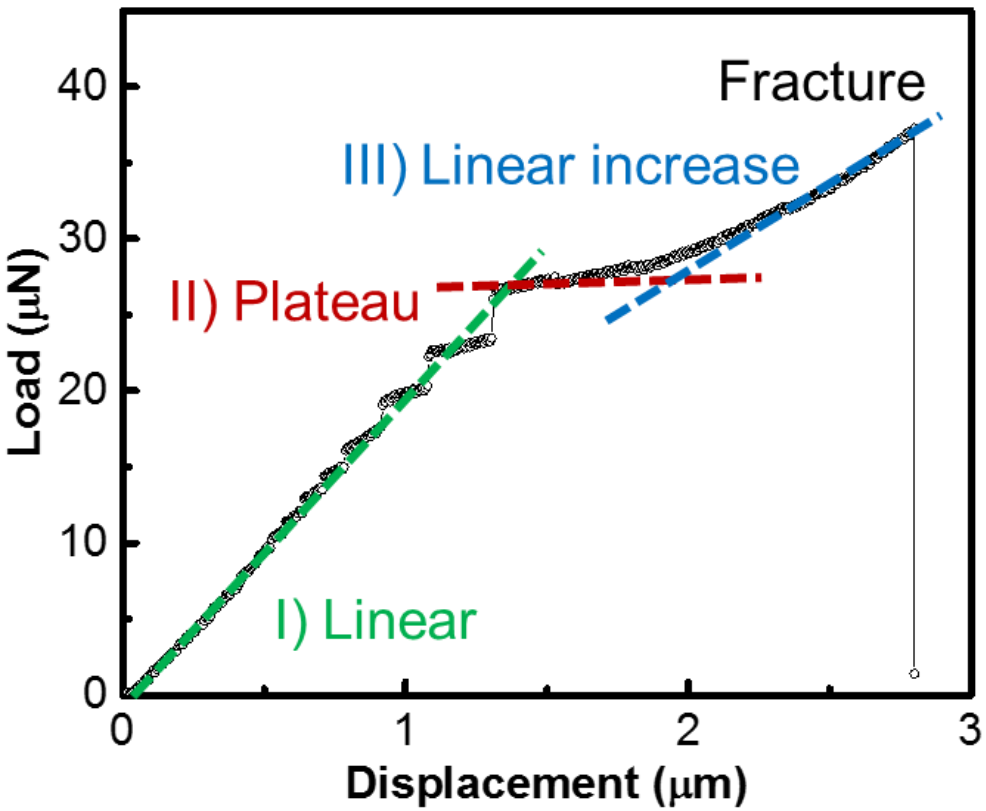
Filler particles

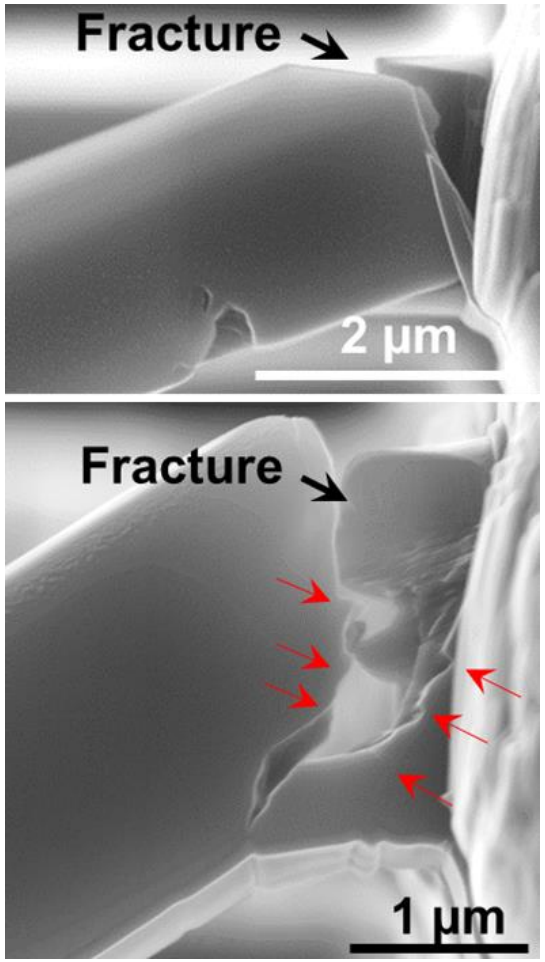




PGA graphite (Irradiated: matrix)

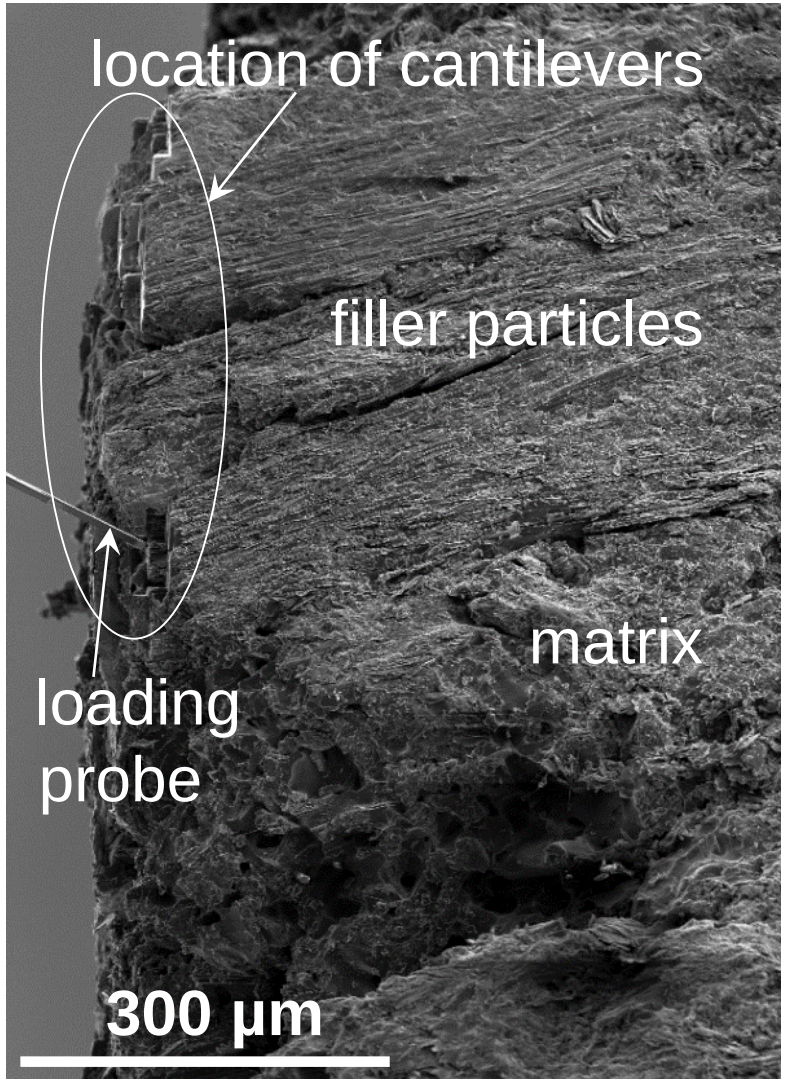




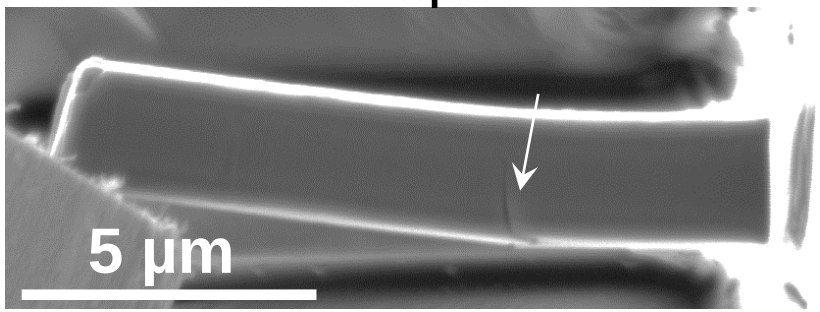


- Cantilevers are made inside the matrix
- Modulus and flexural strength are found to be lower than the unirradiated condition

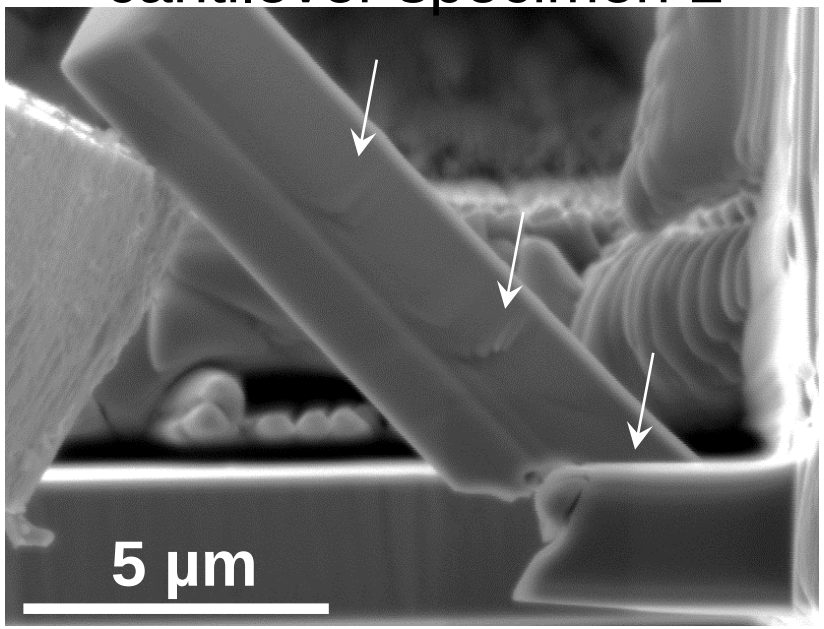
PGA graphite (Irradiated: filler particle)

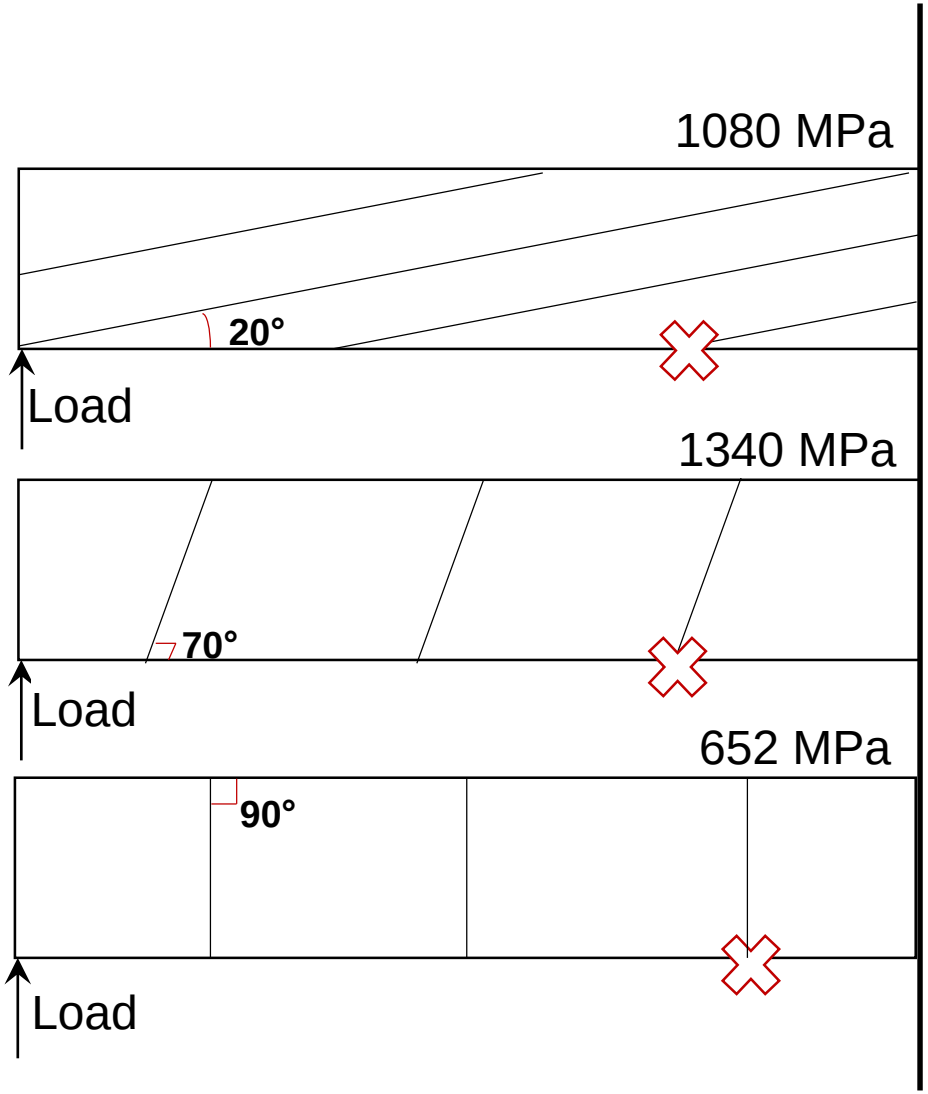


cantilever specimen 1

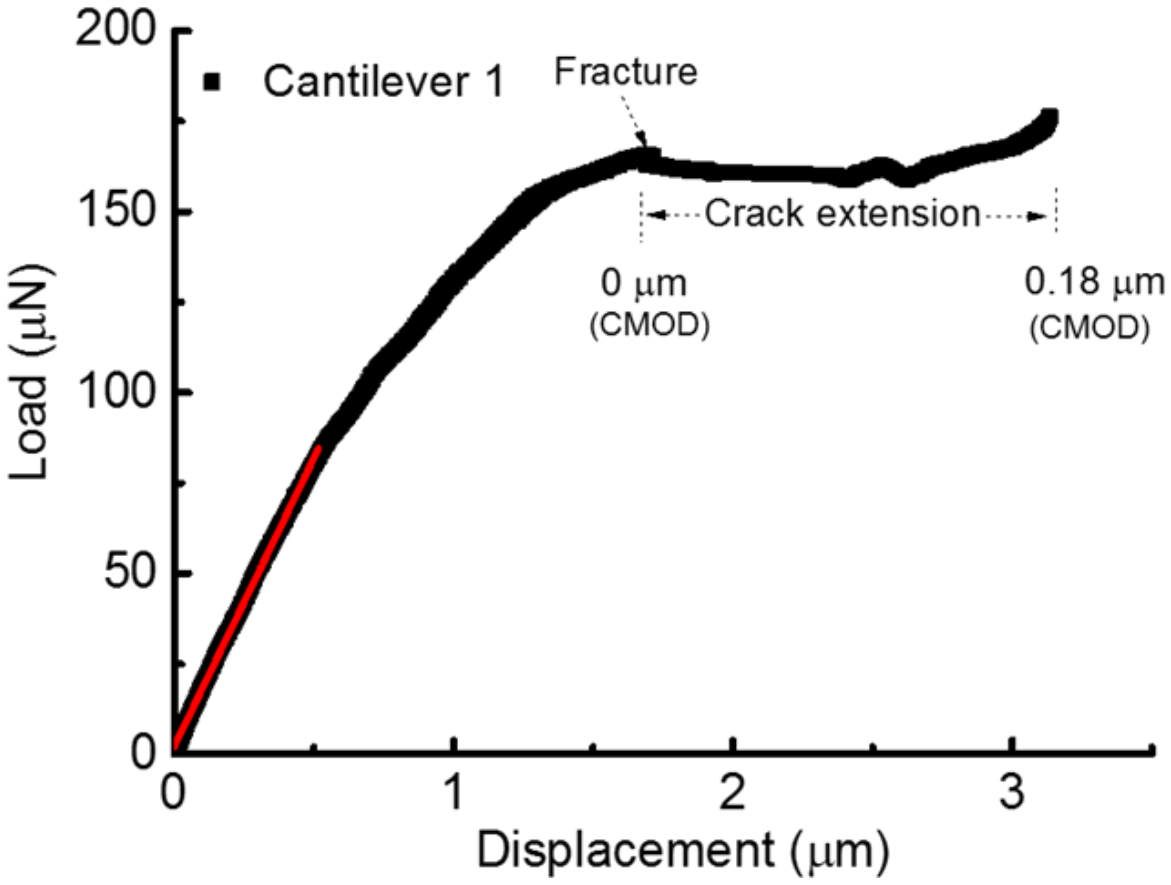


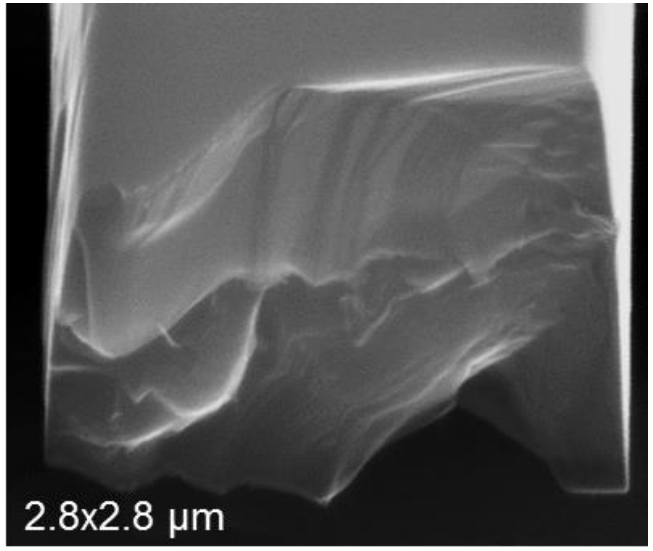
cantilever specimen 2



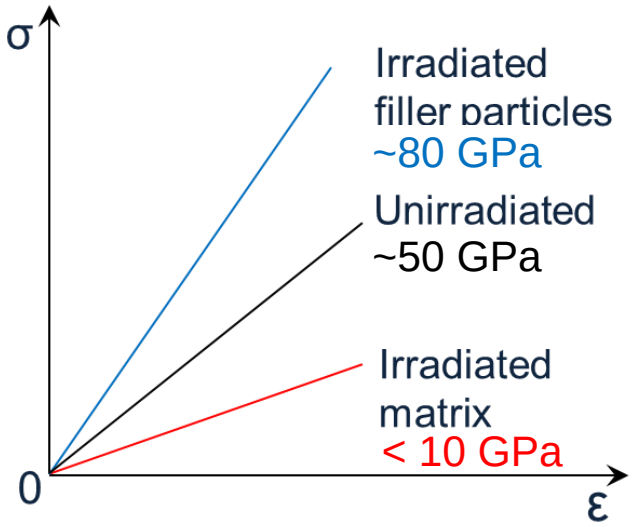


PGA graphite (Irradiated: filler particle)





Elastic modulus:

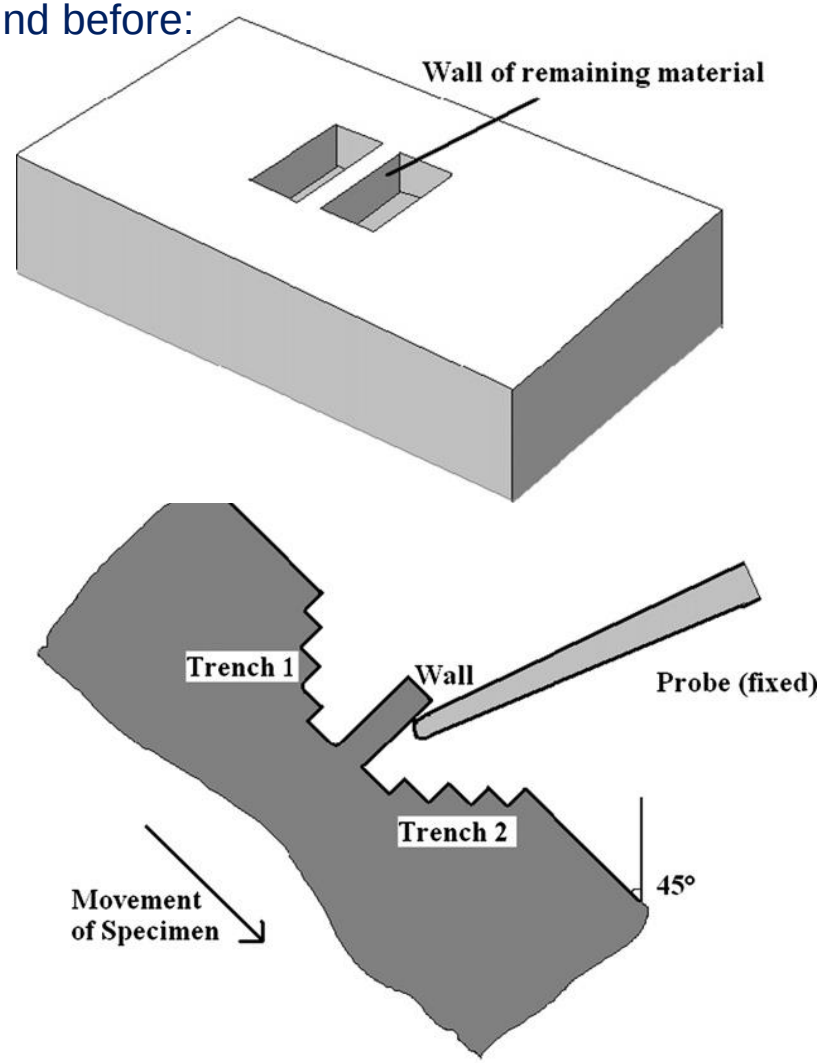


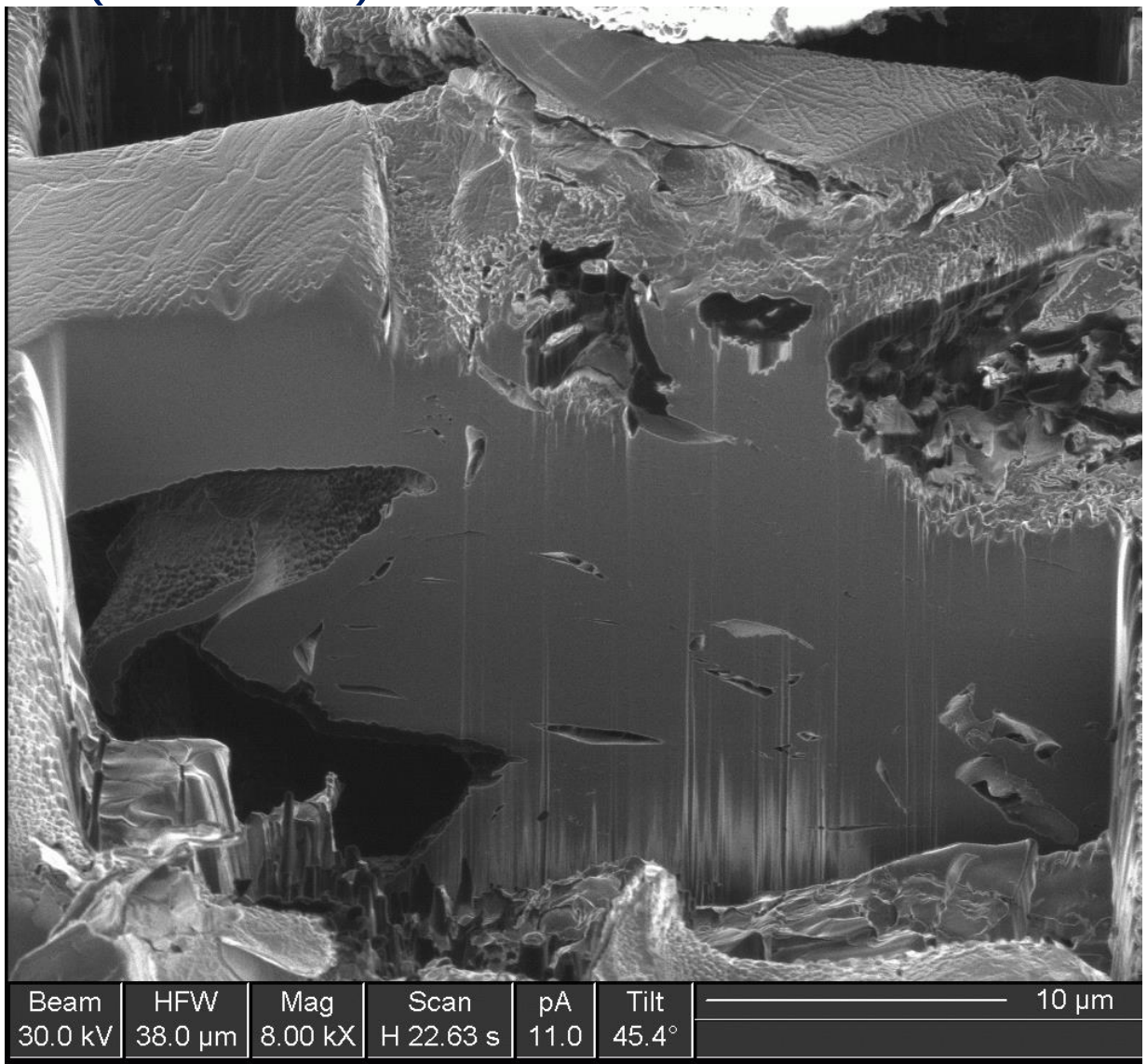
- After neutron irradiation, the matrix becomes more compliant while the filler particles becomes stiffer compared with the unirradiated condition

Liu et al, submitted to Carbon, under review

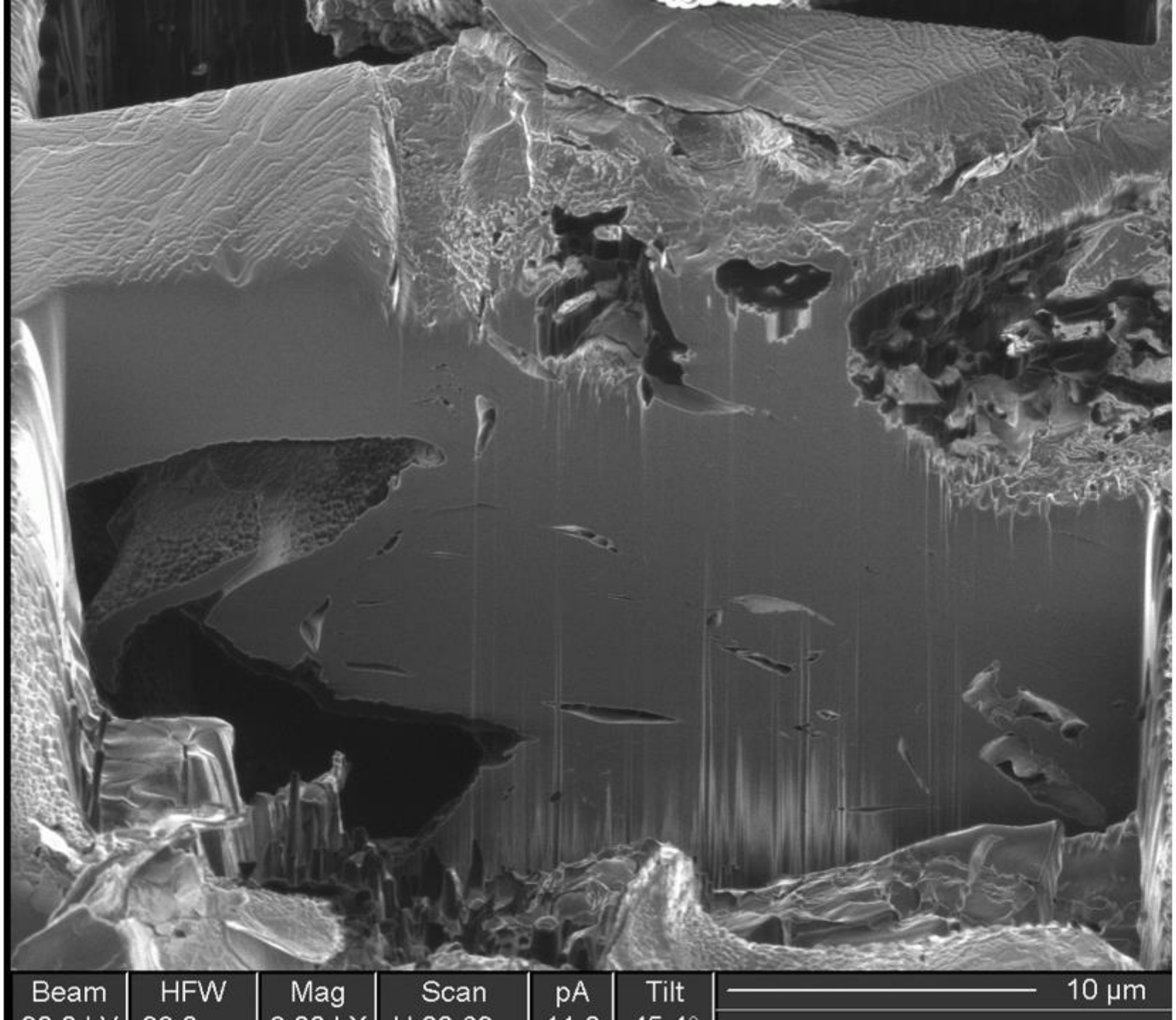
PGA graphite (Irradiated)

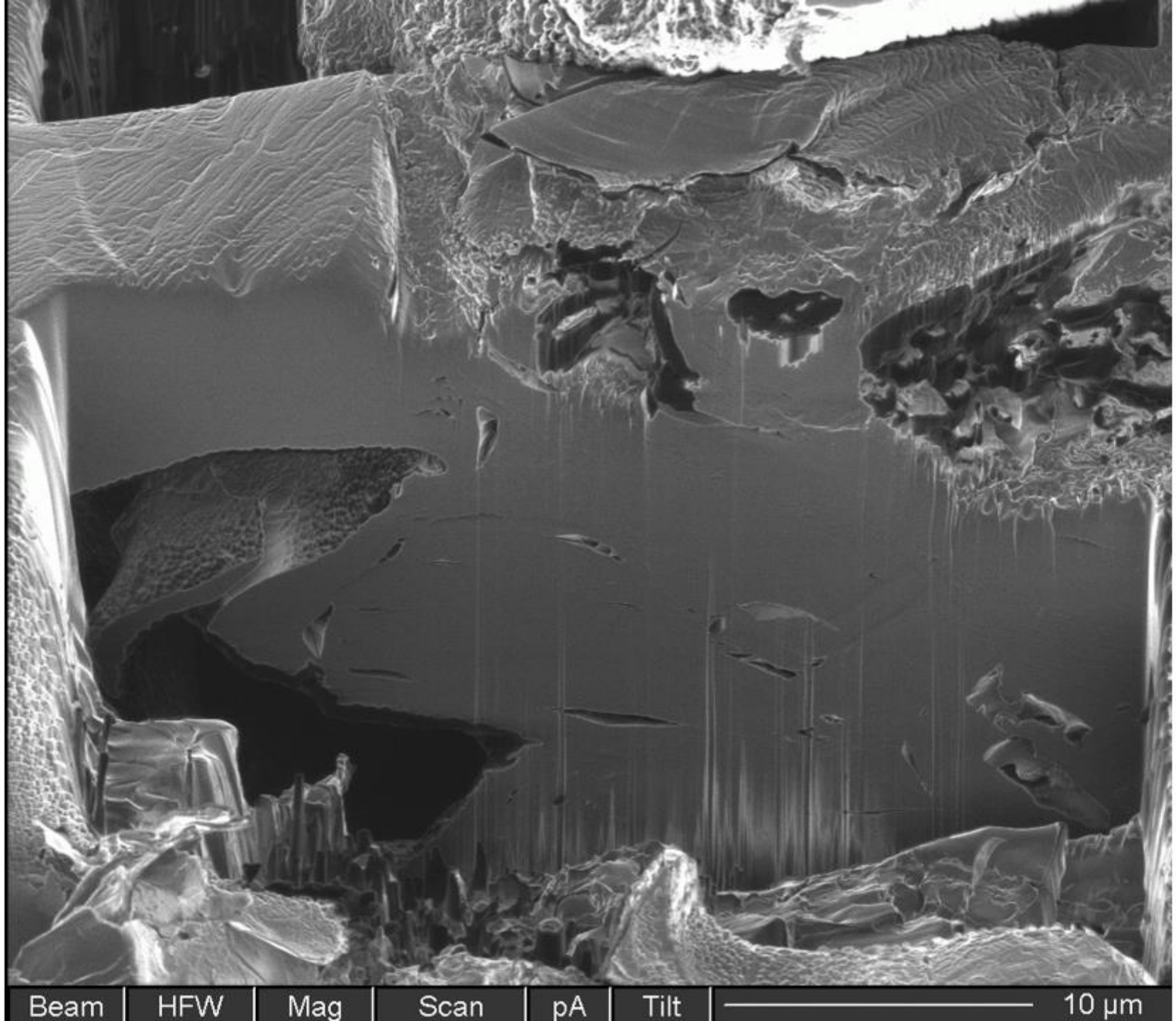
What we found before:

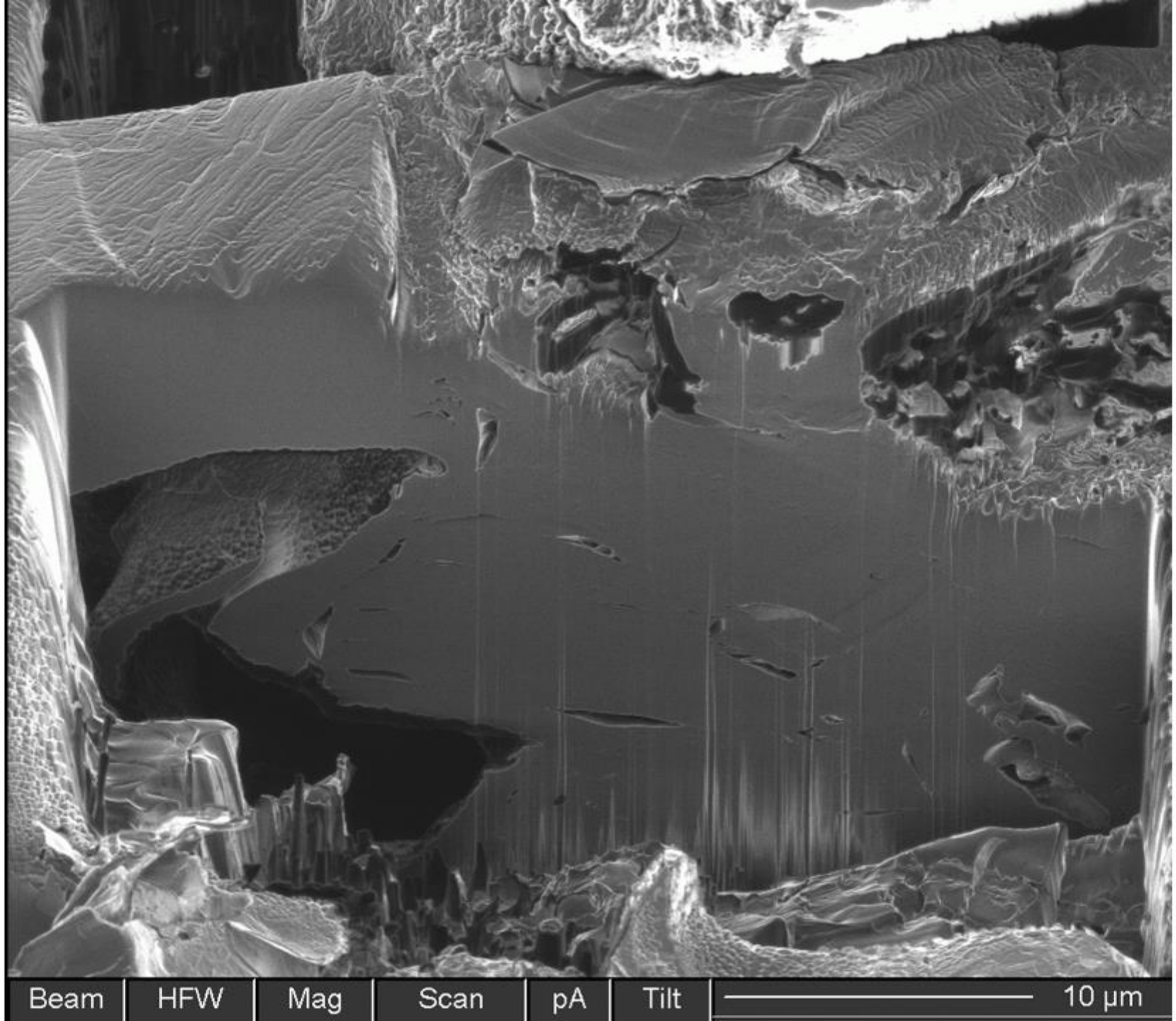


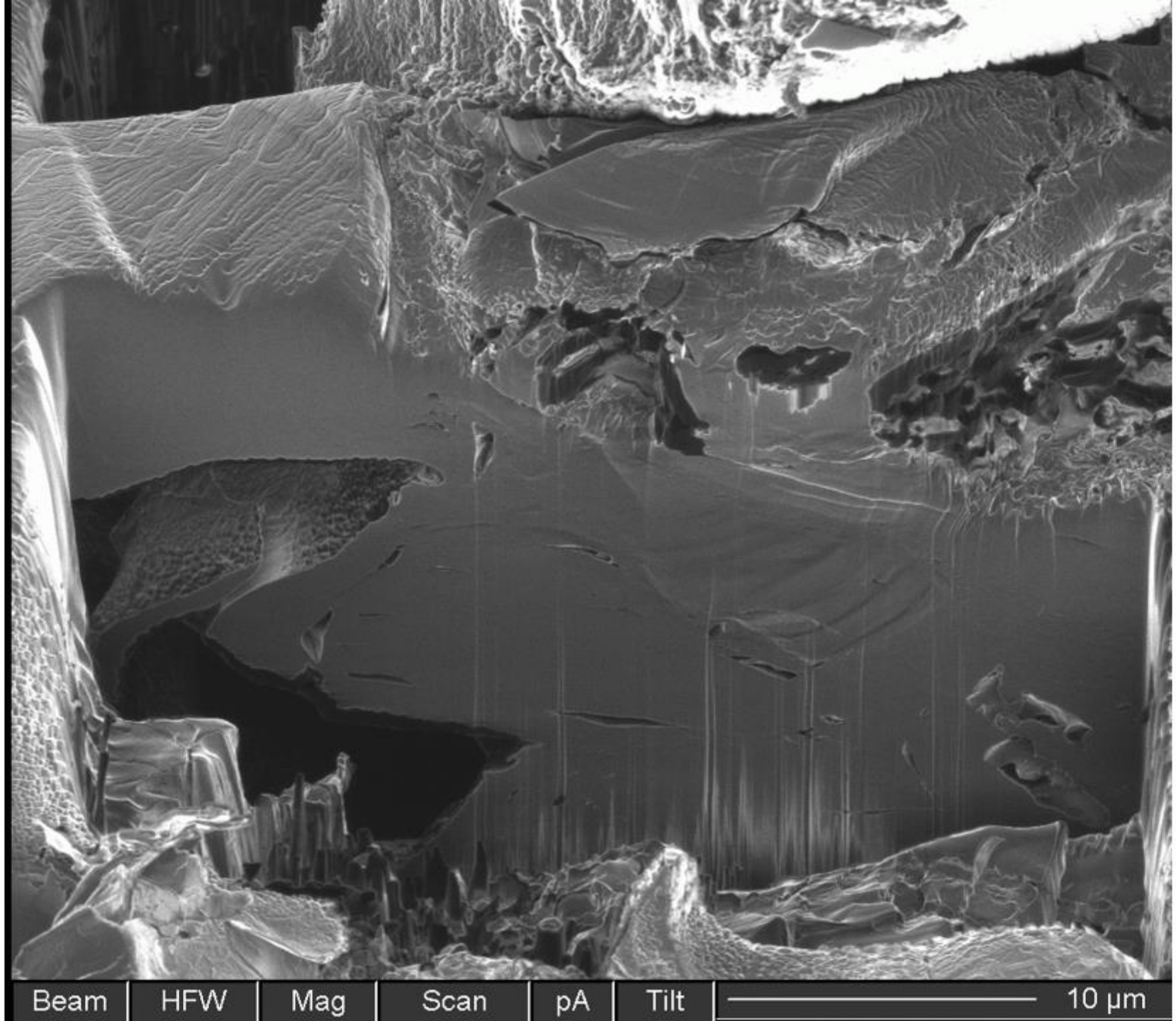


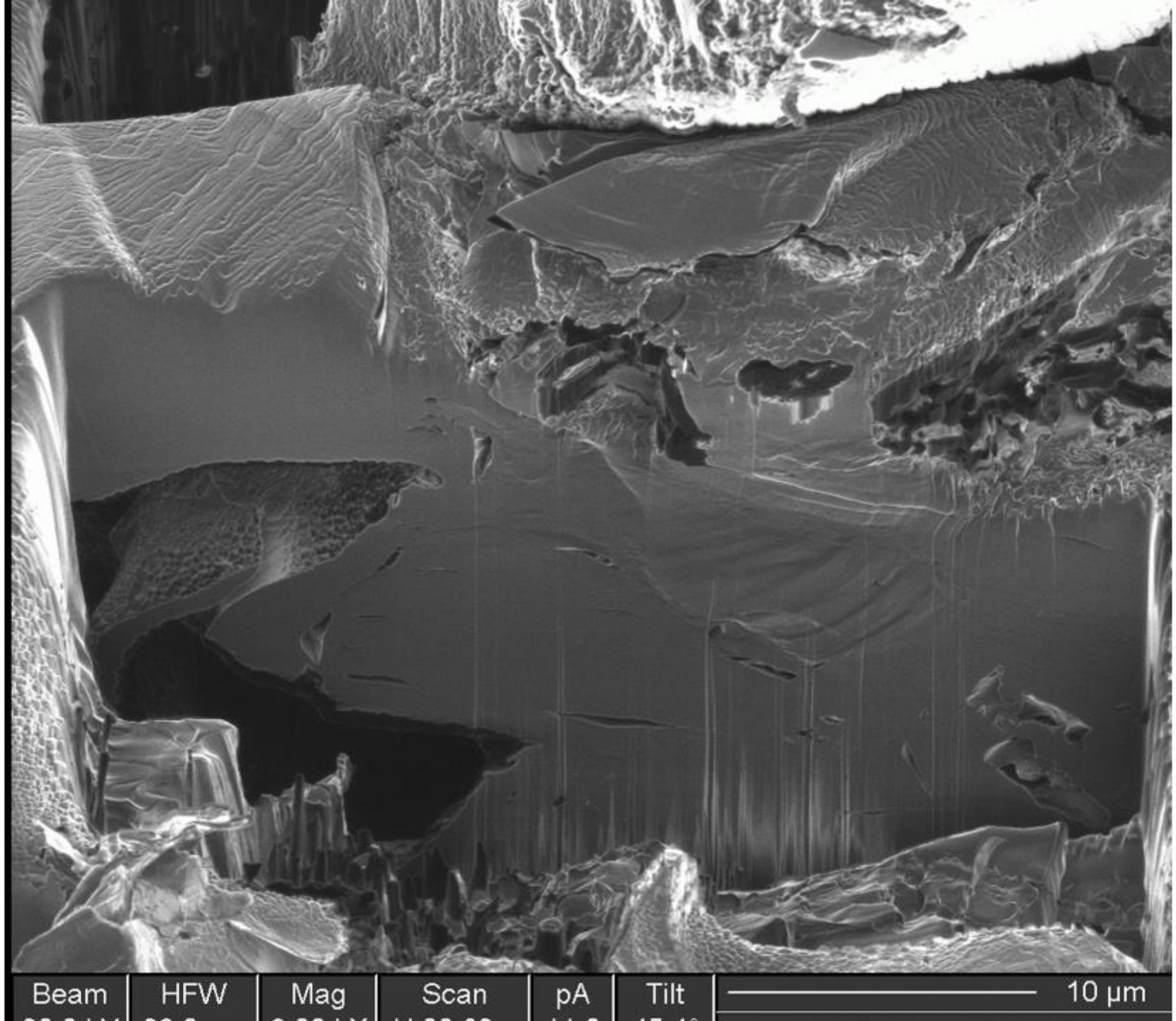
- *Heard et al, J Nucl Mat 2011, 418 (223)*

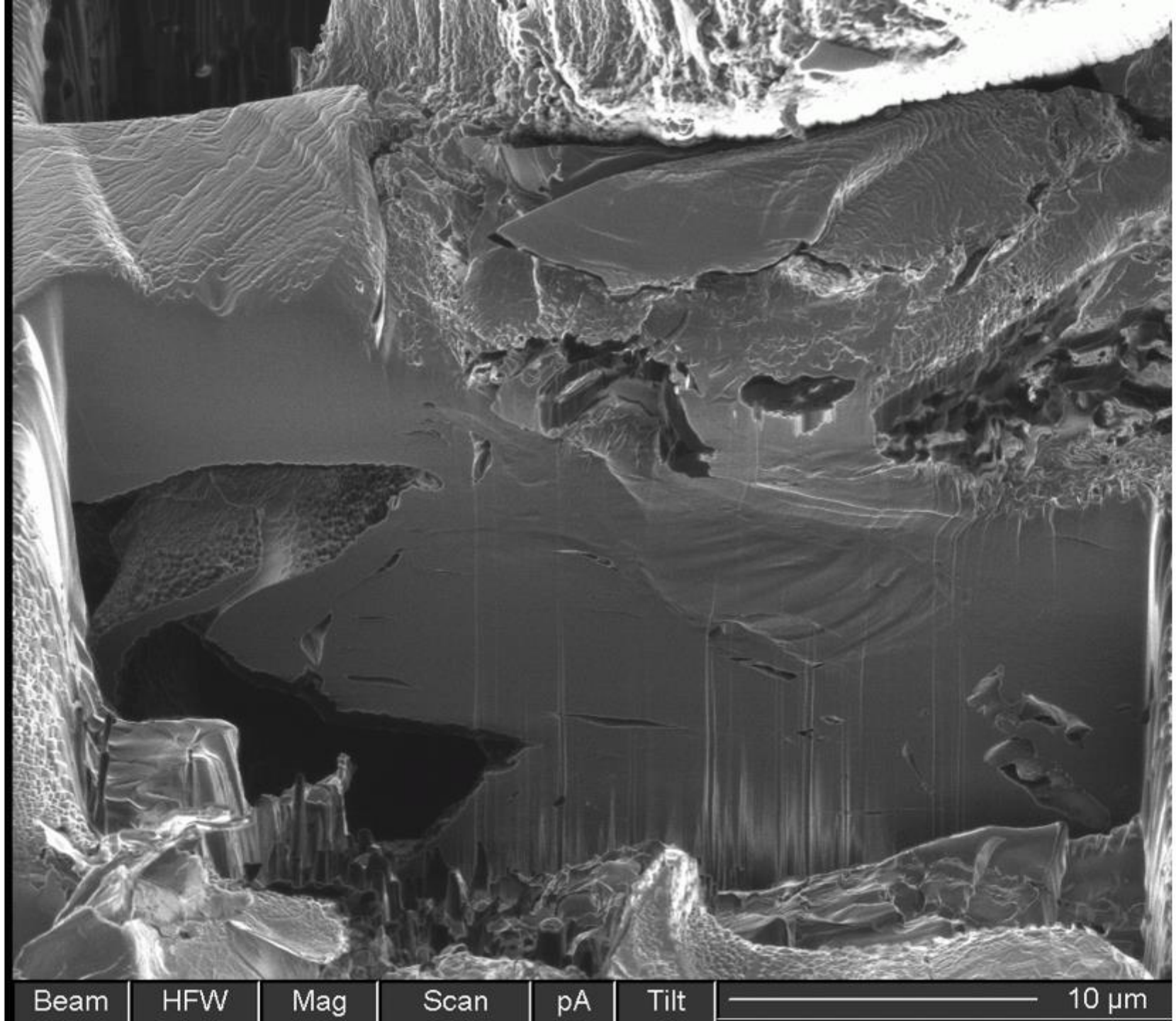

Beam
HFW
Mag
Scan
pA
Tilt
10 µm

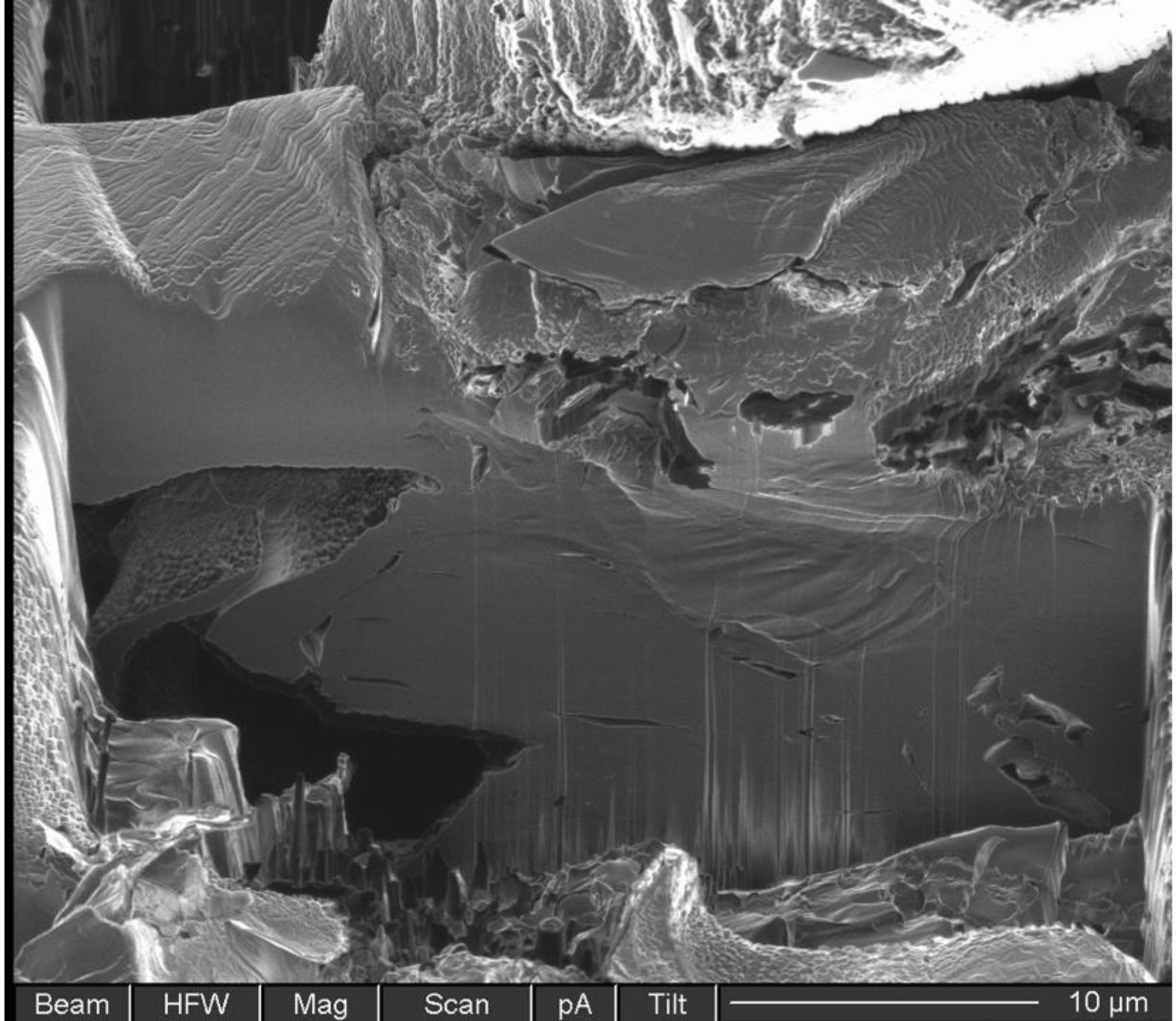

Beam
HFW
Mag
Scan
pA
Tilt
10 µm

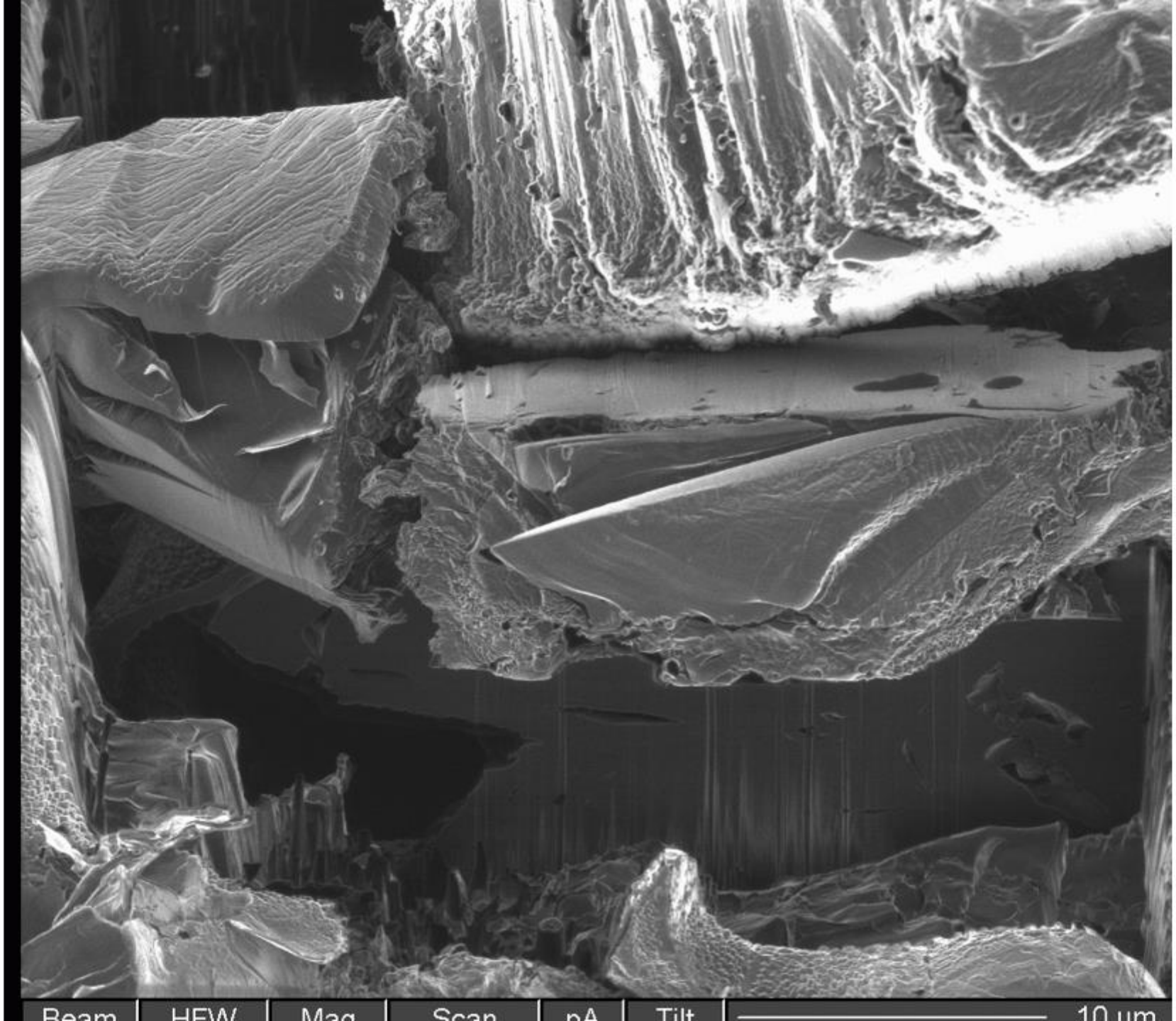

Beam
HFW
Mag
Scan
pA
Tilt
10 µm


Beam
HFW
Mag
Scan
pA
Tilt
10 µm


Beam
HFW
Mag
Scan
pA
Tilt
10 µm

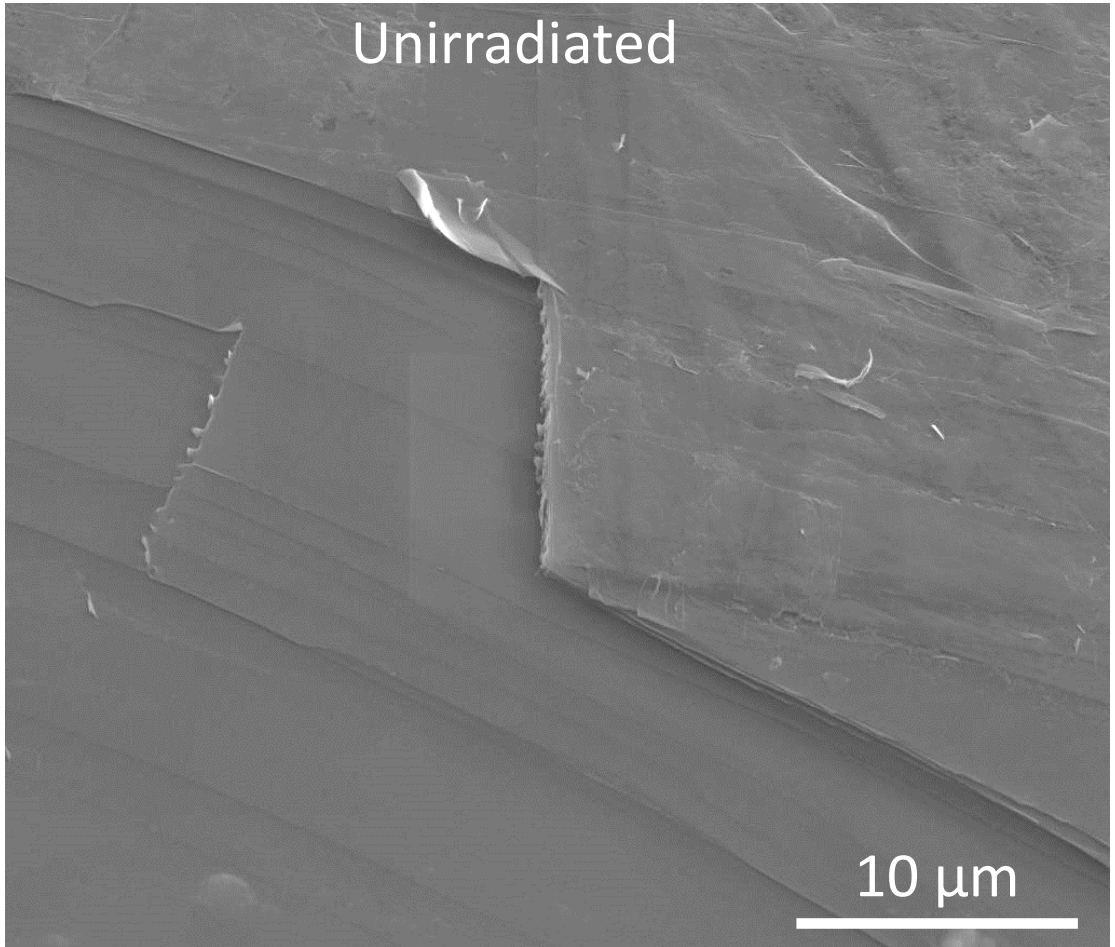

Beam
HFW
Mag
Scan
pA
Tilt
10 µm

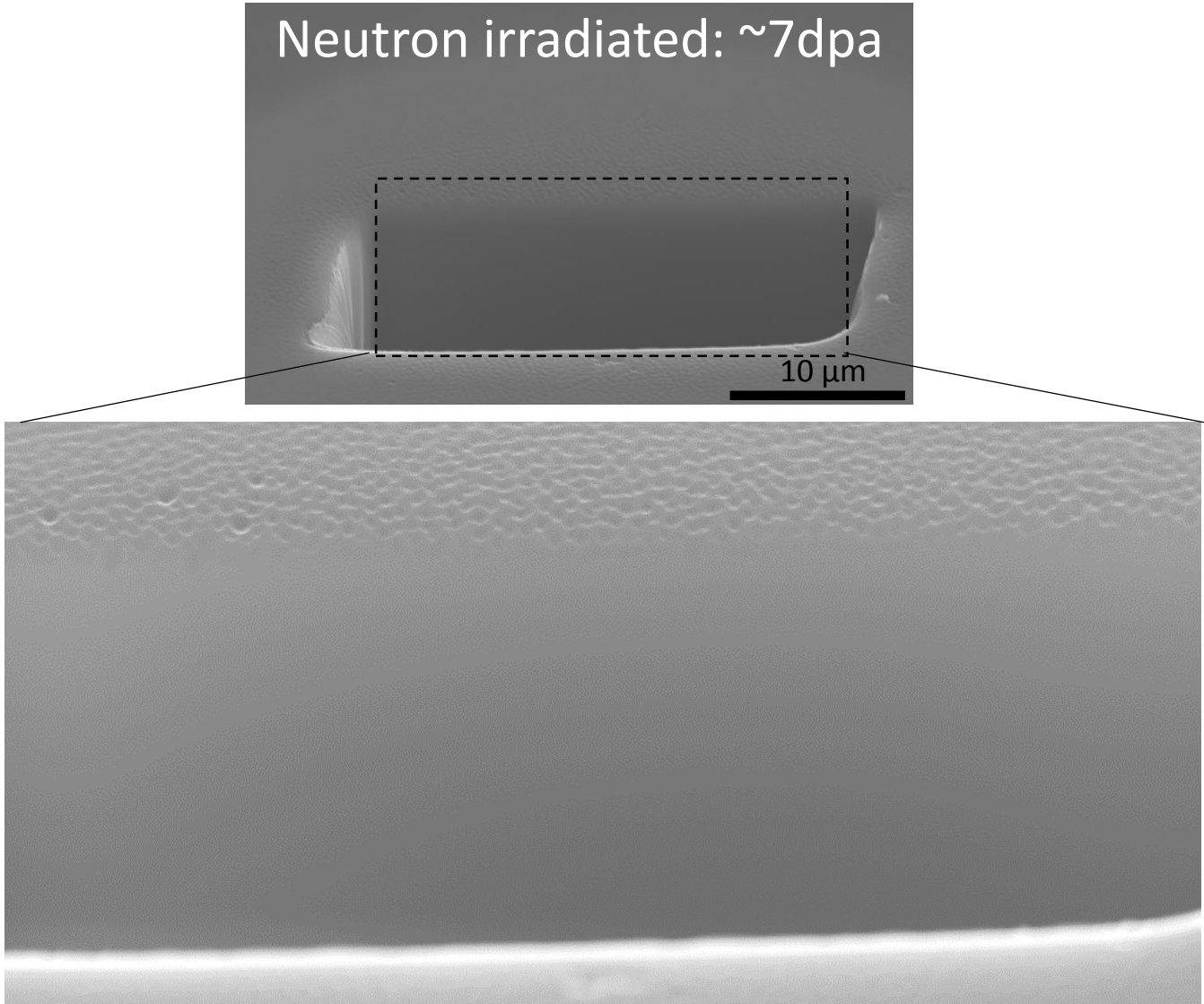

Beam
HFW
Mag
Scan
pA
Tilt
10 µm


Beam
HFW
Mag
Scan
pA
Tilt
10 µm

HOPG graphite (Unirradiated and irradiated)

- **Highly oriented pyrolytic graphite**

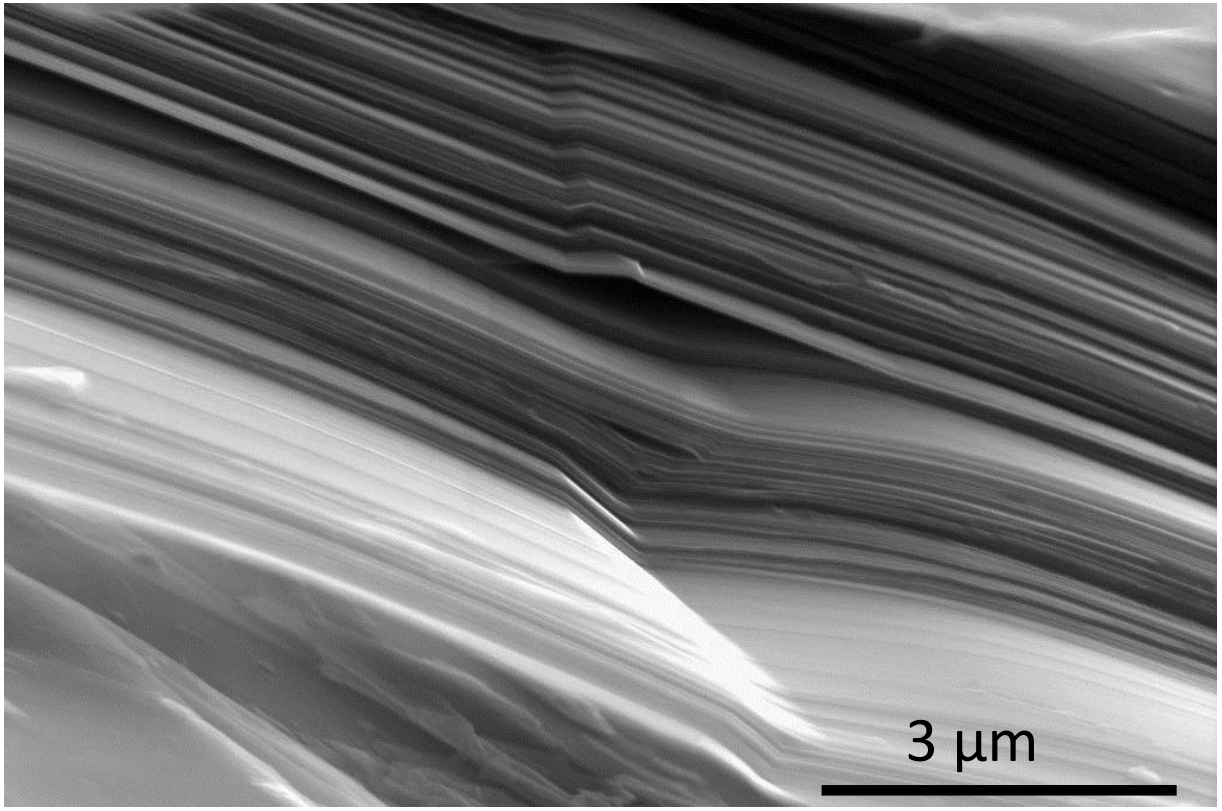


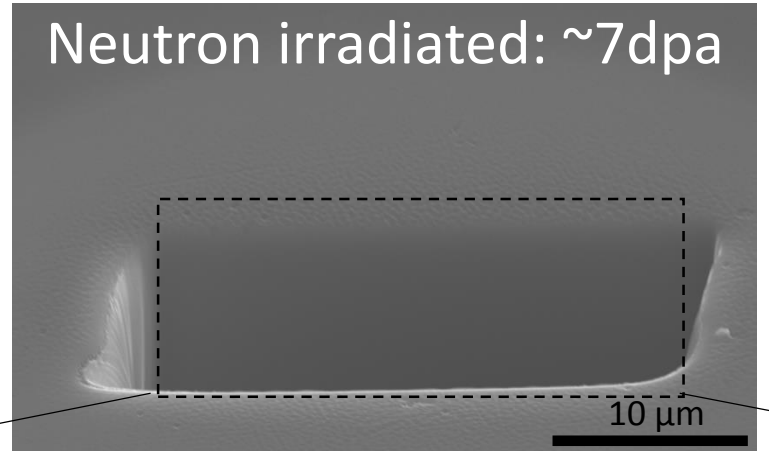


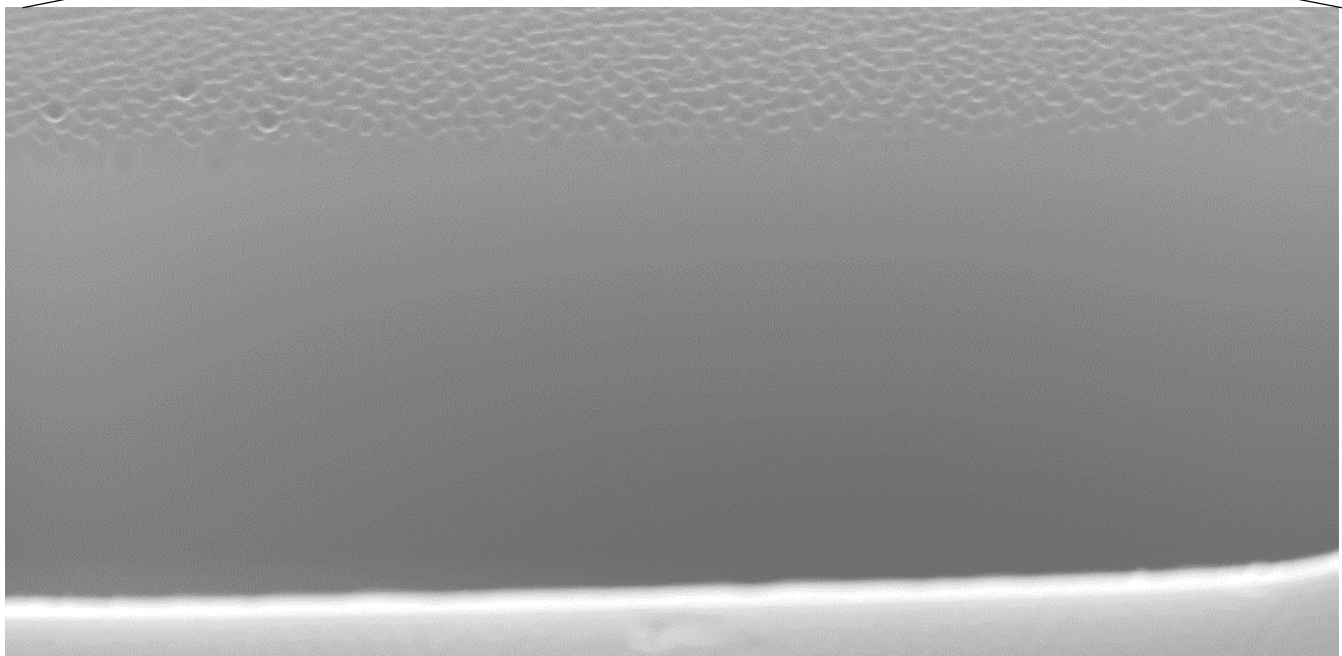
HOPG graphite (Unirradiated and irradiated)

- **Highly oriented pyrolytic graphite**

Unirradiated

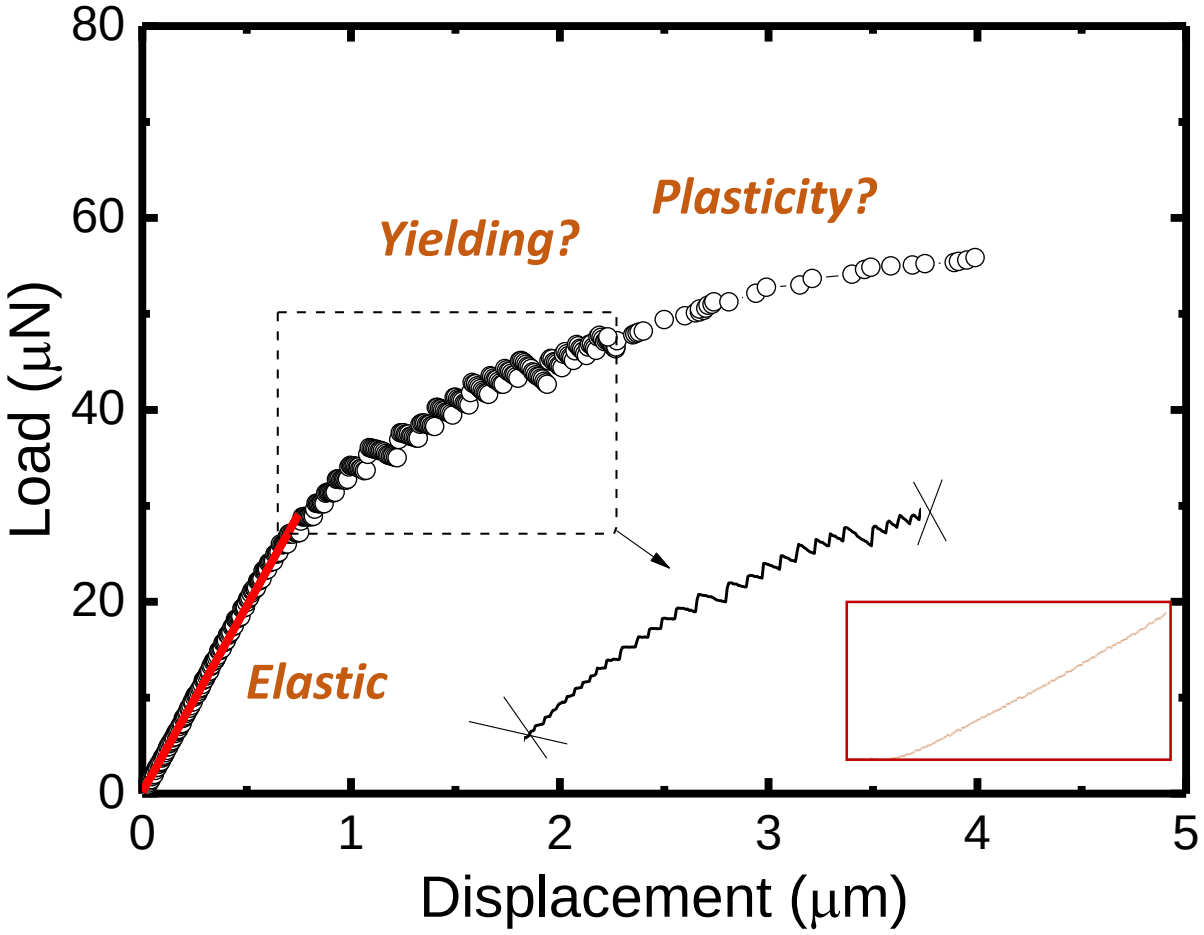


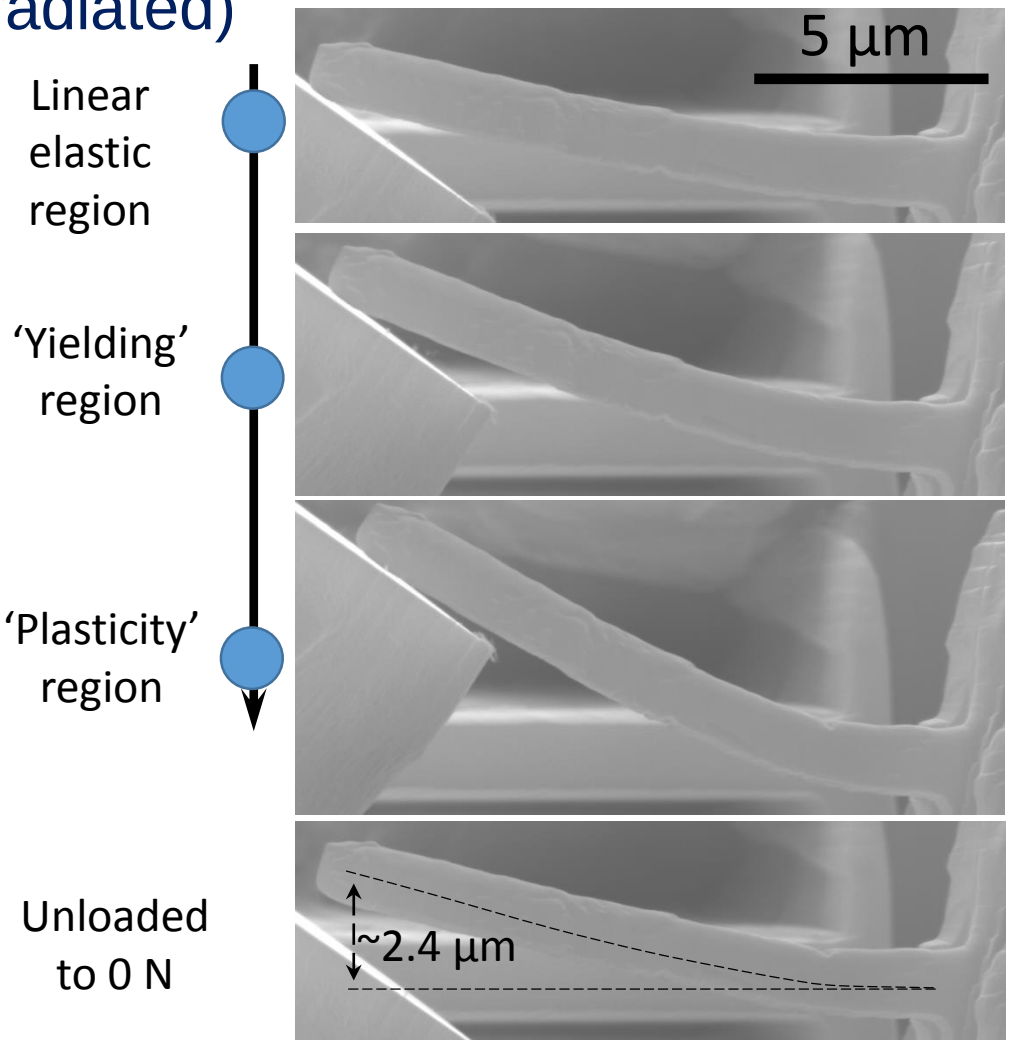




HOPG graphite (Irradiated)

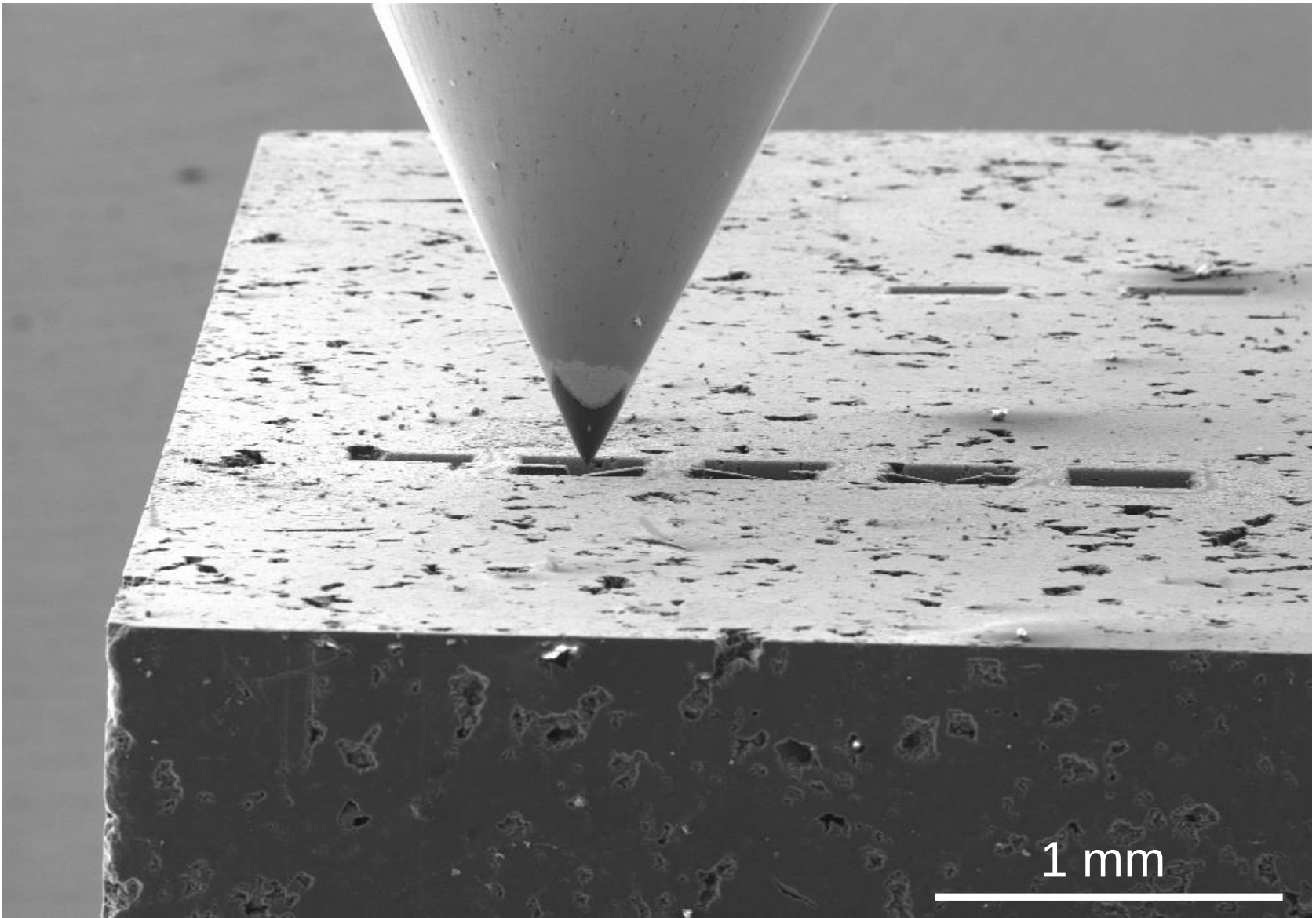
- **Deformation and fracture**





Permanent displacement (~2.4 μm) after load removal

Scale up to larger size



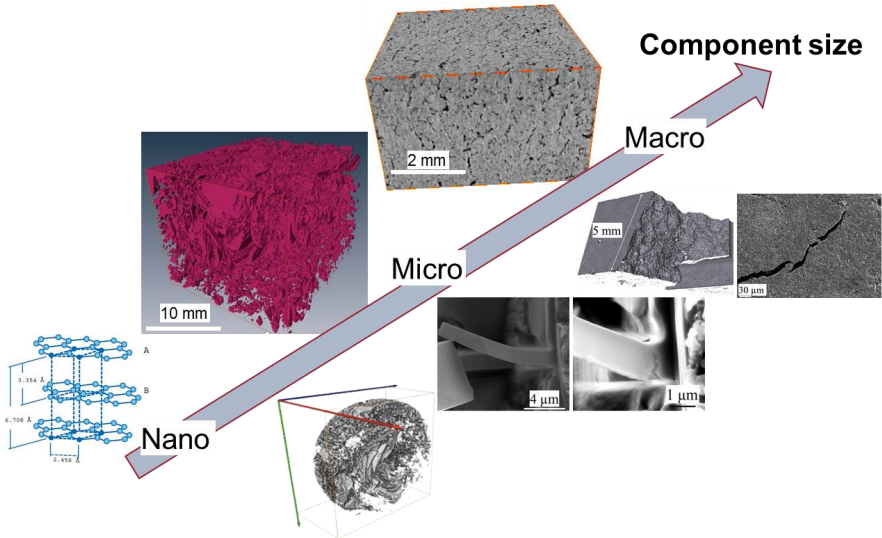
- **Cantilever size:**

  2x2x10 µm

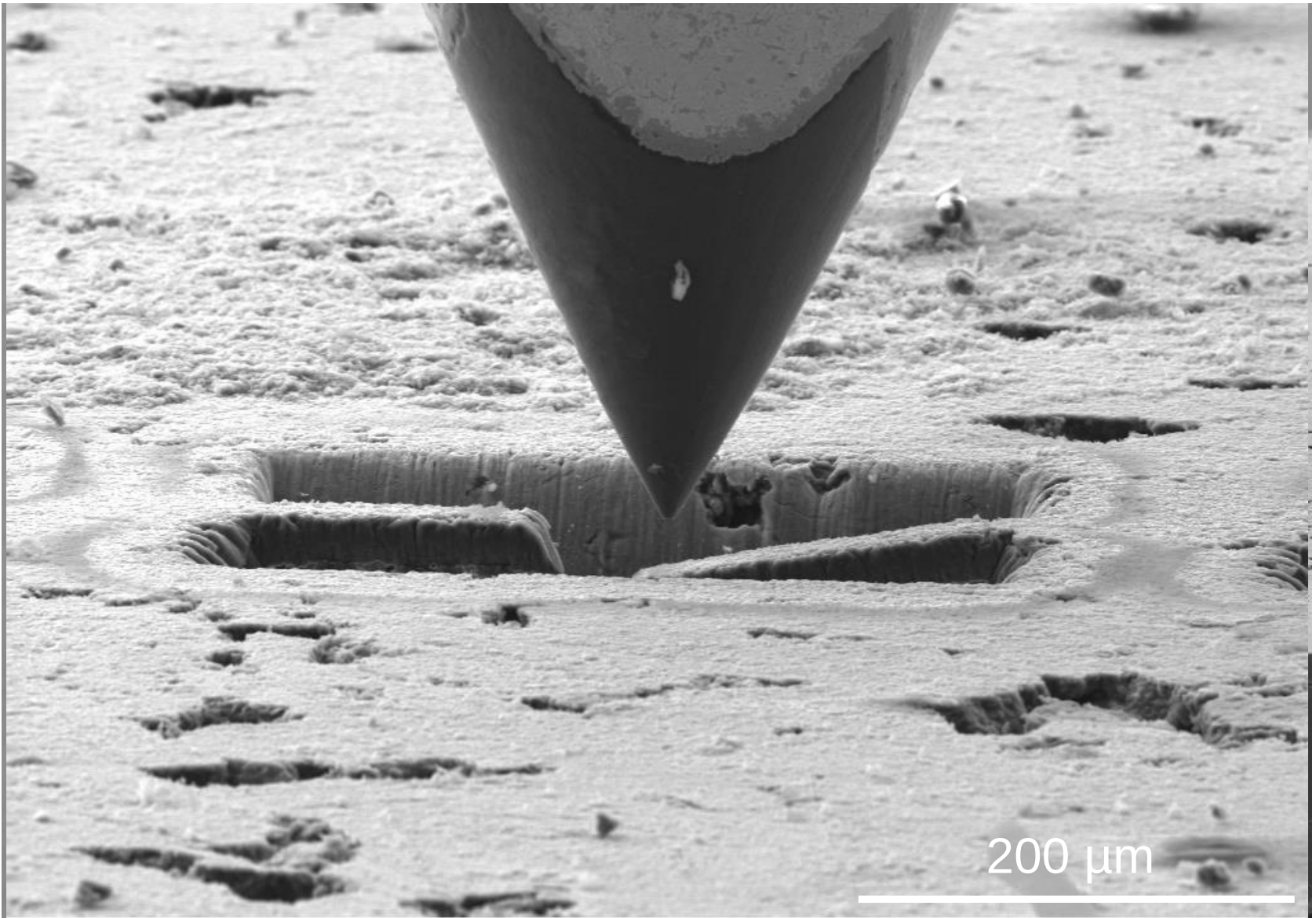
  ↓

  40x40x200 µm

- ***In situ* testing using nano-indentation inside SEM**



Scale up to larger size



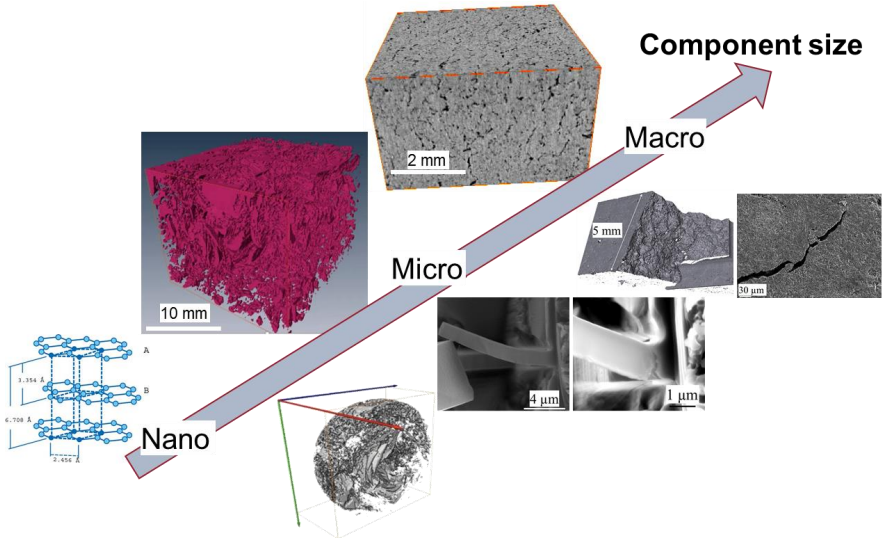
- **Cantilever size:**

  2x2x10 µm

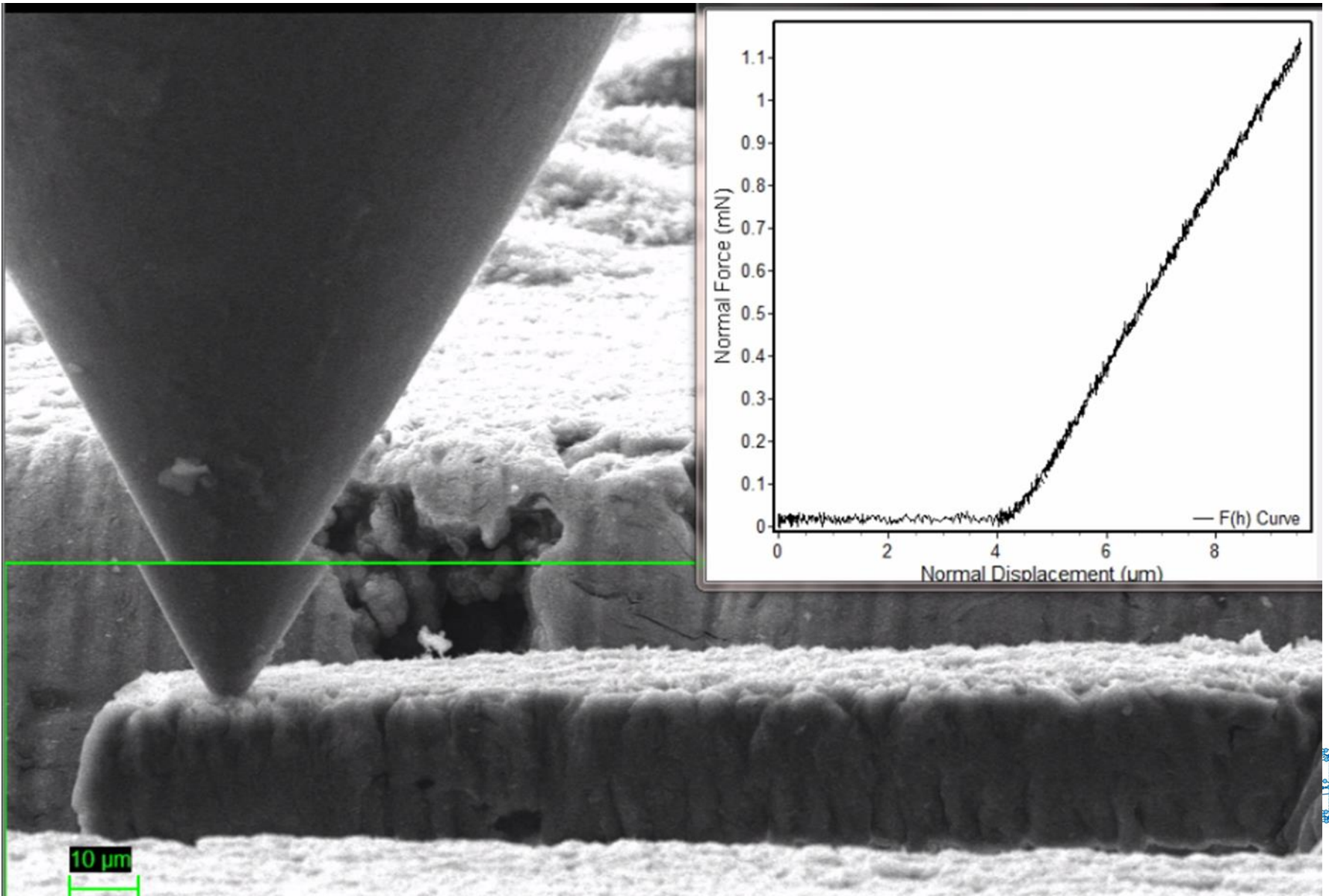
  ↓

  40x40x200 µm

- ***In situ* testing using nano-indentation inside SEM**



Scale up to larger size



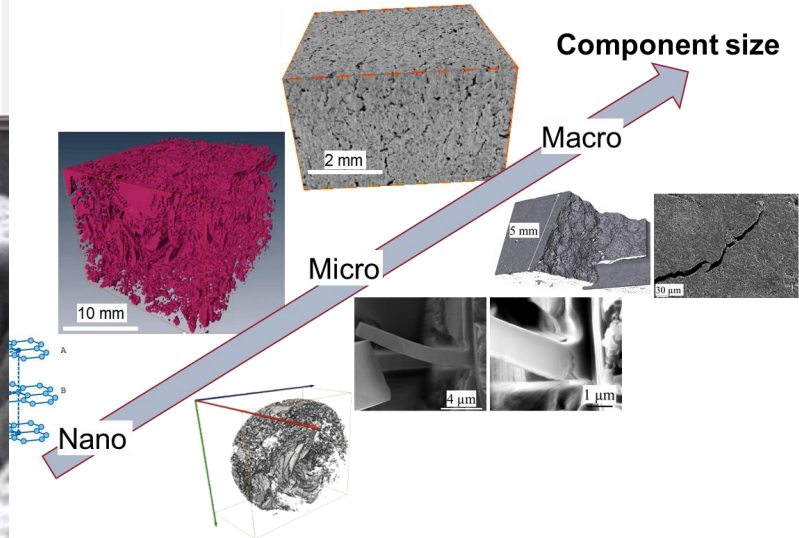
- **Cantilever size:**

  2x2x10 µm

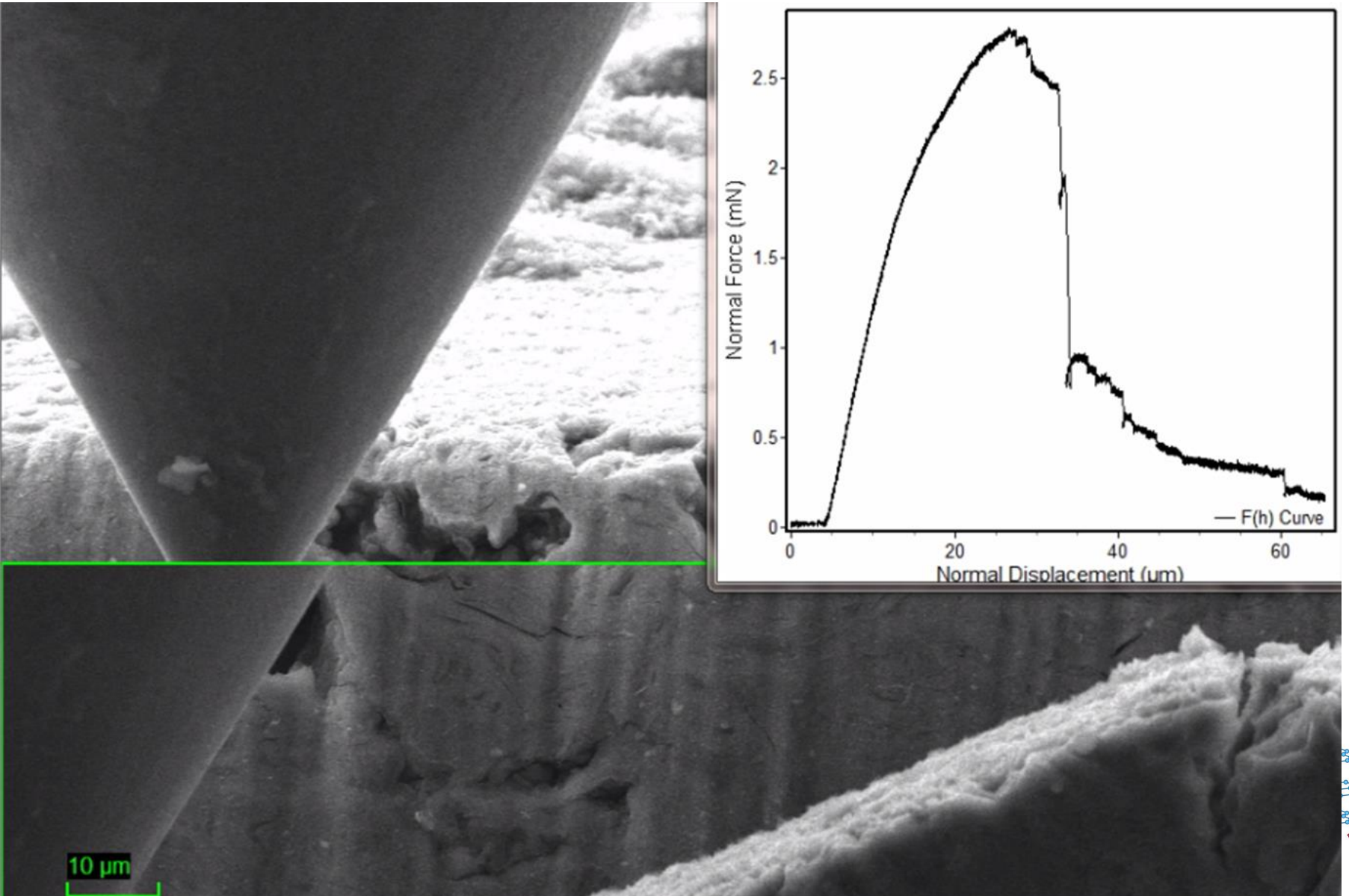
  ↓

  40x40x200 µm

- ***In situ* testing using nano-indentation inside SEM**



Scale up to larger size



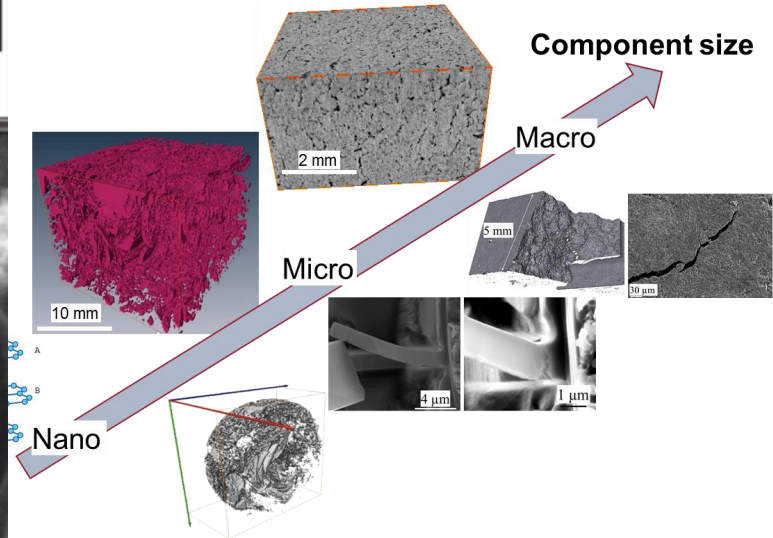
- **Cantilever size:**

  2x2x10 µm

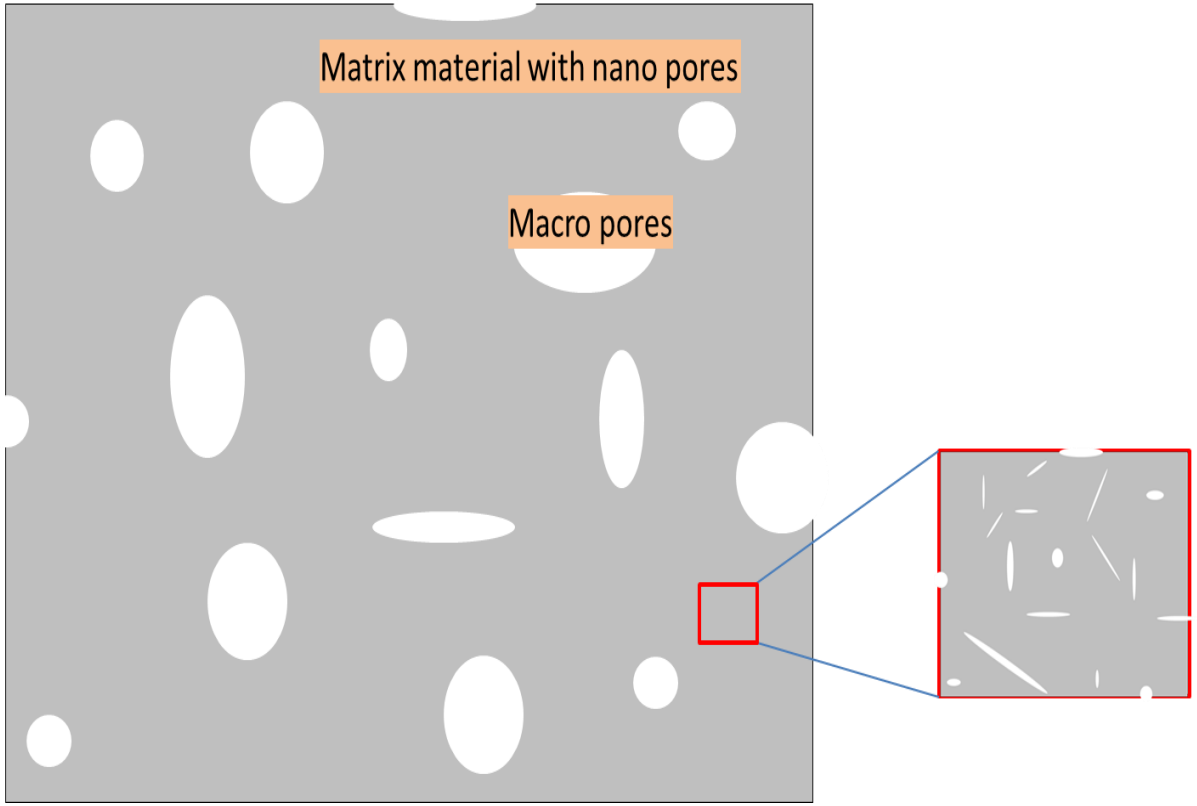
  ↓

  40x40x200 µm

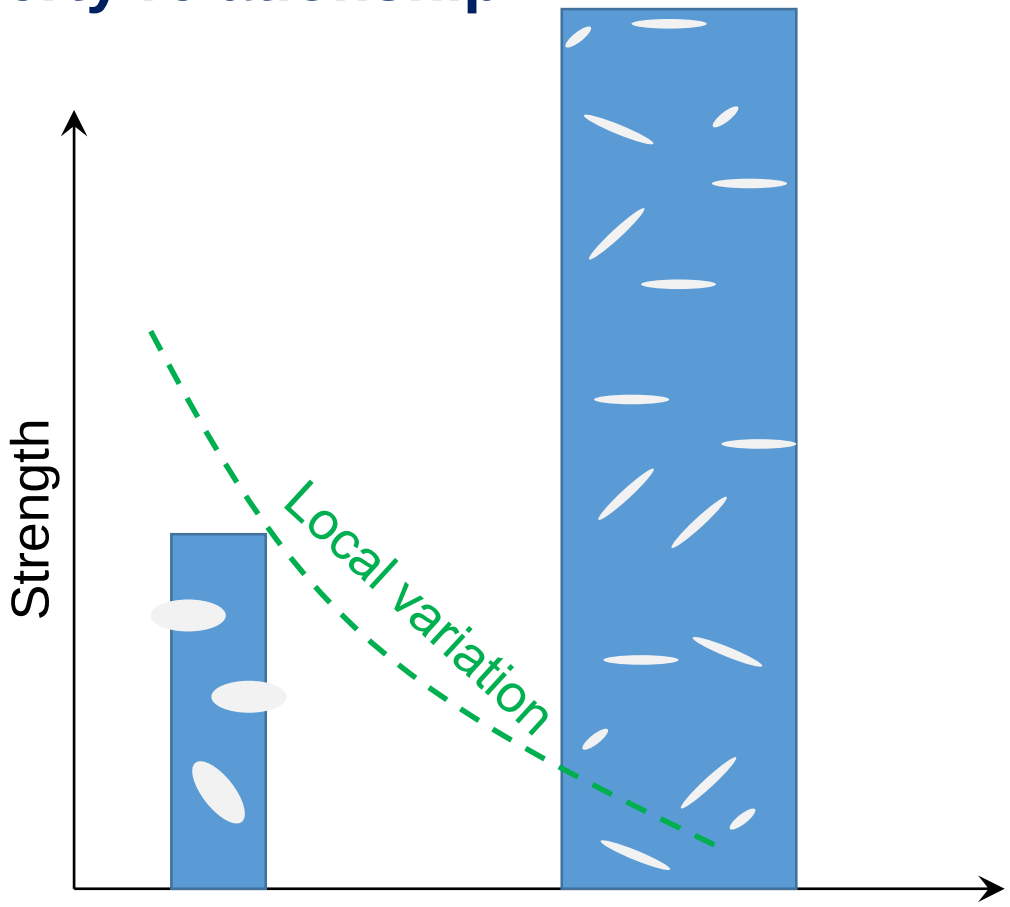
- ***In situ* testing using nano-indentation inside SEM**



Microstructure – property relationship

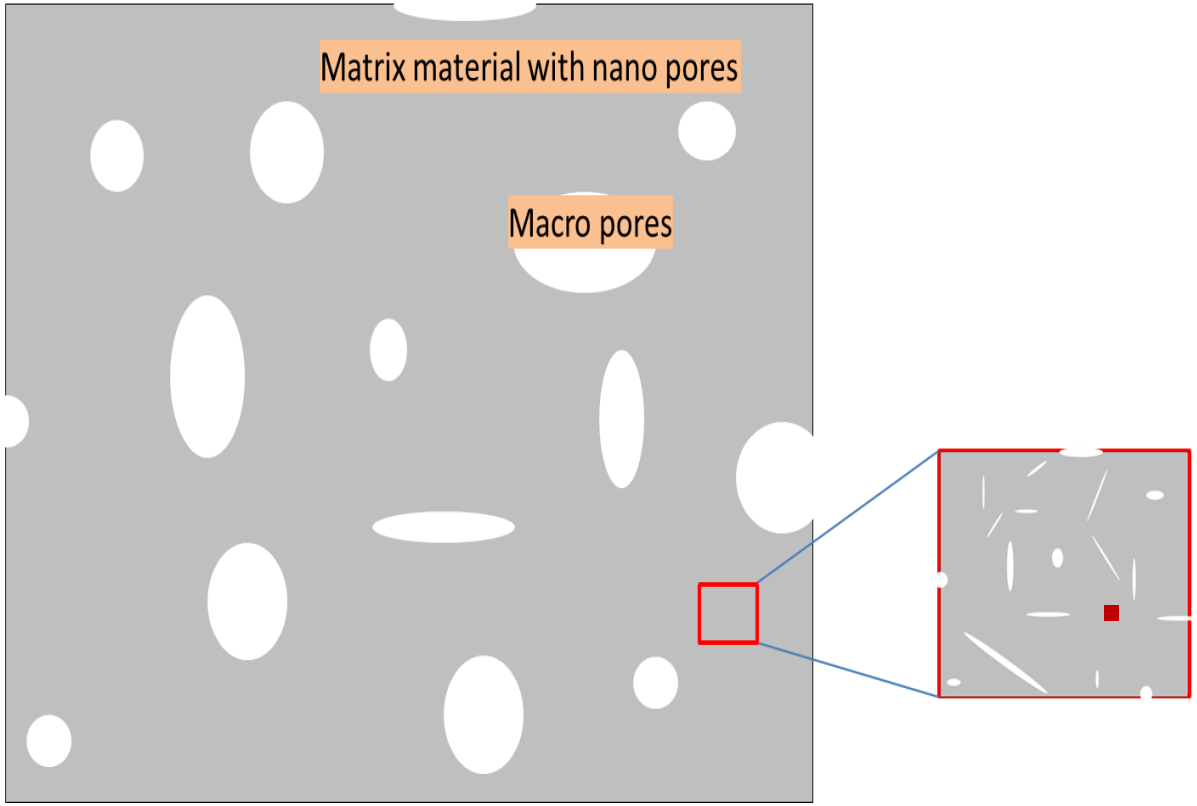


Schematic of the structure

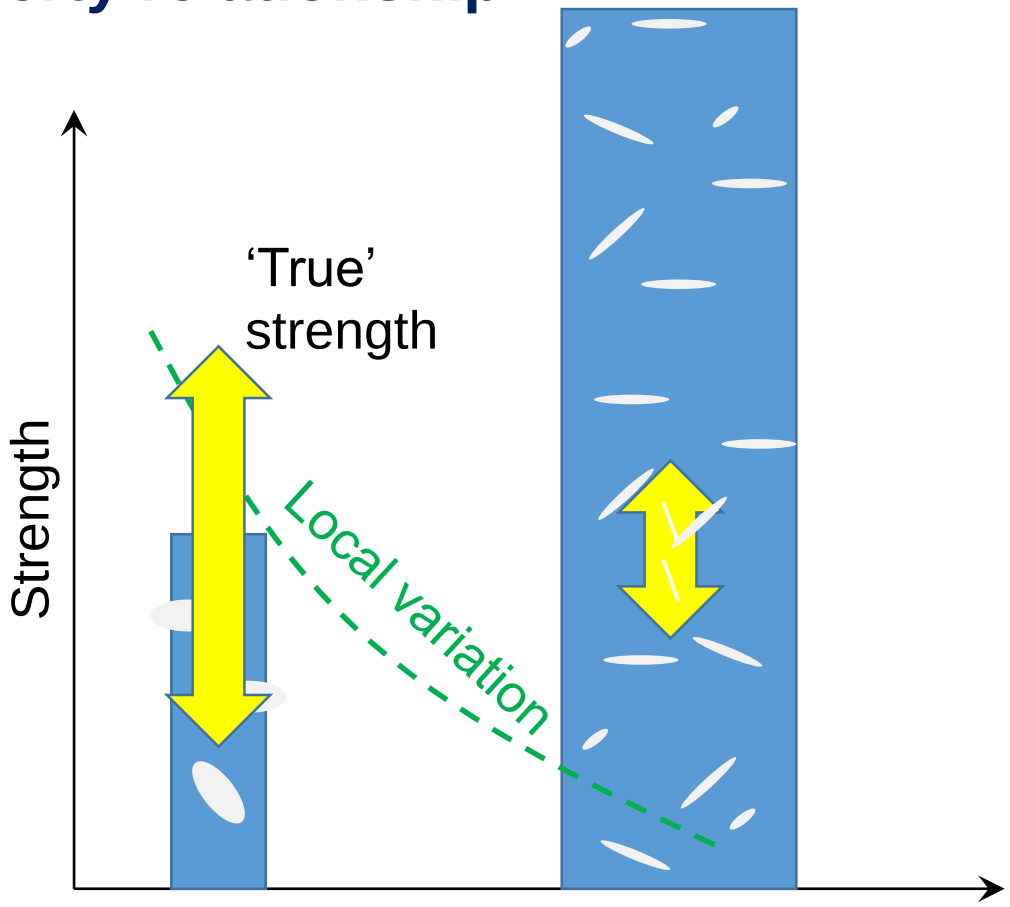


In situ micro-mechanical testing provides first hand information

Microstructure – property relationship



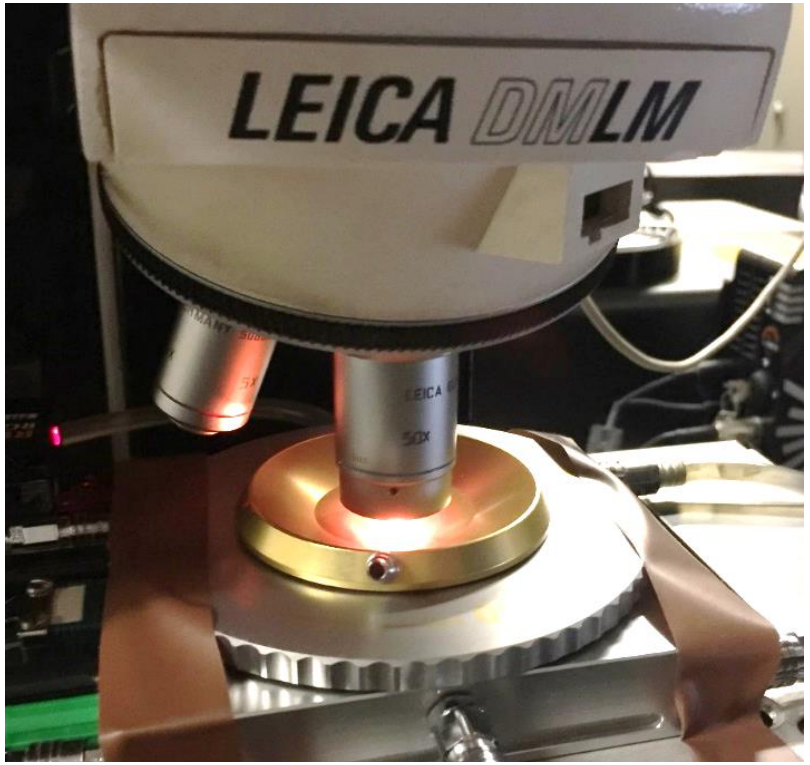
Schematic of the structure

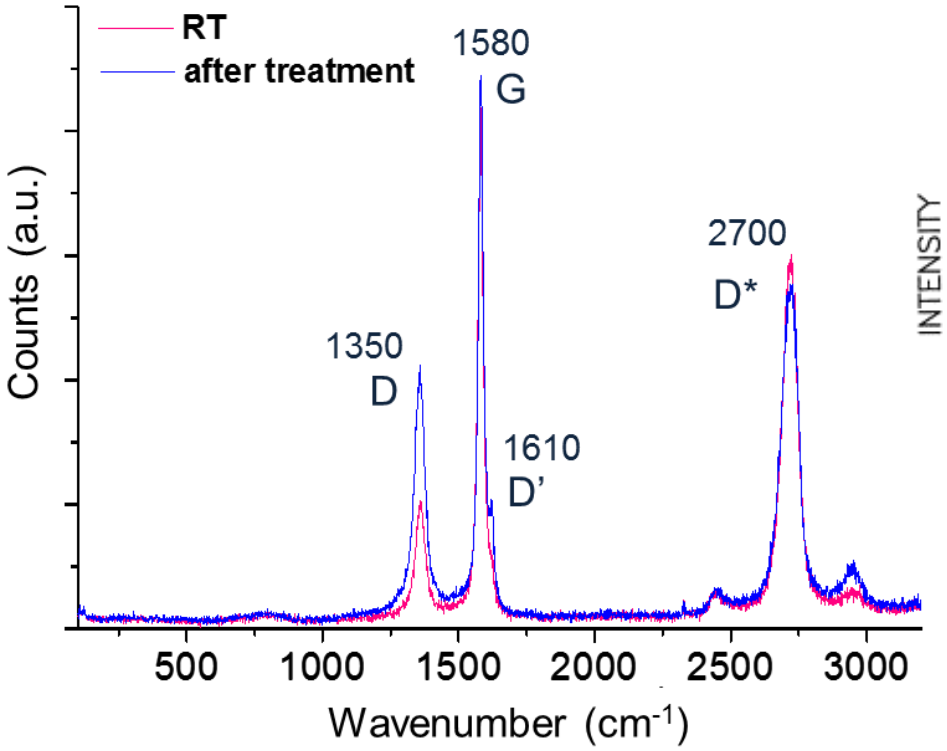


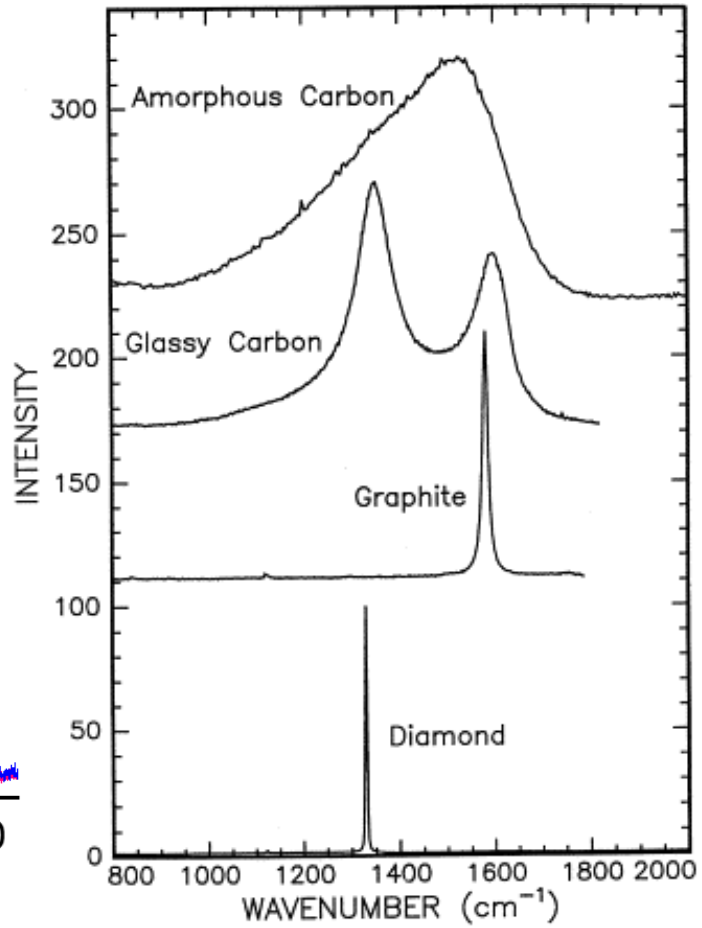
In situ micro-mechanical testing provides first hand information

Raman spectroscopy: Applications

- Detect collective vibration modes of the atoms in the lattice
- App I: Residual stress/strain measurements at RT and at high temperature
- App II: Polarised Raman to measure the preferred orientation of crystals

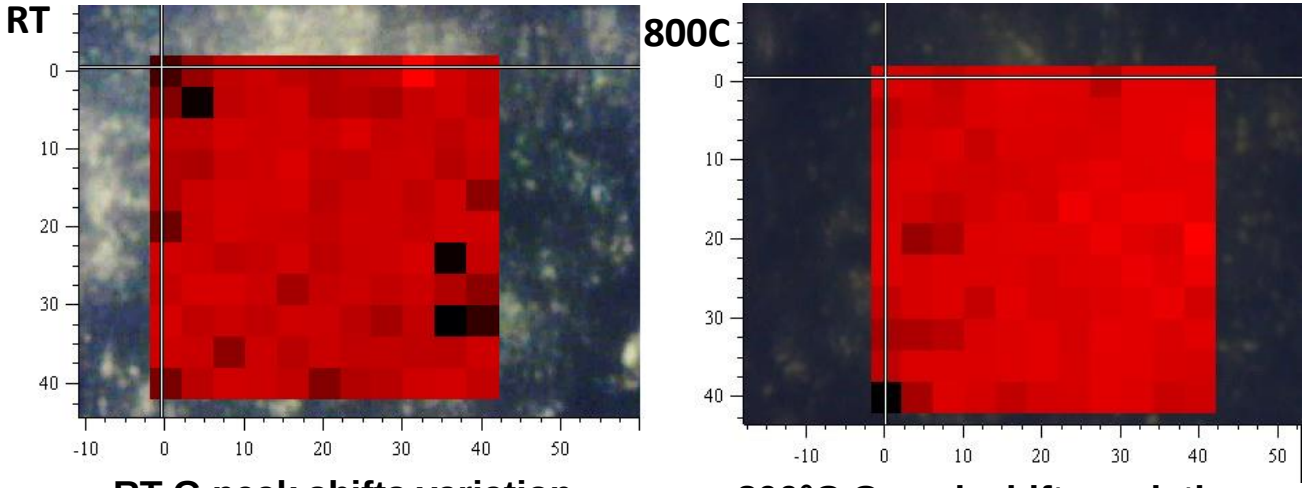


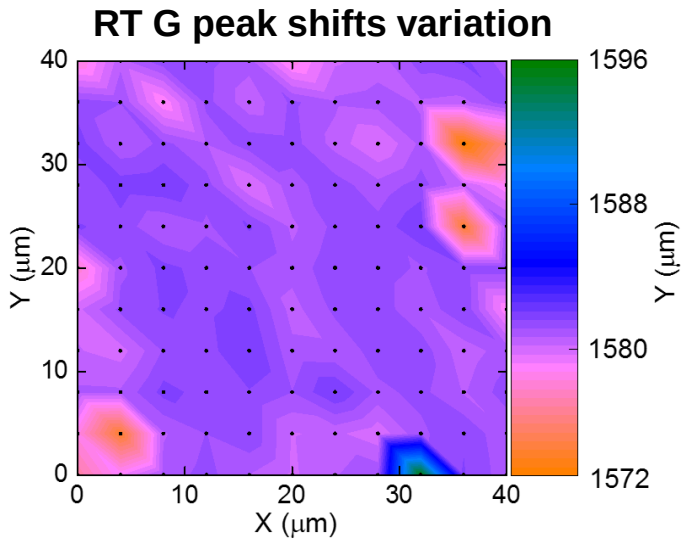


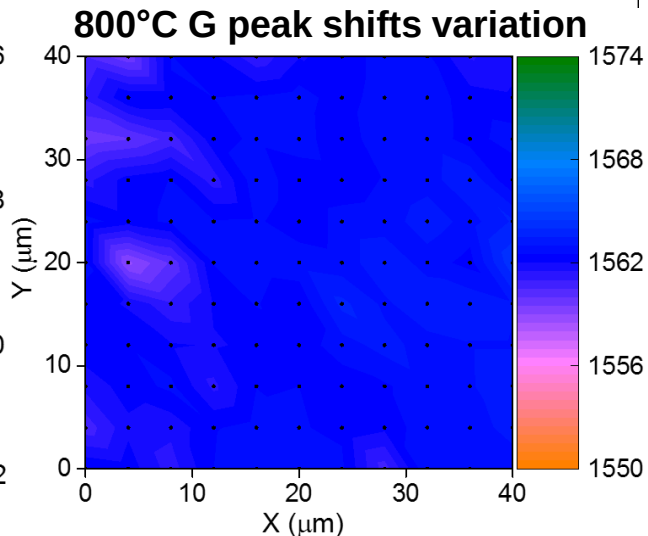


Raman spectroscopy: Residual strain

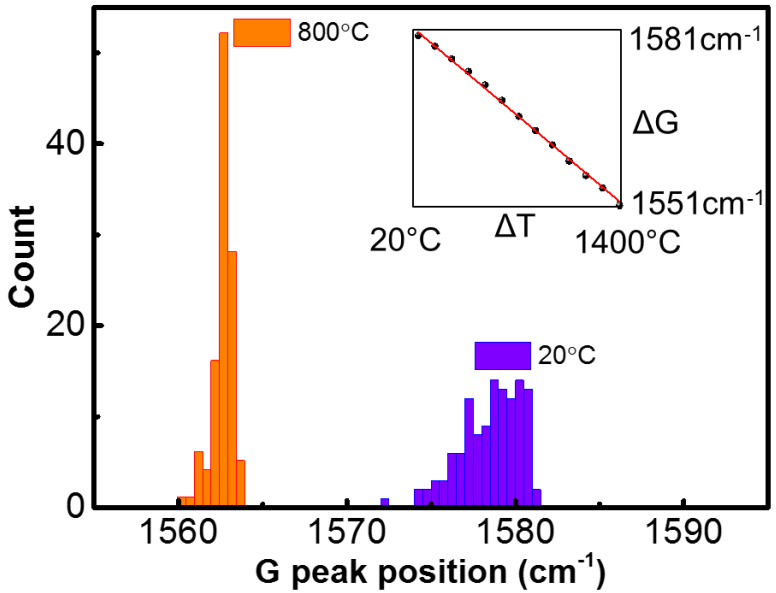
- Residual stress/strain measurements: G peak shifts





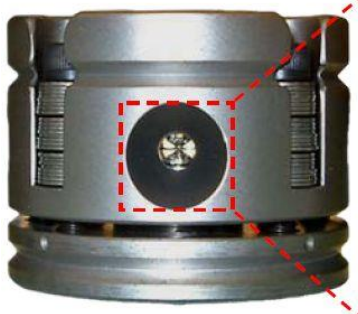


- G peak position change – local strain
- At 800°C, the histogram distribution of the 121 measurements appear narrower in the map
- Residual stress in the material is relaxed when heated up, and this will affect the mechanical behaviour of graphite in service at high temperature

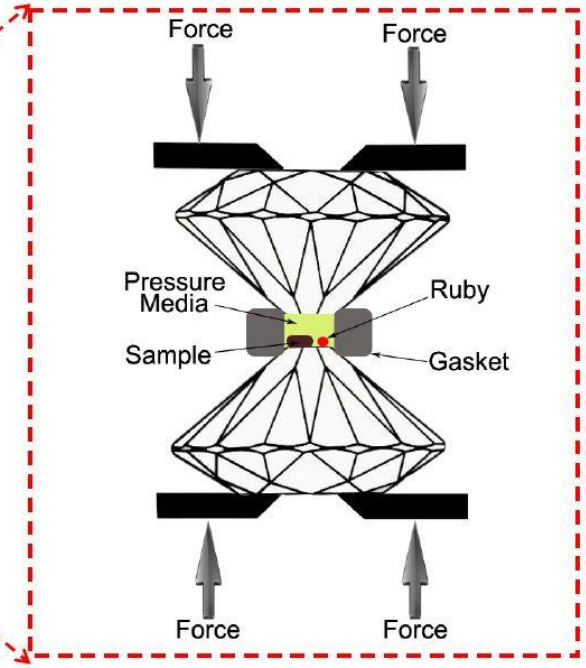


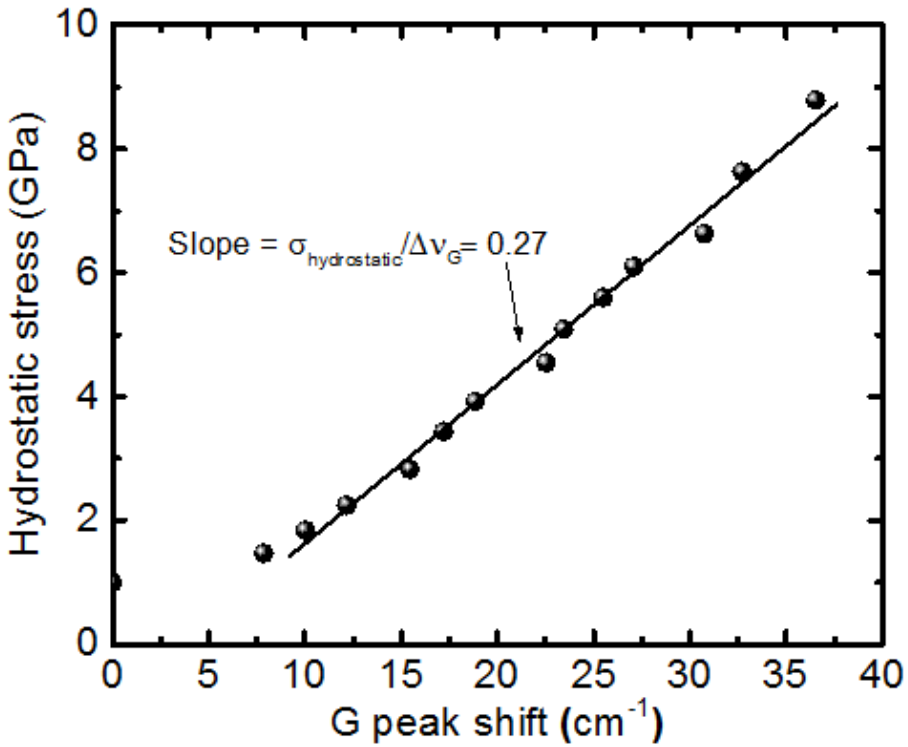
Raman spectroscopy: Quantify the residual stress

Diamond Anvil Cell



Yang et al, Nanowires – Fundamental Research, Chapter 23, 2011



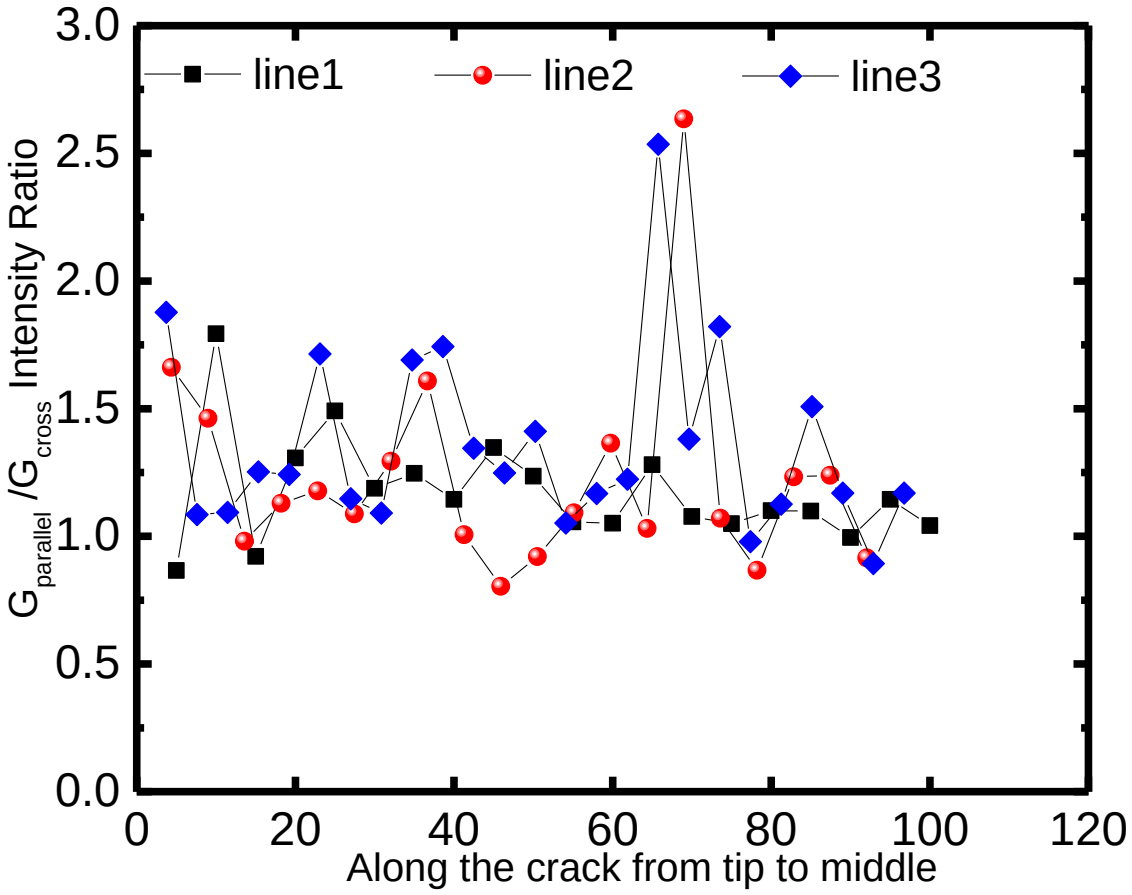


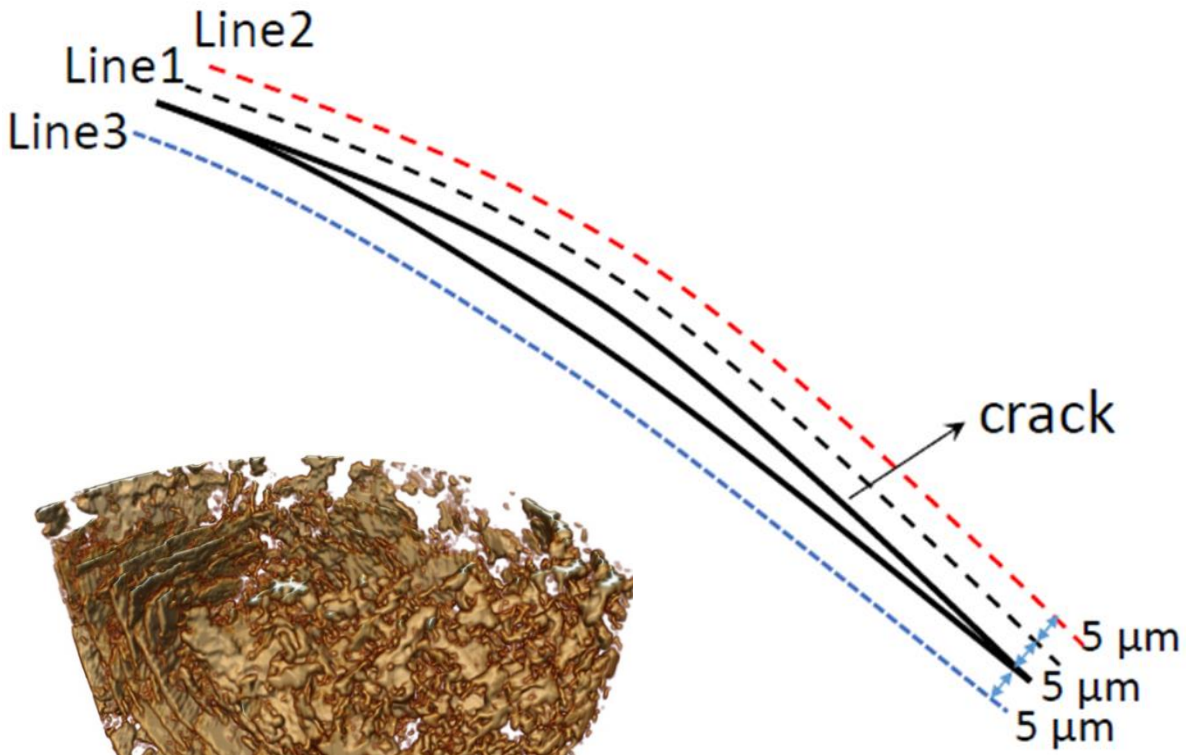
HT Standard deviation	RT Standard deviation	Change between HT and RT	Equivalent hydrostatic compressive stress MPa
0.62	1.93	1.31	**235.01**
0.69	2.02	1.32	**237.44**
0.85	1.99	1.15	**205.40**

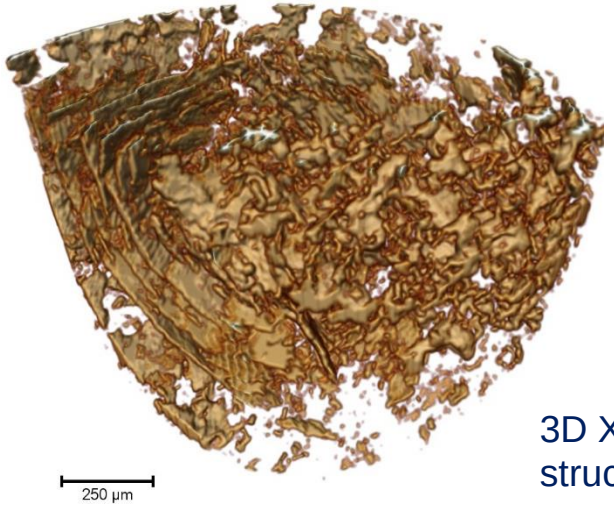
- Graphite sample of the size of tens of microns;
- DAC was used to apply pressure on the sample;
- Ruby grains to give indication of the stress while the Raman spectra of the graphite is monitored;

Raman spectroscopy: Polarisation and preferred orientation

- Measurements along a crack

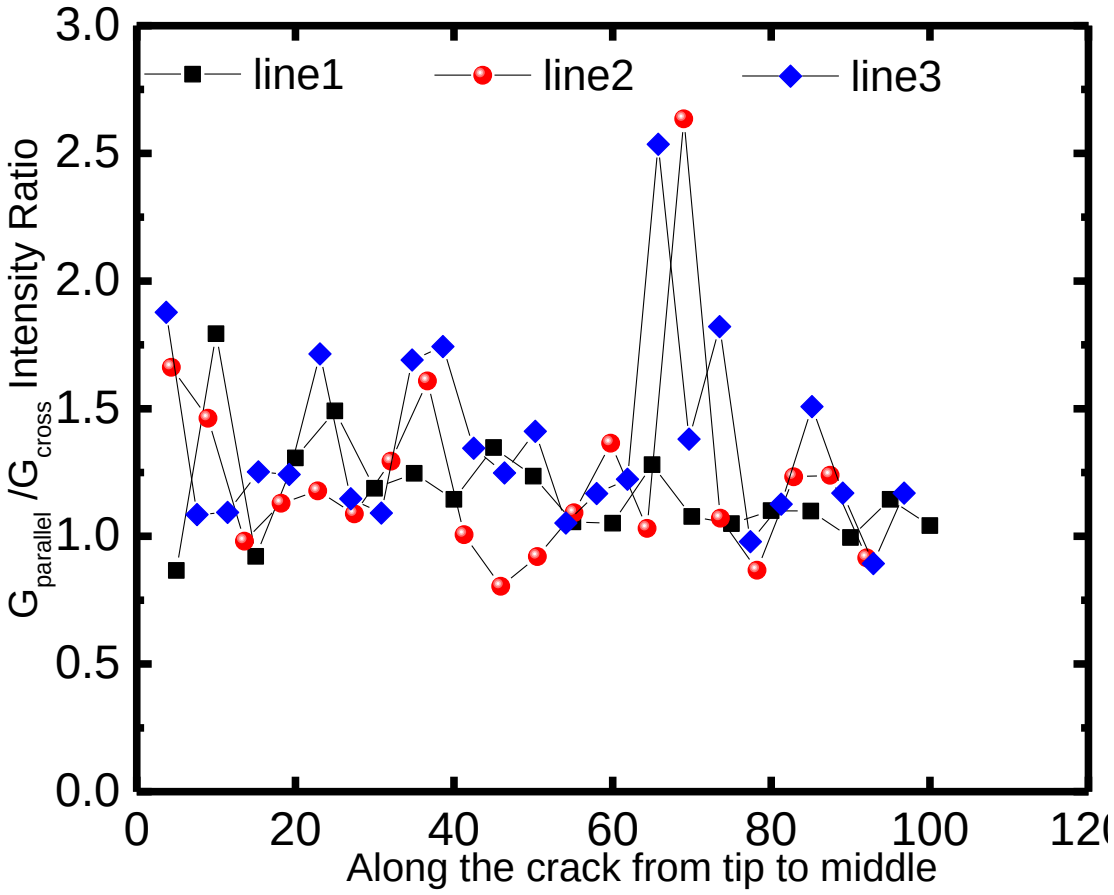


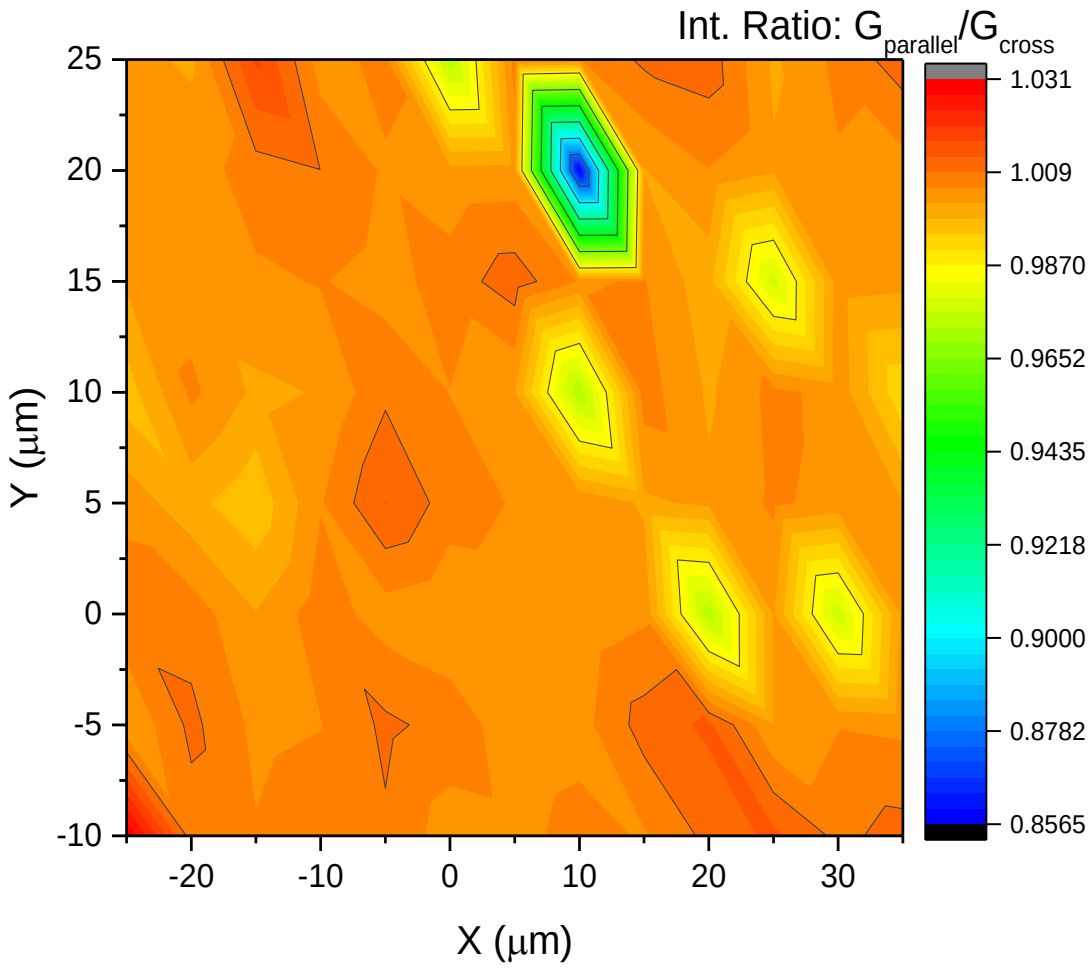




3D X-ray tomography of the pore structure inside a filler particle

Raman spectroscopy: Polarisation and preferred orientation





Key Messages

- A *in situ* micro-mechanical test approach has been developed and successfully applied to a range of carbon and graphite materials to measure the ‘true’ local properties for multi-scale modelling input and to explore the microstructure-property relationship
- Raman spectroscopy is a powerful tool for residual stress/strain measurements in carbon/graphite based material and polarization provides information on the preferred orientation of local crystals in polycrystalline graphite
- A range of techniques have been used to study the microstructure and properties of various graphites, from micro-scale to macro-scale, from unirradiated to a range of radiation conditions, from room temperature to high temperatures

Acknowledgements

EPSRC grant: EP/J019891/1;
EPSRC fellowship grant: EP/N004493/1;
Royal Commission for the Exhibition of 1851 Research Fellowship scheme;

Collaborators:

Lawrence Berkeley National Laboratory, USA
Prof. Robert Ritchie
Idaho National Laboratory, USA
Dr. Joshua Kane, Dr. William Windes
Centre for Device Thermography and Reliability, Bristol, UK
Prof. Martin Kuball, Dr. James Pomeroy, Ms. Maire Power
Interface Analysis Centre, Bristol, UK
Prof. Peter Flewitt
Earth Sciences, University of Bristol, UK
Dr. Oliver Lord
National Physical Laboratory, UK
Dr. Ken Mingard, Dr. Mark Gee
Oxford Materials, UK
Prof. James Marrow