# WORKSHOP ON GRAPHITE RESEARCH

# UK and European Research Activities

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# Overview

- European Nuclear Graphite Research Initiatives
- UK Specific Nuclear Graphite Research
- Nuclear Graphite Research at Manchester
- Conclusions

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# Nuclear Graphite Research in Europe

- The main drivers for nuclear graphite research in Europe are:
  - The continued safe operation of the UK AGRs and remaining Magnox reactors, including the possibility of life extension
  - The European Framework Programmes FP5, FP6, FP7
    - RAPHAEL
    - CARBOWASTE
  - The decommissioning and waste disposal of irradiated graphite waste from graphite moderated reactors (including operational waste) in the UK, France, Lithuania, Italy, Spain and Germany
- Depending on the definition of Europe there are operating RBMK reactors in Western Russia and Lithuania as well as shutdown RBMK reactors in the Ukraine
  - These activities also have issues of continued safe operation and final decommissioning and waste disposal

# RAPHAEL-IP

- RAPHAEL-IP
  - ReActor for Process heat, Hydrogen And ELectricity generation
- European Commission's 6th Euratom Framework Programme
  - support research co-operation and integration of research efforts in the nuclear fission and fusion area
  - April 2005 – April 2009
- 33 Partners or organisations
  - 10 countries
    - Belgium, Czech Republic, France, Germany, Italy, The Netherlands, Slovak Republic, Spain, Switzerland, UK

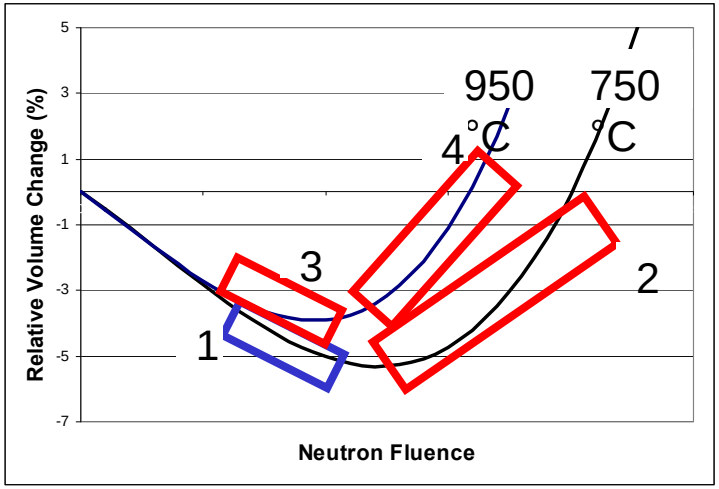
# RAPHAEL-IP

- 8 Sub-projects
  - coupled reactor physics and core thermo-fluid dynamics (SP CP)
  - fuel technology (SP FT)
  - back-end fuel technology (SP BF)
  - materials development (SP ML)
  - component development (SP CT)
  - safety (SP ST)
  - system integration (SP SI)
  - project management (SP PM)

- Materials development (SP ML)
  - 4 work packages
    - vessel materials (WP-ML1)
    - high temperature materials (WP-ML2)
    - graphite materials (WP-ML3)
    - codes and standards for graphites and composites (WP-ML4)

# RAPHAEL-IP

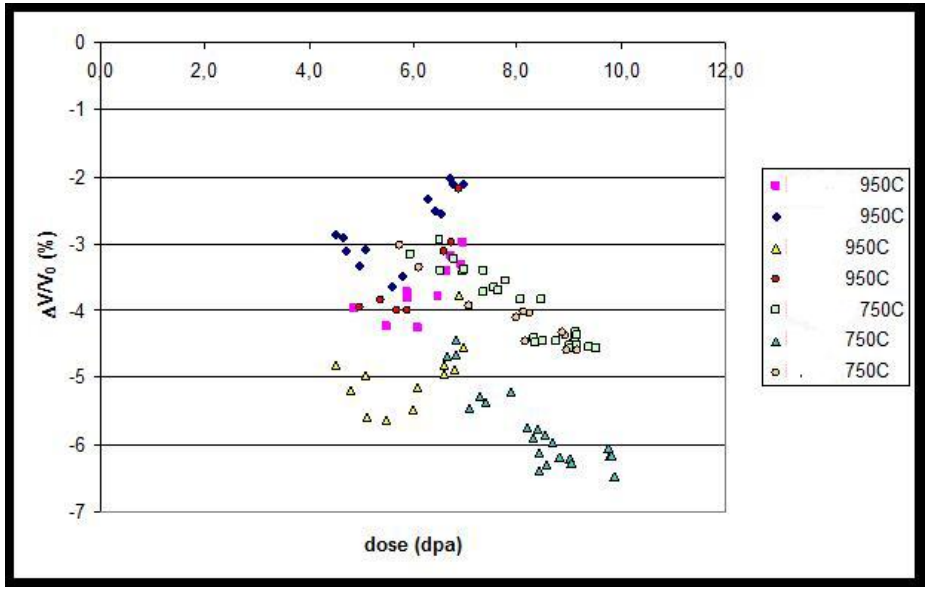
- Graphite materials (WP-ML3)
  - 4 tasks
    - continuation of 750ºC irradiation tests (Task 1)
    - graphite irradiation test at higher temperatures (Task 2)
    - corrosion and heat-up tests (Task 3)
    - graphite modelling (Task 4)
  - 8 partners
    - University of Manchester (UK), NRG (The Netherlands), AMEC (UK), FZJ (Germany), Framatome ANP (France), CEA (France), SGL Carbon (Germany), UCAR (France)
  - 2 observers
    - NRI Rez (Czech Republic), Paul Scherer Institut (Switzerland)




| | |
|---|---|
| INNOGRAPH-1A: (FP5) | 750°C, low/medium dose |
| INNOGRAPH-1B: | 750°C, high dose |
| INNOGRAPH-2A: | 950°C, low/medium dose |
| INNOGRAPH-2B: | 950°C, high dose |

# RAPHAEL-IP

- Codes and standards (WP-ML4)
  - 7 partners
    - NNC (UK), JRC (The Netherlands), Framatome ANP (France), Framatome ANP (Germany), EA (Spain), SGL Carbon (Germany), UCAR (France)




**750°C and 950°C Turnaround**

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# Carbowaste EU FP7

- Aims to develop a solution for integrated irradiated graphite waste management through investigation of:
  - The nature of the contamination (how it is contained within the graphite? What are its release mechanisms?)
  - The mobility and immobility of the various species within the graphite
  - Seek opportunities for safe and fit for purpose disposal solutions
  - Assist predictability of long-term disposal performance
  - Develop opportunities for more economic solutions for legacy waste and future use of the material.
  - Investigate recycling possibilities
- Membership: 28 partners, from the UK, France, Germany, Italy, Spain, Lithuania, Belgium Romania, the Netherlands, Sweden and South Africa
- Funding Total Funding 12,081,363€ (6,000,000€ EU)
  - Manchester **Funding 623,062 € (470,833 € EU)**

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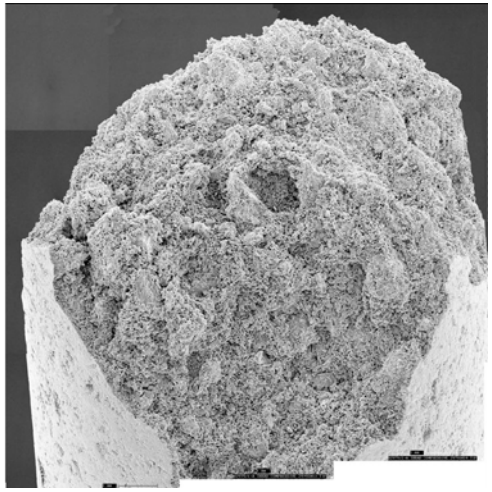
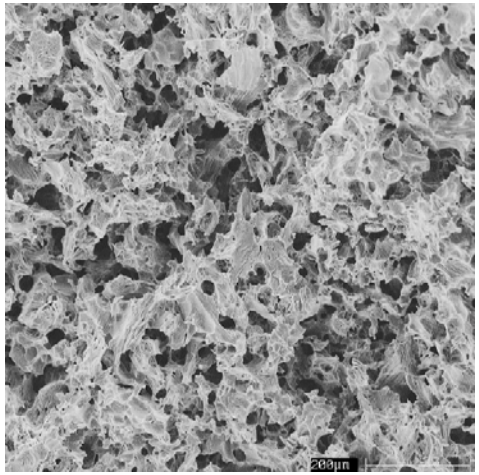
# Some Examples of Nuclear Graphite Research in the UK

**Licensees AGR and Magnox reactors**

- Statistical analysis – prediction of brick cracking rates
- Graphite irradiation Data
  - Development of semi-empirical models for use in graphite component structural integrity assessments including irradiation creep
- Statistical analysis of reactor installed and trepanned data of component dimensional change, weight loss and property changes for use in structural integrity assessments
- Whole core modelling
- Refuelling trace monitoring
- Seismic modelling (numerical analysis and proposed rigs)
- Component life prediction (numerical finite element modelling)





**PGA Graphite ~40% weight loss Magnox North/SERCO**

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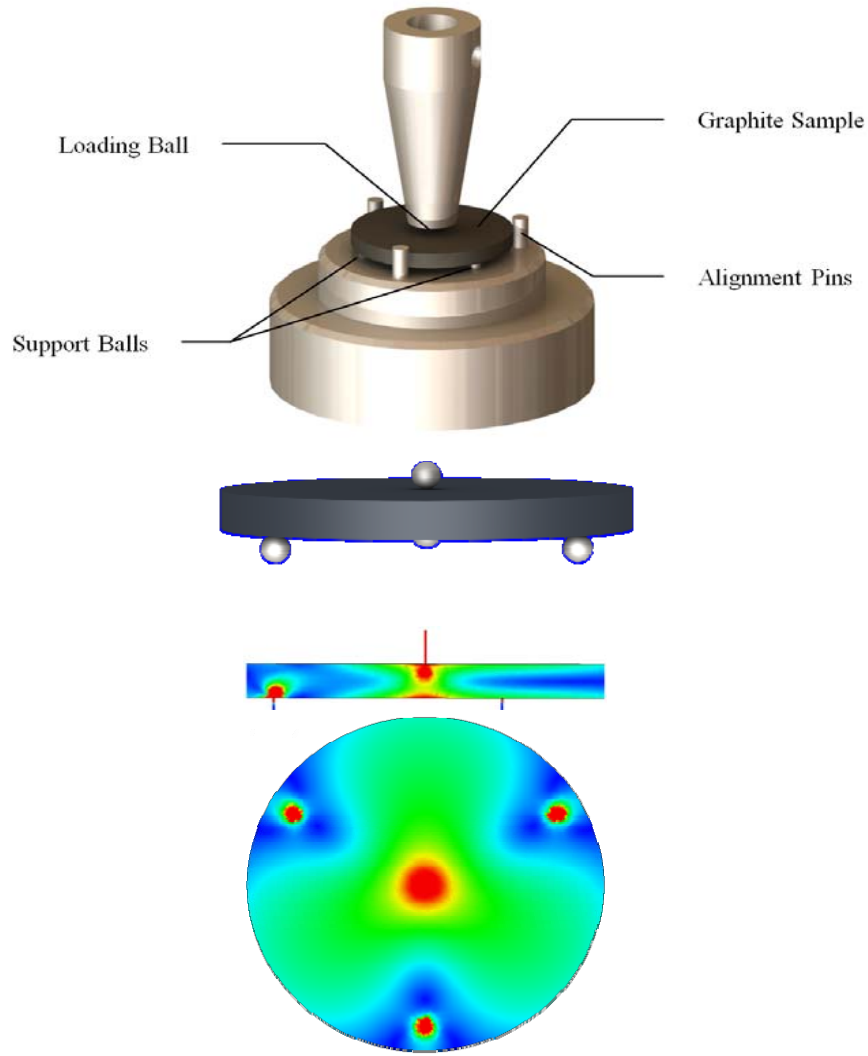
# Some examples of Nuclear Graphite Research in the UK

**Licensees AGR and Magnox reactors**

- Inspection methods (crack detection using eddy currents)
- AGR Gilsocarbon graphite property MTR programme
- Possible AGR Gilsocarbon graphite irradiation creep MTR programme
- Microstructural – property investigation in highly oxidised (~40% weight loss) Magnox PGA graphite
- Improved methods of property measurement, particular Young's modulus and Poisson's ratio.
- Biaxial testing of graphite strength
- Atomistic modelling of defects in irradiated graphite

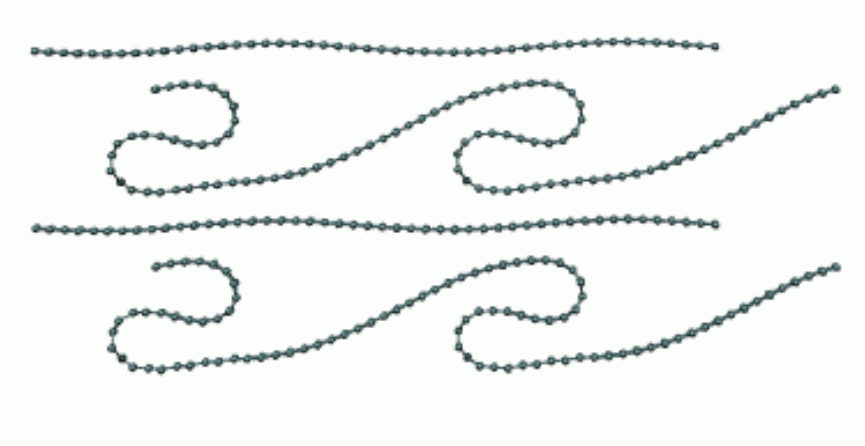



**Biaxial testing due to Gareth Neighbour University of Hull**

# Research Contractors to the UK Licensees

- AMEC Nuclear
- Atkins
- British Energy Generation Ltd (EDF)
- Doosan Babcock
- Frazer-Nash Consultancy Ltd
- Jacobs Engineering UK Ltd
- Magnox North
- Magnox South
- National Nuclear Laboratory (NNL)
- NRG Petten
- Nuclear Decommissioning Authority (NDA)
- Nuclear Technology Consultancy
- Quintessa Limited
- Serco
- University of Birmingham
- University of Bristol
- University of Glasgow
- University of Hull
- University of Manchester
- University of Strathclyde
- University of Sussex

**One quarter size rig of AGR core AMEC**



**Malcolm Heggie (University of Sussex)**
**Atomistic Modelling**

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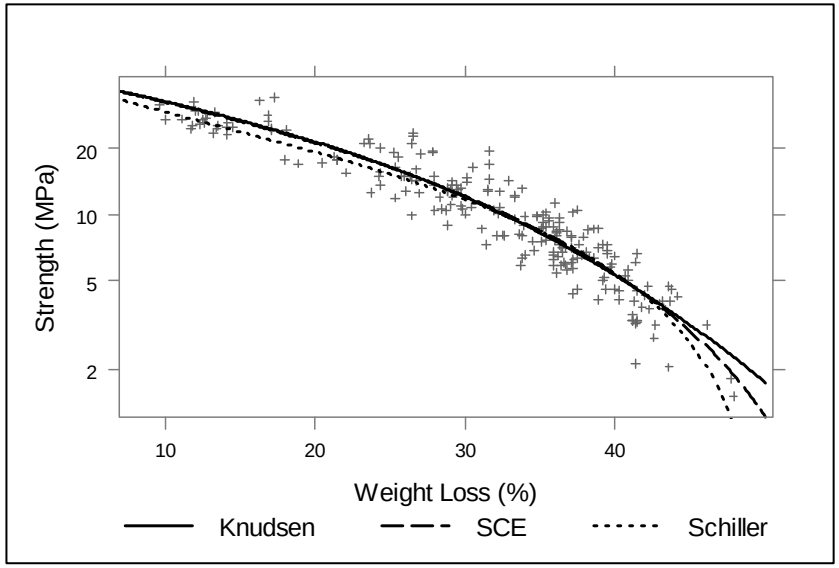
# HSE(ND)
# Independent Nuclear Research

- The Graphite Technical Assessment Group (GTA)
  - Hosted by the University of Manchester
- Statistical assessment of irradiated graphite properties
  - The University of Manchester and Models and Computing Services (Ernie Eason)
- Fracture in graphite
  - The University of Birmingham
- AGR Brick cracking network
  - The University of Manchester
  - The University of Birmingham
  - The Health and Safety Laboratory (HSL)
- Development of Whole Core Models
  - The University of Manchester




**High weight loss strength data showing evidence "percolation limit"**

**Due to HSL/HSE**

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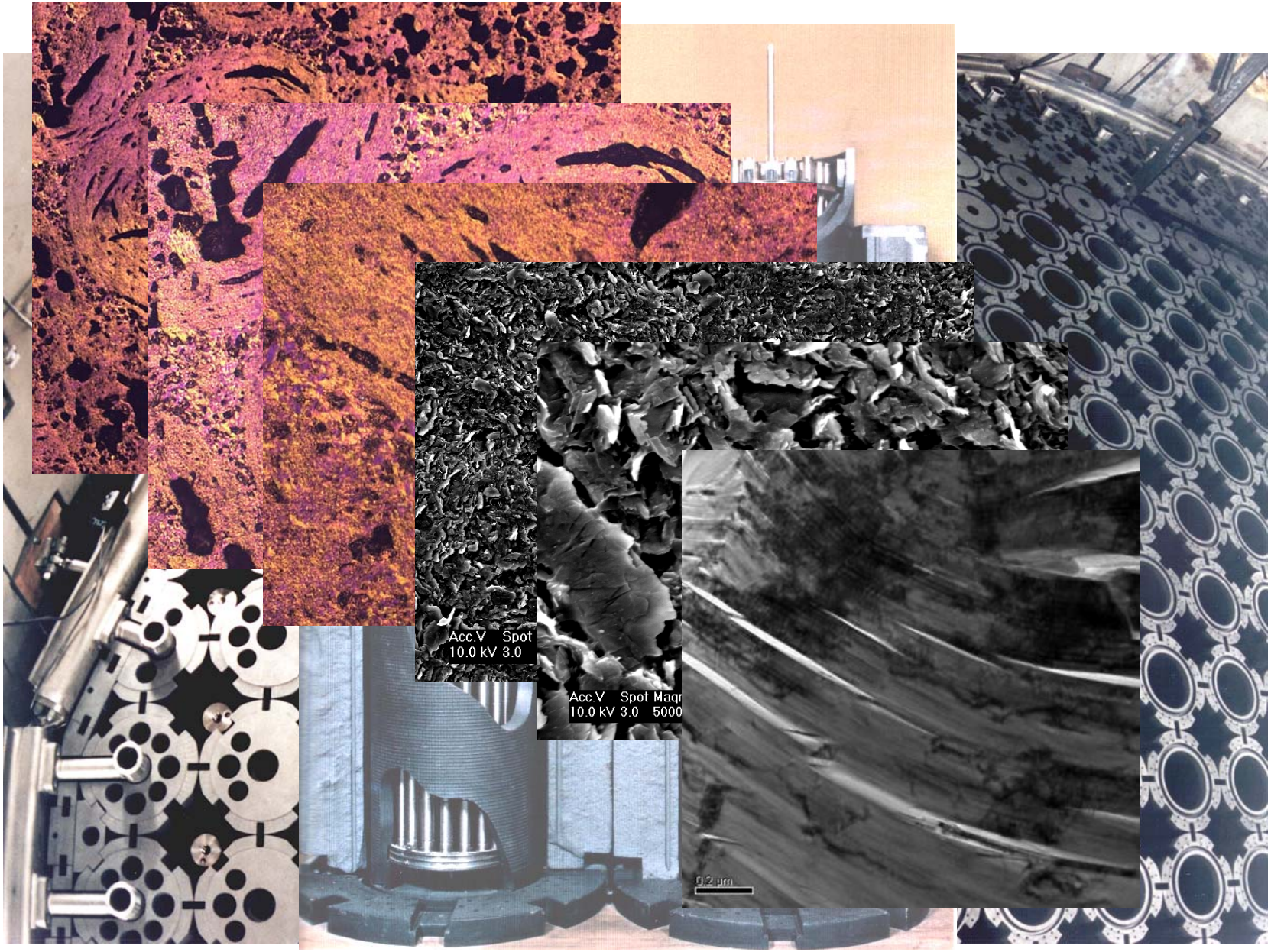

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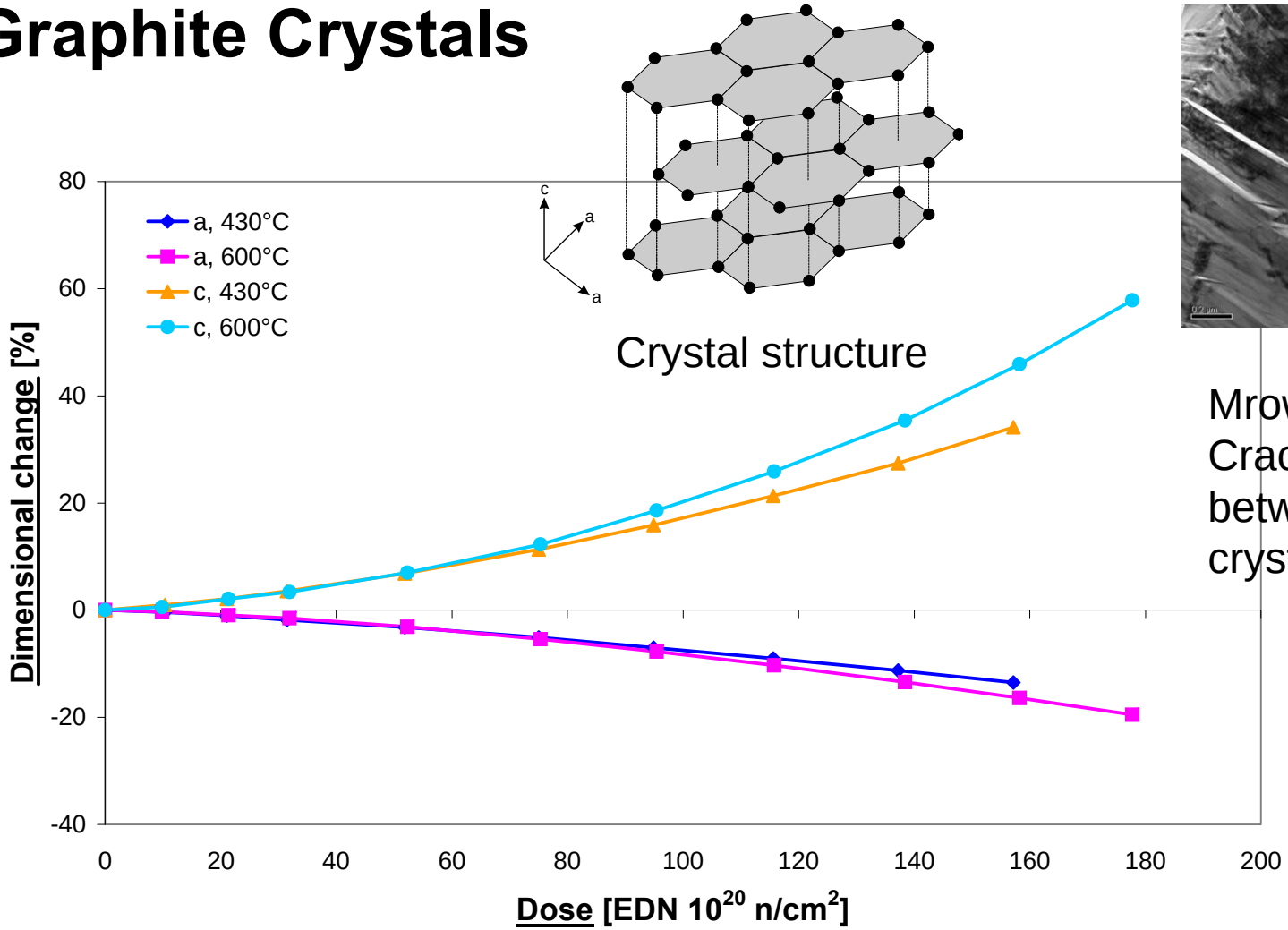
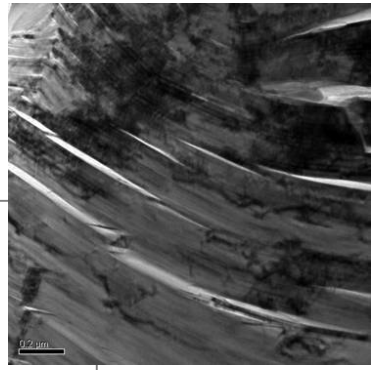
# Irradiation Induced Dimensional Changes in Graphite Crystals







Crystal structure



Mrowozski Cracks between crystallites

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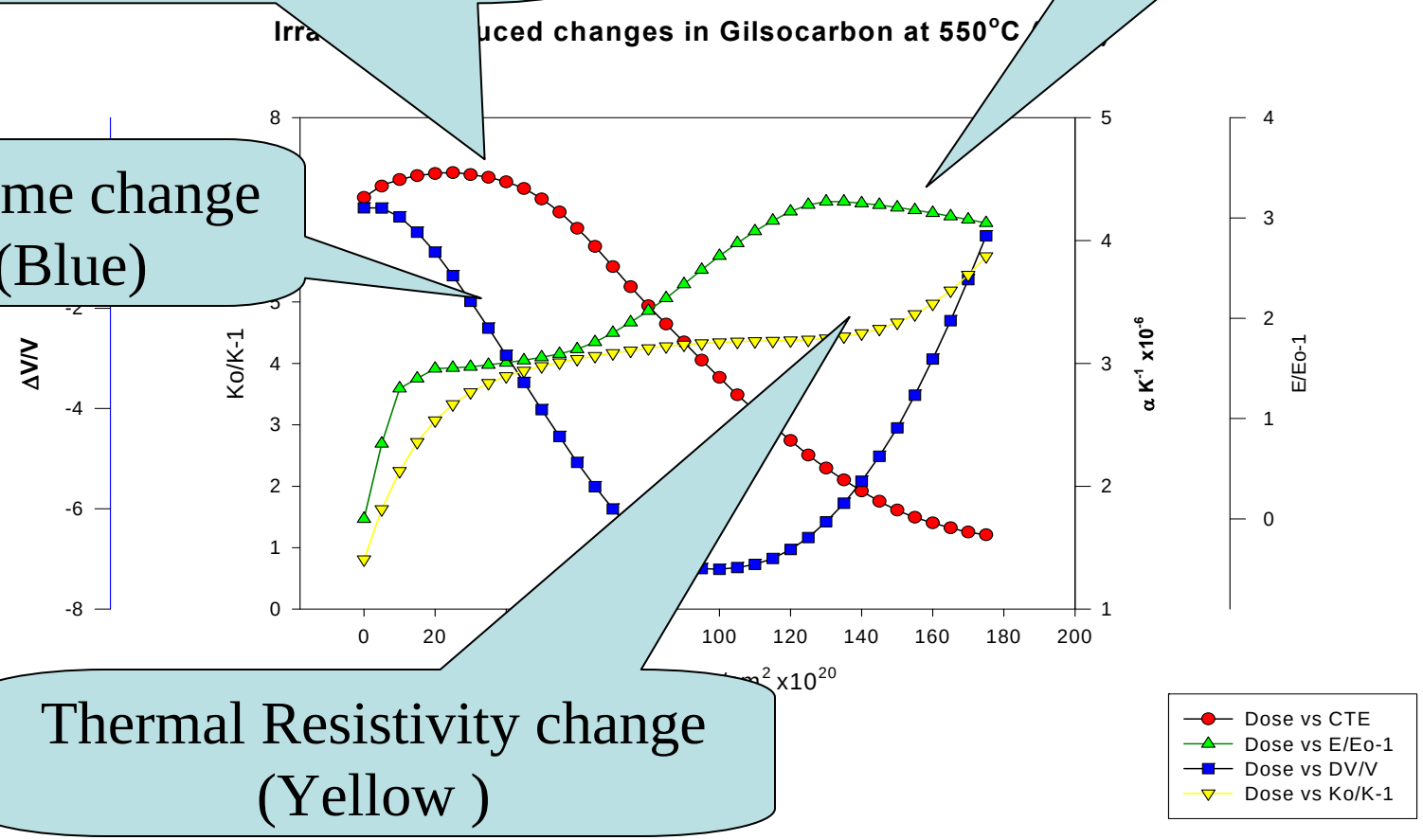
# Graphite Irradiation Behaviour – Observed Bulk Graphite Property Changes

Coefficient of Thermal Expansion change (Red)

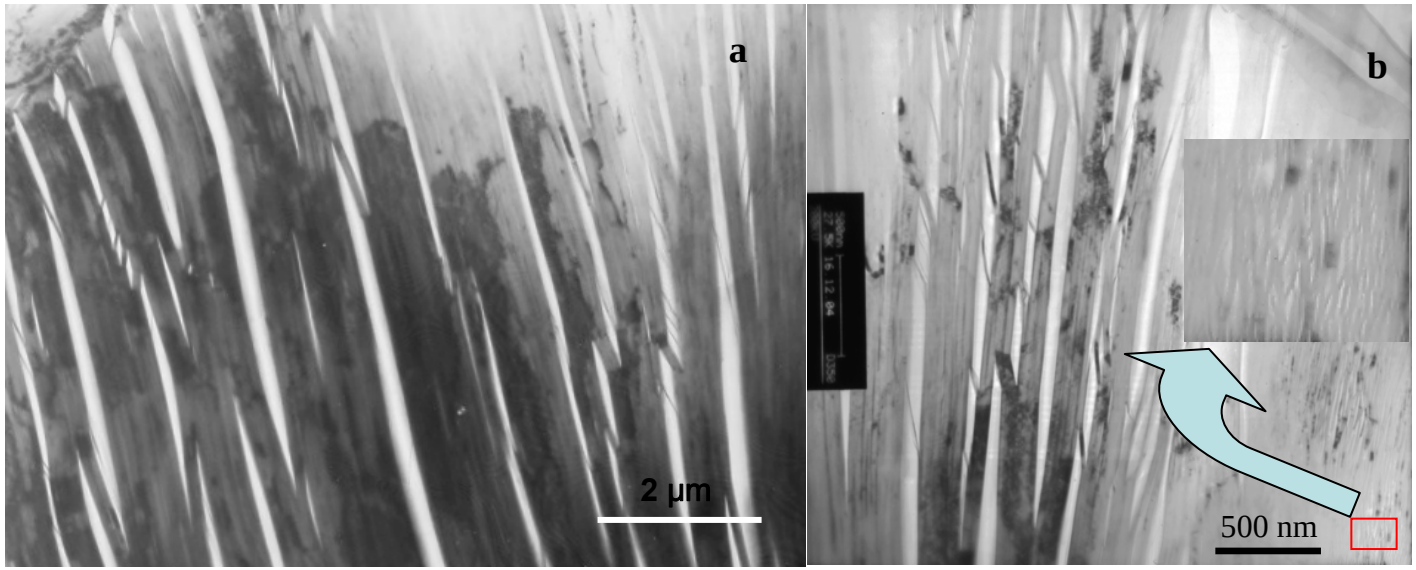
Young's modulus change (Green)

Volume change (Blue)

Thermal Resistivity change (Yellow )



# Study of the influence of micro-cracks on the behaviour of nuclear graphite




- TEM images of Mrozowski cracks in Pile Grade A Graphite
- Mrozowski cracks have an important role in determining both the unirradiated and irradiated the properties nuclear graphite
- Microcracks were formed by cleavage along basal plane during graphitisation
- The length of the cracks varies from tens of nanometres to more than 10 mm
- The width of the cracks varies from less than 50 nm to ~200 nm.
- The very fine crystallites and cracks in the inset of the figure on the left may be in the binder.

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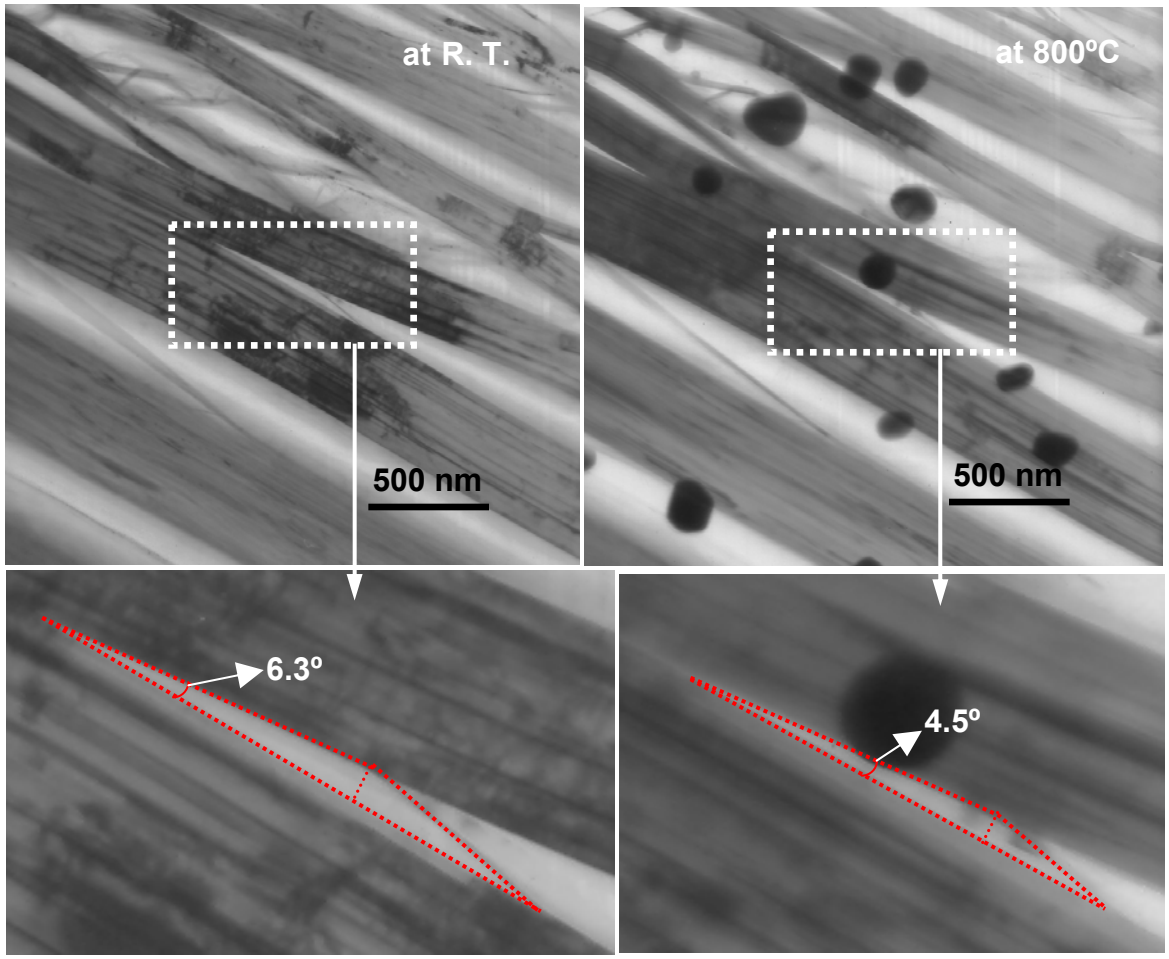
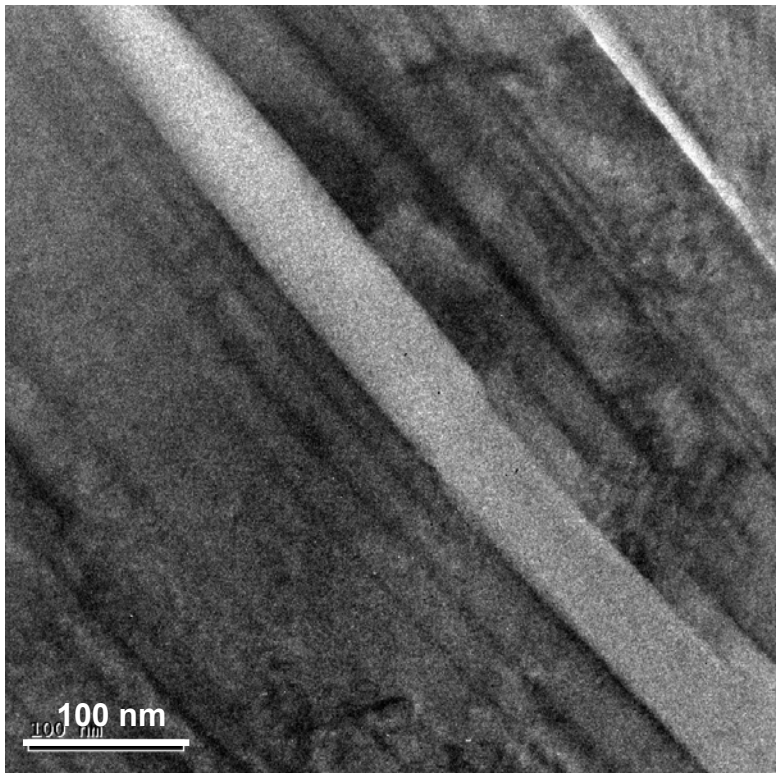
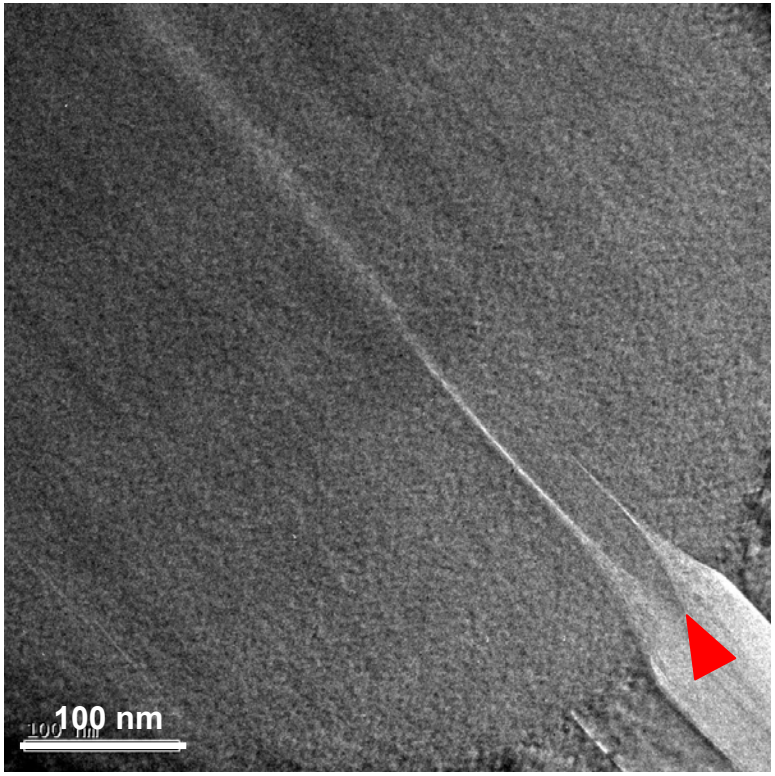
# **Results:** in situ heating




Upon heating, a gradual closure of cracks is observed because of the thermal expansion of the graphite crystallites surrounding the cracks.

# **Results:** in situ electron irradiation




Closure of a crack in Gilsocarbon after In-situ electron irradiation.

The feature with bright contrast does not disappear completely.

Note a small part of crack (indicated by arrow), which was covered by the electron beam has not closed completely..

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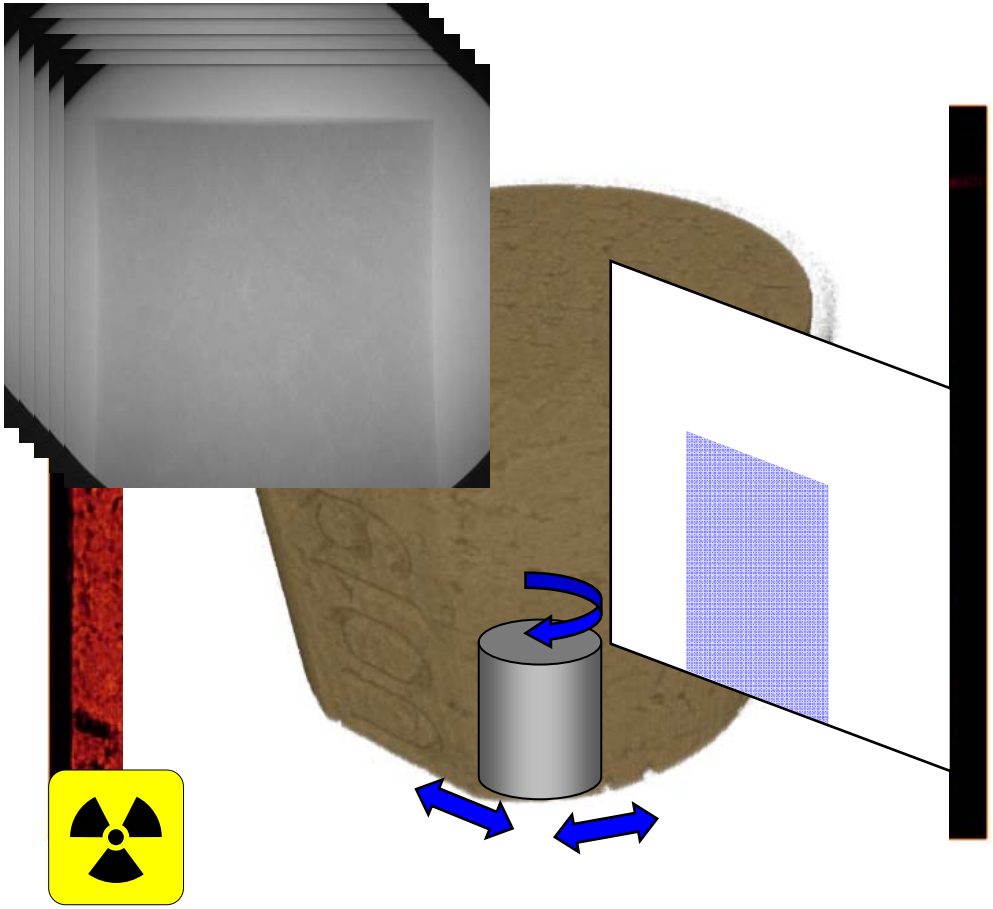
# Characterisation and modelling of microstructure heterogeneity in nuclear graphite

- Synchrotron tomography
  - Non-destructive
  - 3D microstructure
  - Technique
    - sample
    - X-ray source
    - detector
    - reconstruction



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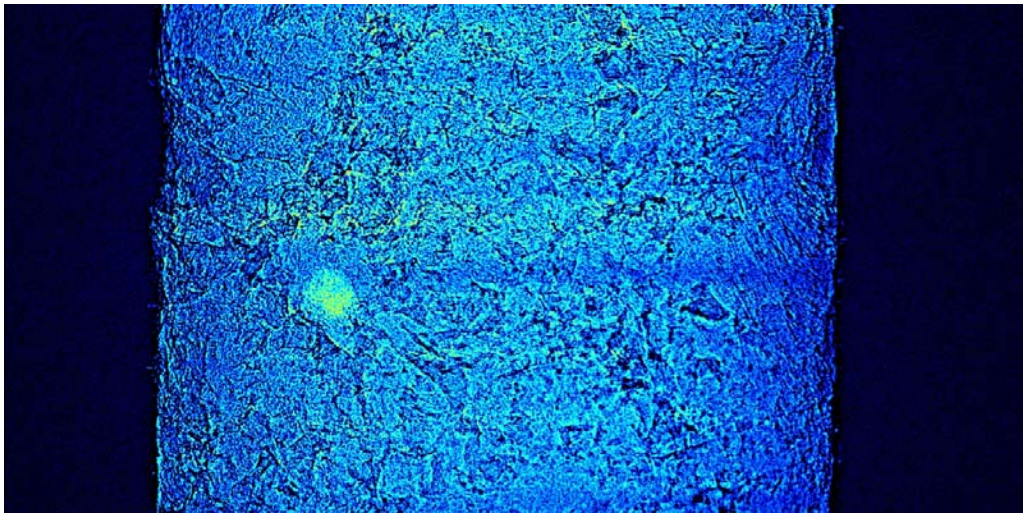
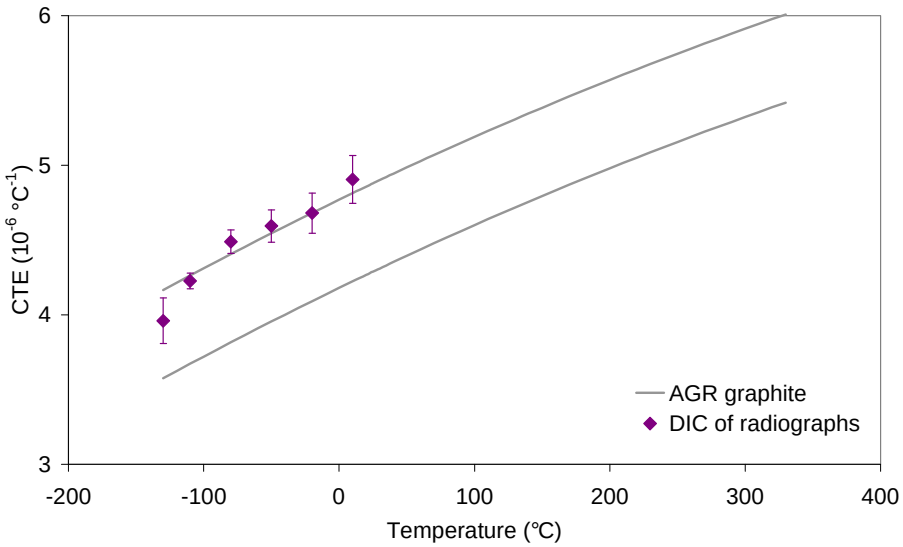
# Synchrotron tomography

- Swiss Light Source (SLS)
  - Paul Scherrer Institut, Villigen
- TOMCAT beamline
  - TOmographic Microscopy and Coherent rAdiology experimenTs
- Thermal experiments
  - Gilsocarbon samples
    - ø1mm × 2mm region of interest
  - CT scanned at different temperatures
    - 0°C, -30°C, -60°C, -90°C, -120°C, -140°C

# Synchrotron tomography
# Bulk CTE

- Bulk CTE changes
  - radiographs
  - digital image correlation (DIC)
    - DaVis
  - compared well with literature data





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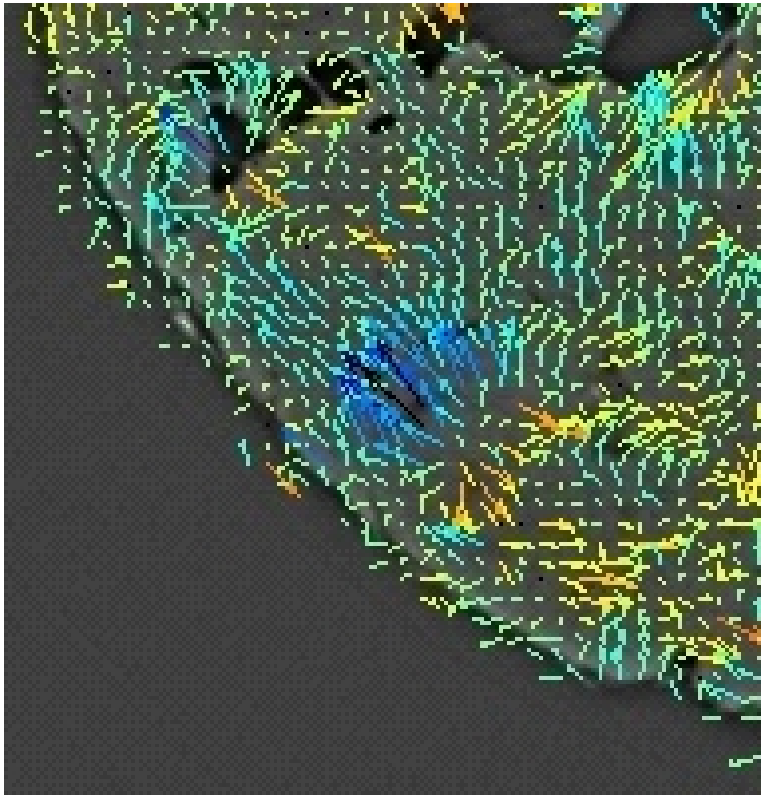
# Synchrotron Tomography Localised CTE

- Local CTE
  - reconstructions
  - regions of well-defined microstructure
  - digital image correlation (DIC)
  - heterogeneity in thermal strains



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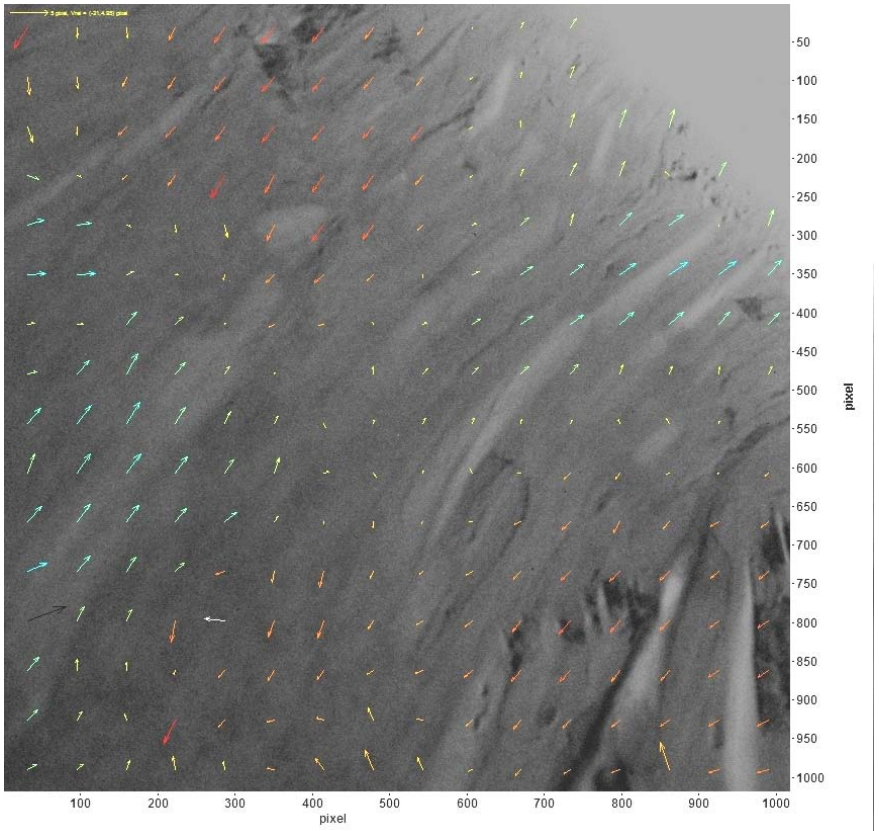
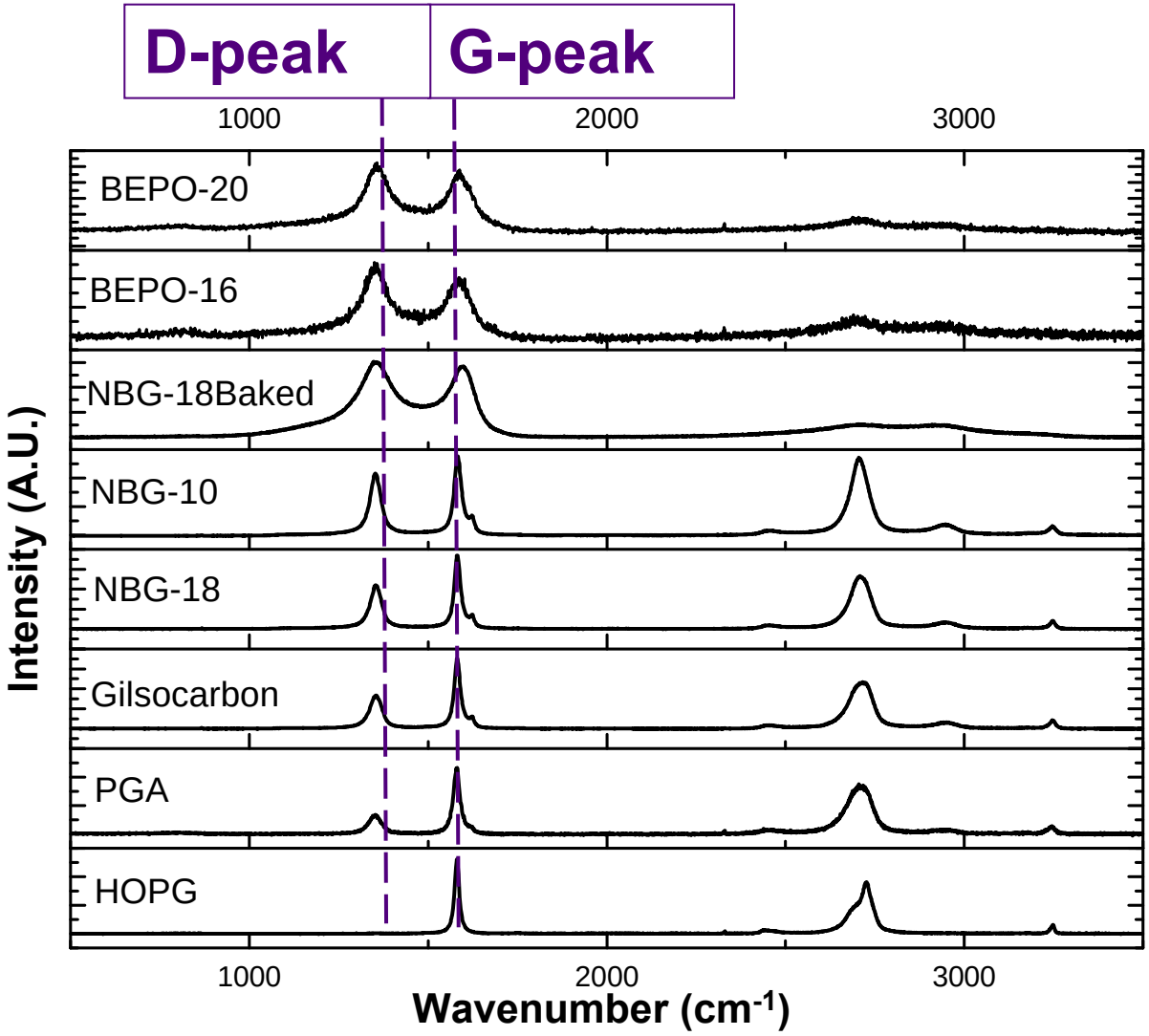
# Transmission electron microscopy - Localised CTE

- Microstructural thermal strain
  - sample heated to 600°C
  - closure of Mrozowski cracks
  - directionality
    - Digital Image Correlation (DIC)
  - local CTE (non-cracked)
    - $11.7 \times 10^{-6}$ $K^{-1}$
  - local CTE (cracked)
    - *c*-axis $34 \times 10^{-6}$ $K^{-1}$
    - *a*-axis $-0.5 \times 10^{-6}$ $K^{-1}$




**400-500°C**

# Raman Spectroscopy – structural characterisation, phase purity and crystallite size.




- Raman scattering measurements were performed using a Renishaw inVia Raman microscope using an Argon 514.5nm laser.
- G-peak noted at 1580 $cm^{-1}$ indicative of in plane bond stretching of C $sp^2$ atoms.
- D peak noted at 1350 $cm^{-1}$ is the breathing node of $sp^2$ and disordered carbon.

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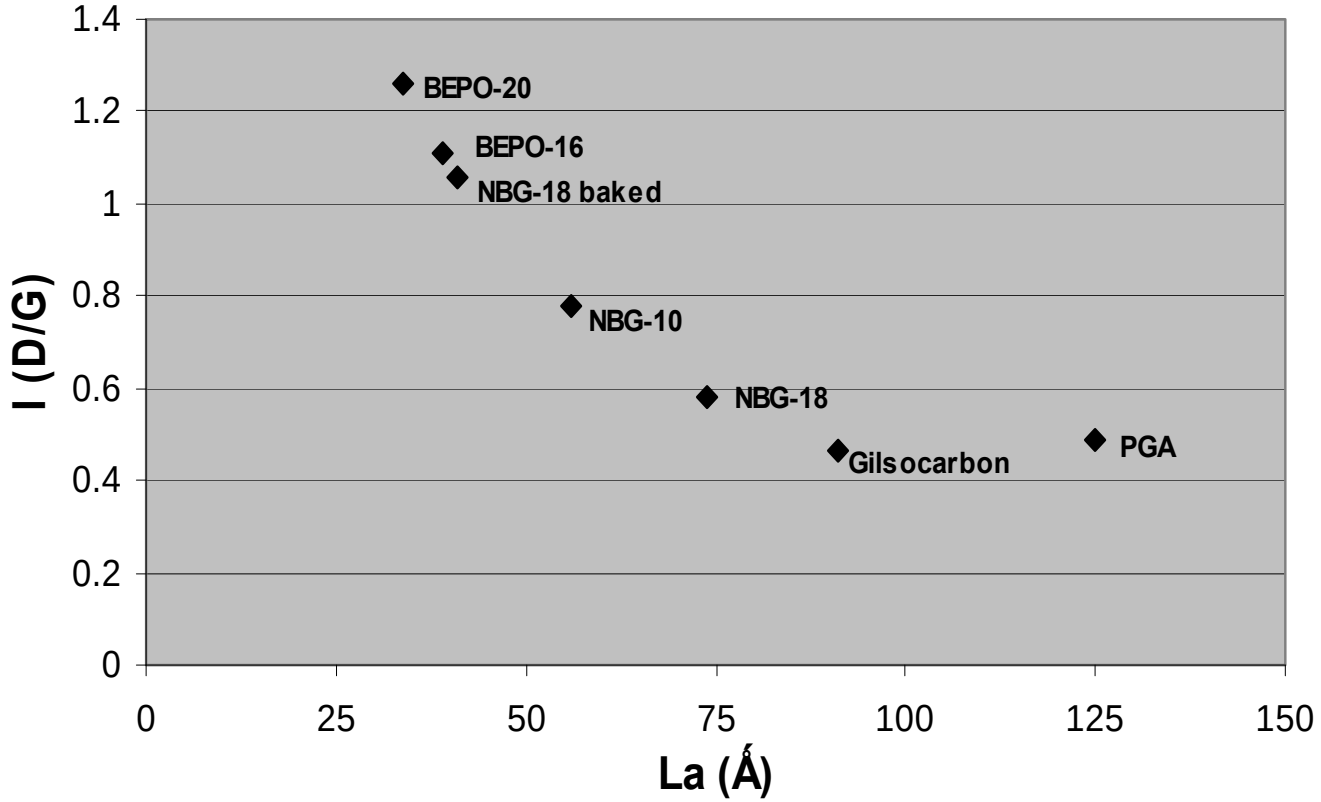
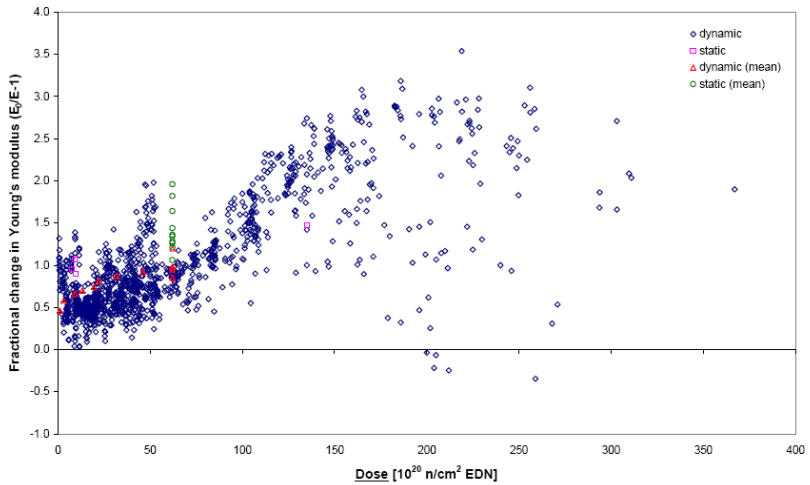
# Raman crystallite size




- I(D)/(G) is an indication of the structural disorder.
- Structural disorder increases a crystallite size decreases.

# Models of Young's Modulus for Gilsocarbon Graphite grades Irradiated in an Inert Environment

- Ernest D. Eason, Modeling & Computing Services LLC Boulder, Colorado USA
- Graham Hall, Barry Marsden, Nuclear Graphite Research Group The University of Manchester
- Funded by HSE(ND)
- Properties being investigated are: dimensional change, CTE, Young's modulus, strength and thermal conductivity
- Later analysis will also include irradiation in an oxidising atmosphere
- Only Young's modulus discuss here
- Database
  - UKAEA MTR data

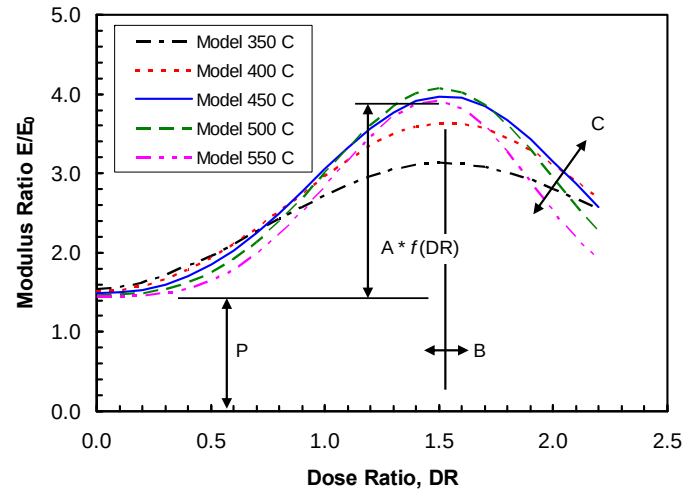



**Young's modulus inert MTR data**

# Inert Model for Young's Modulus

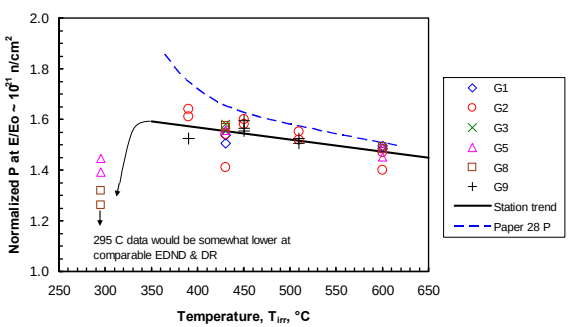
**The model below was fitted to the inert MTR data**

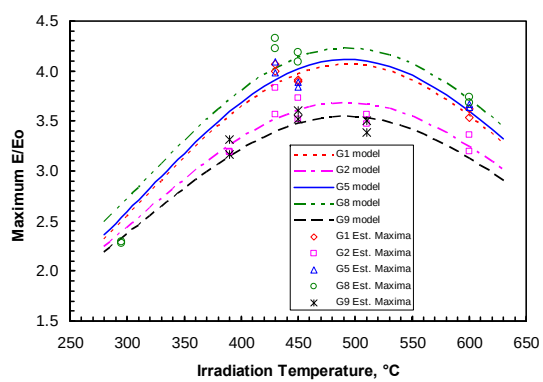
$$\frac{E}{E_0} = P(T_{irr}) + A(T_{irr}) \cdot \left(\frac{DR}{B}\right)^{C-1} \exp\left[-\left(\frac{DR}{B}\right)^{C}\right]$$

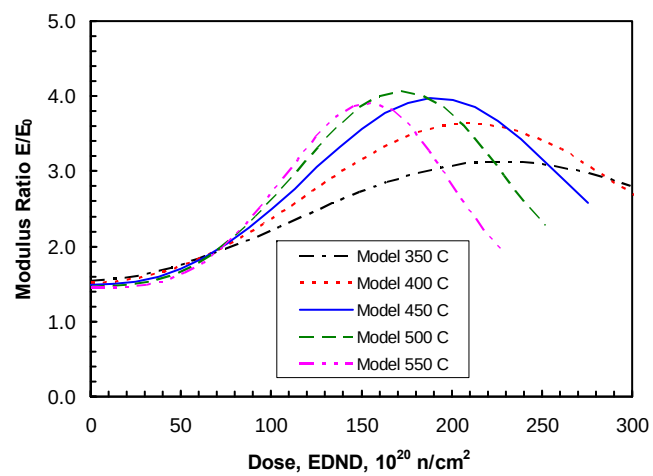



**Dose ratio DR, is dose normalised to dimensional change "turnaround"**

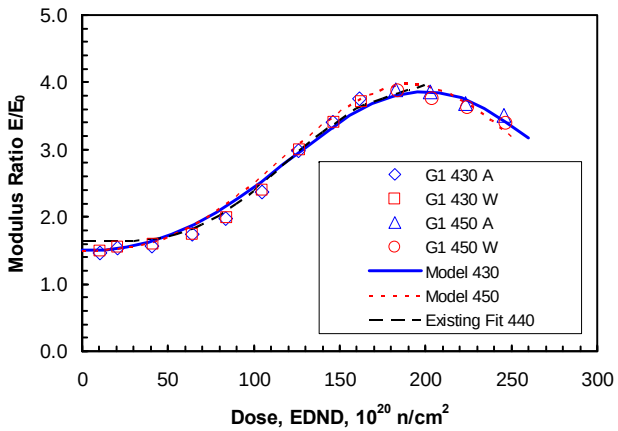
**Functions *P* and *T* were found to be function of graphite grade as well as temperature, see below**



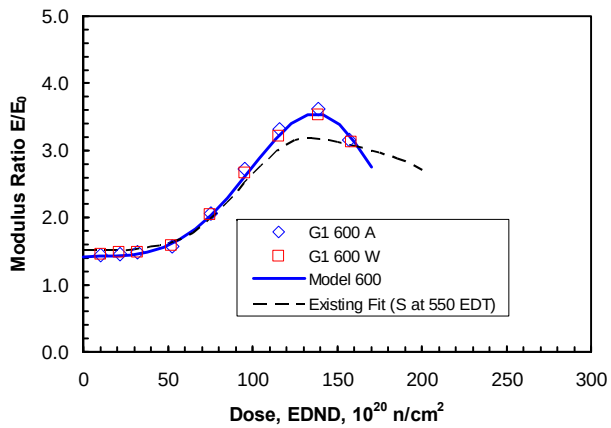



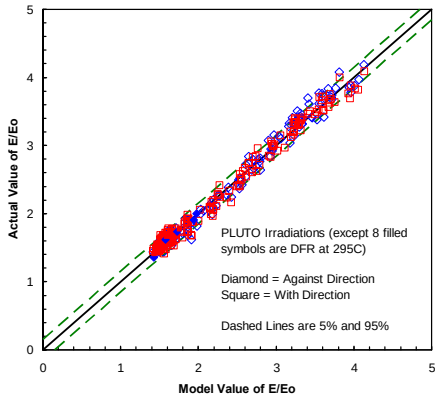
# Model fits to various graphite grades



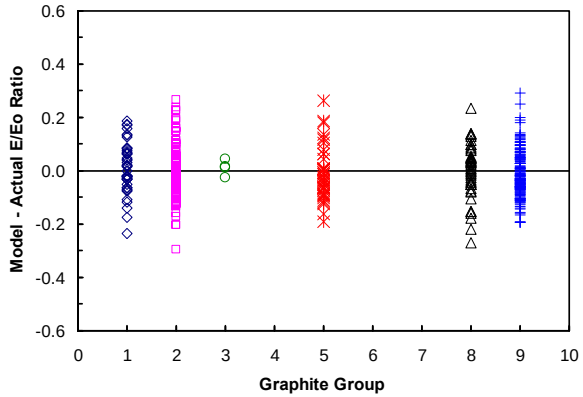

**Inert Environment Model, Graphite Group 5 (HYA), 430 - 450°C Data**




**Inert Environment Model, Graphite Group 5 (HYA), 600°C Data**




**Actual *vs.* Model Values of E/E0 for Station Moderator Data Used for Calibration**




**Residual Plot Showing no Residual Trend with Graphite Group**

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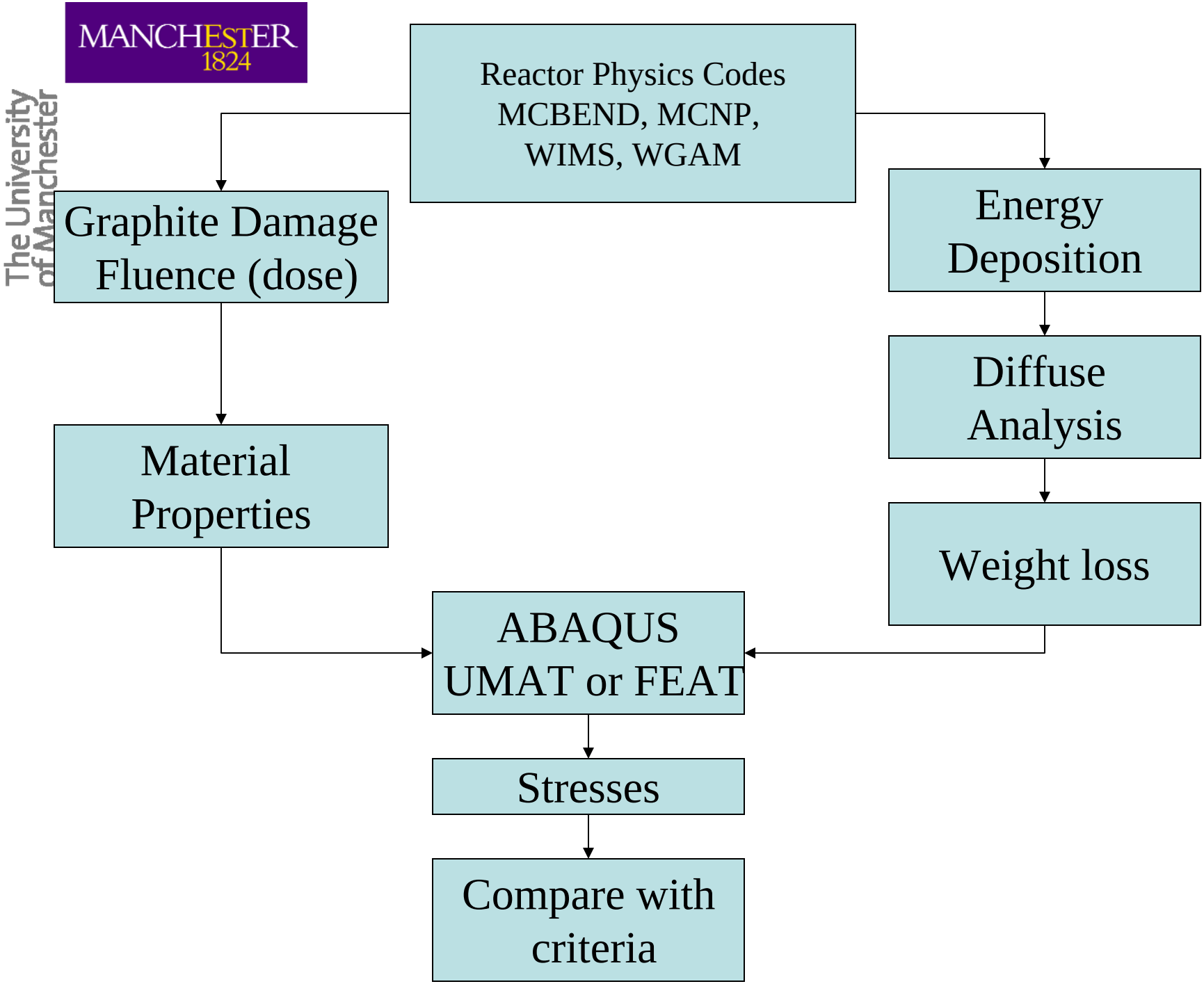
# Graphite Component Stress Analysis

- Nuclear Graphite – is an artificial, porous polycrystalline material
- In reactor graphite properties and dimensions change due to fast neutron irradiation and radiolytic oxidation
- Also in reactor graphite exhibits irradiation creep
- Property changes are a function of:
  - Fast neutron fluence
  - Temperature
  - Radiolytic weight loss
- Irradiation creep is a function of
  - Fast neutron fluence
  - Radiolytic weight loss
  - Stress
- There are other complications related to creep, CTE which are ignored here


Reactor Physics Codes
MCBEND, MCNP,
WIMS, WGAM
Graphite Damage
Fluence (dose)
Energy
Deposition
Diffuse
Analysis
Material
Properties
Weight loss
ABAQUS
UMAT or FEAT
Stresses
Compare with
criteria

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# Total Strain Increment

Elastic Strain

Total Strain

Primary creep strain

$$\{\varepsilon_E\} = \{\varepsilon_{TOT}\} - \{\varepsilon_{pc}\} - \{\varepsilon_{sc}\} - \{\varepsilon_{\gamma}\} - \{\varepsilon_{th}\}$$

Secondary creep Strain

Thermal Strain

Dimensional Change

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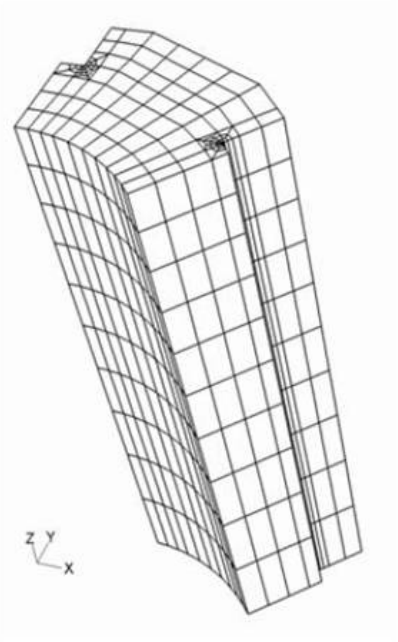
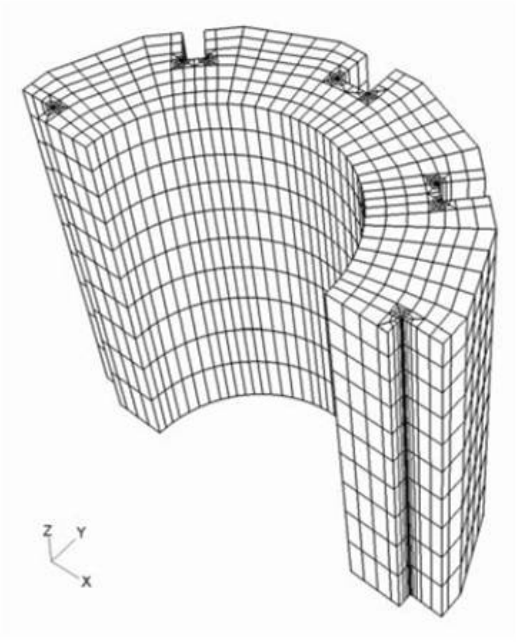
# Example HPB/HNB 3-D Finite Element Meshes

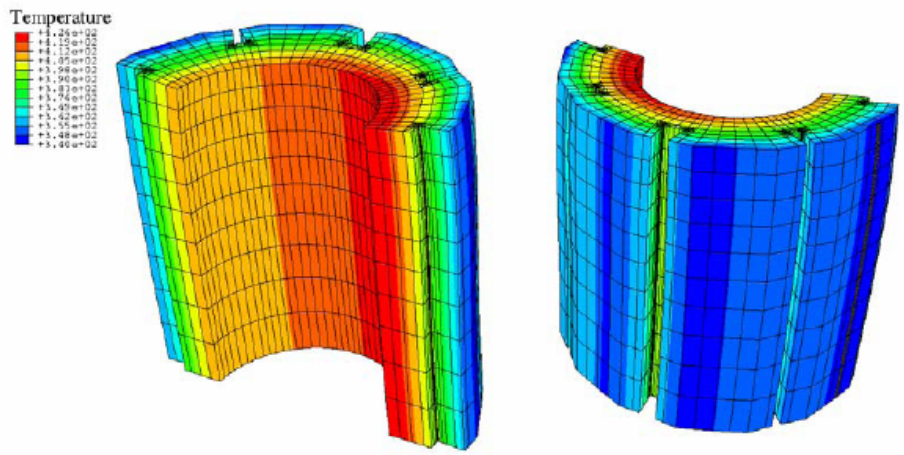



a) Central



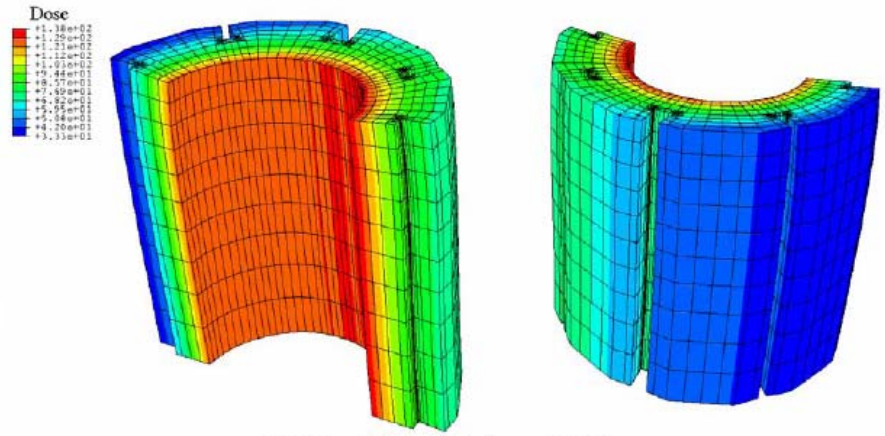

b) Peripheral

# Variation in Fluence (Dose), temperature and weight loss



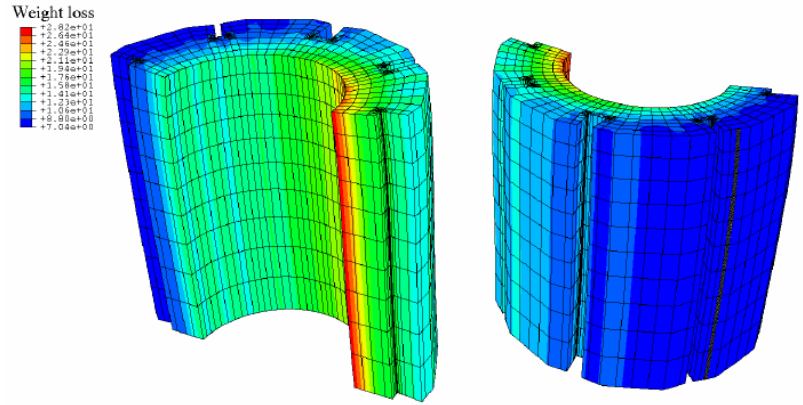

(b) Peripheral brick temperature distribution

**Temperature**




(b) Peripheral brick irradiation fluence distribution

**Fluence**

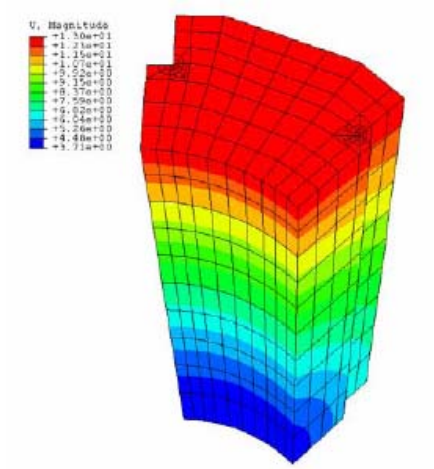



(b) Peripheral brick weight loss distribution

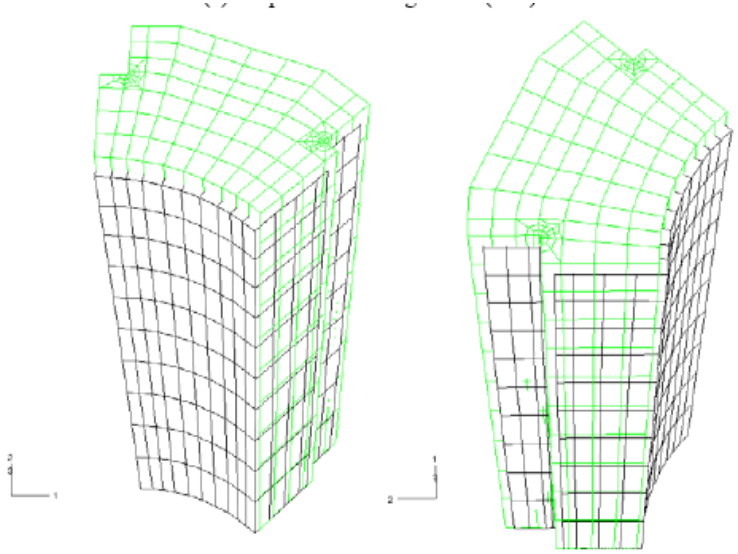
Figure 8: Three-dimensional weight loss distribution at 30.6 fpy

**Weight loss**

# Displacements - Central



(a) Displacement magnitude (mm)



(b) Deformed and undeformed shape

Figure 28: Three-dimensional central brick position displacement after the shutdown step

QuickTime™ and a
decompressor
are needed to see this picture.

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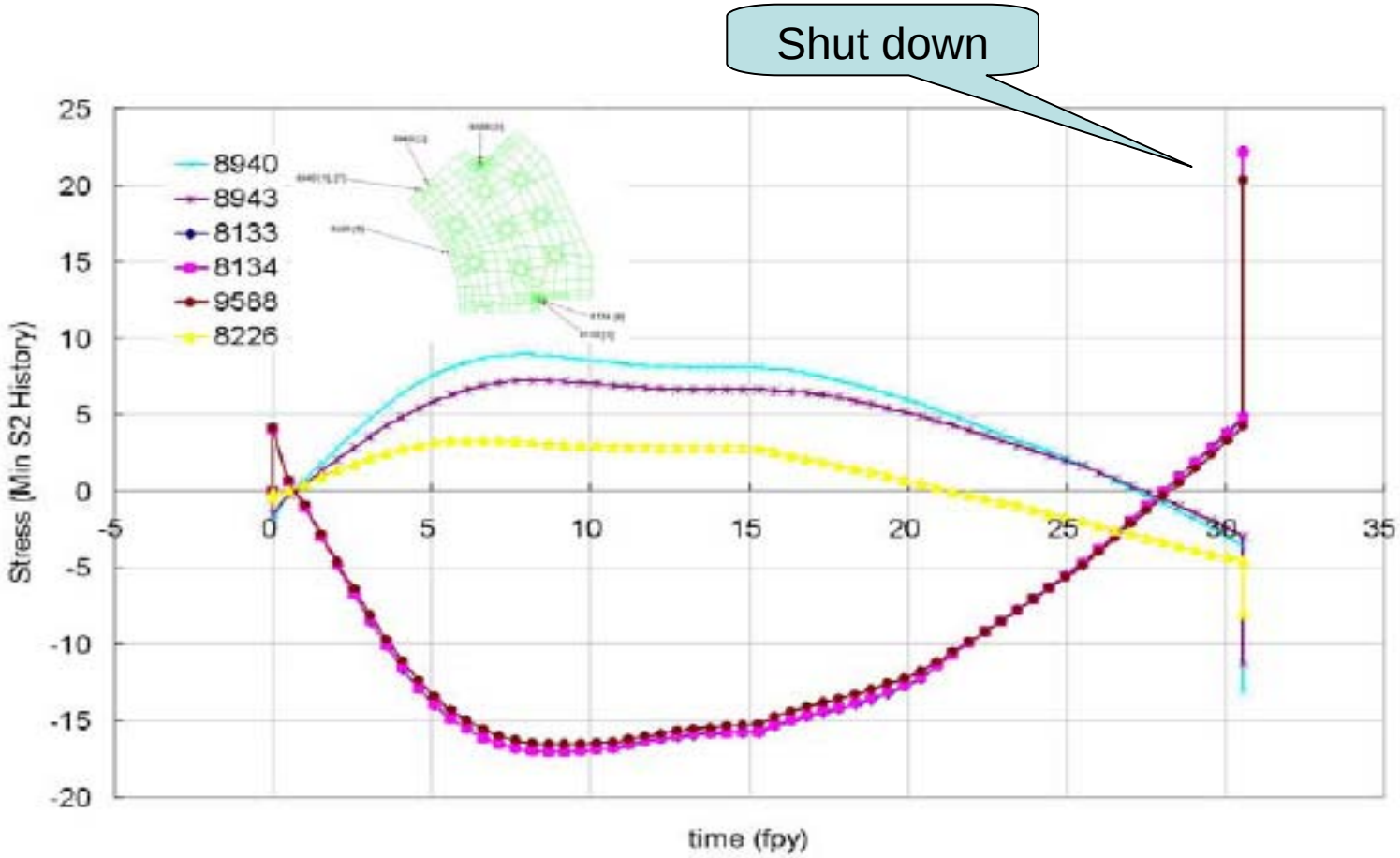
# Hoop stresses – Central Brick – 2D




(b) History profiles for node numbers form the minimum hoop stress curve.

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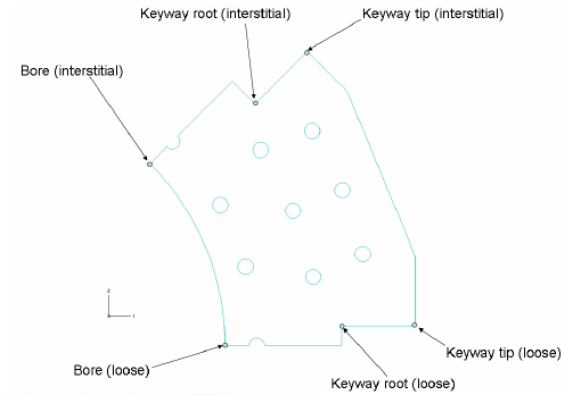
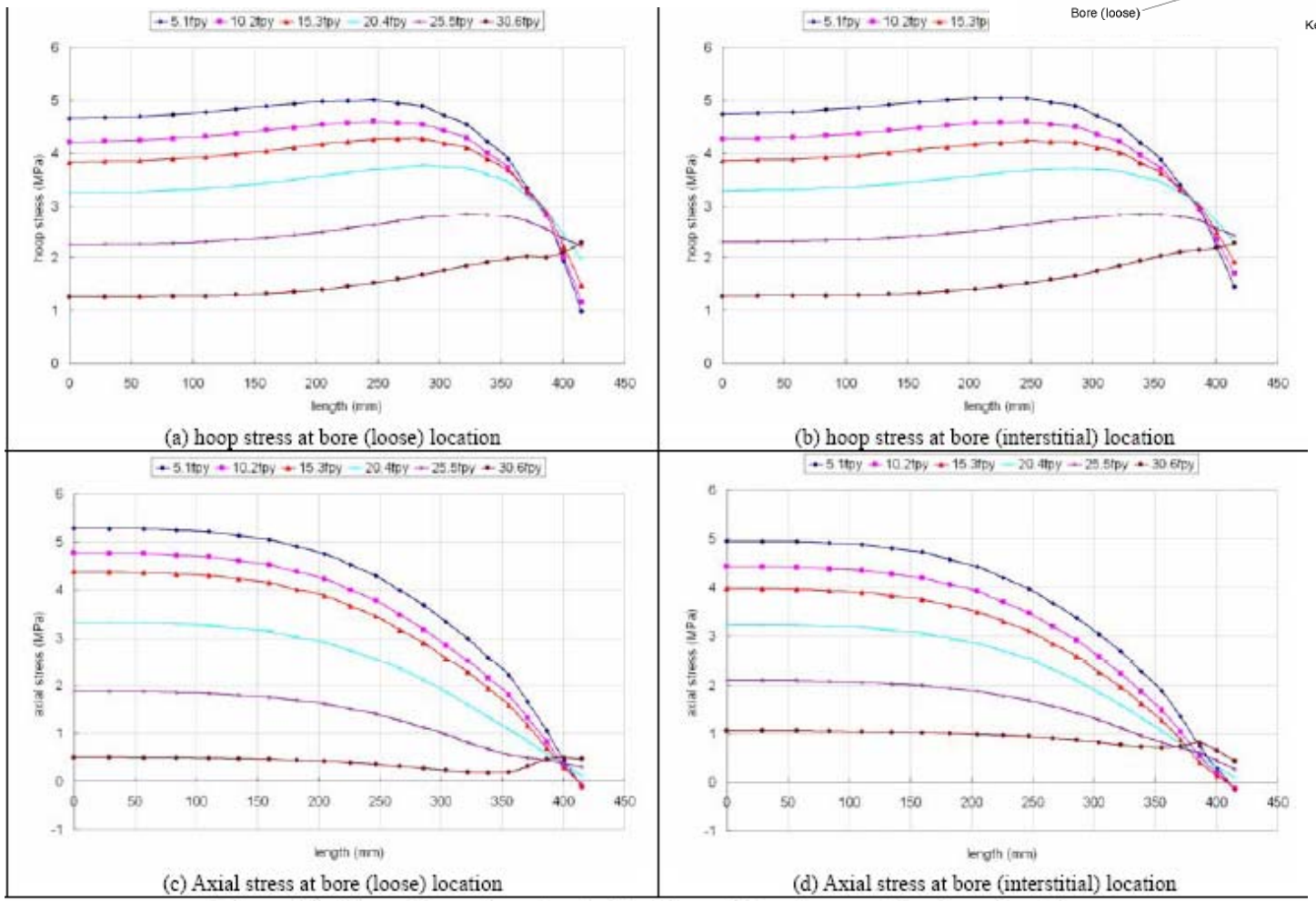
# Central Brick Bore Stresses – 3D




(a) hoop stress at bore (loose) location

(b) hoop stress at bore (interstitial) location

(c) Axial stress at bore (loose) location

(d) Axial stress at bore (interstitial) location

Figure 30: Three-dimensional central brick position stresses along bore locations

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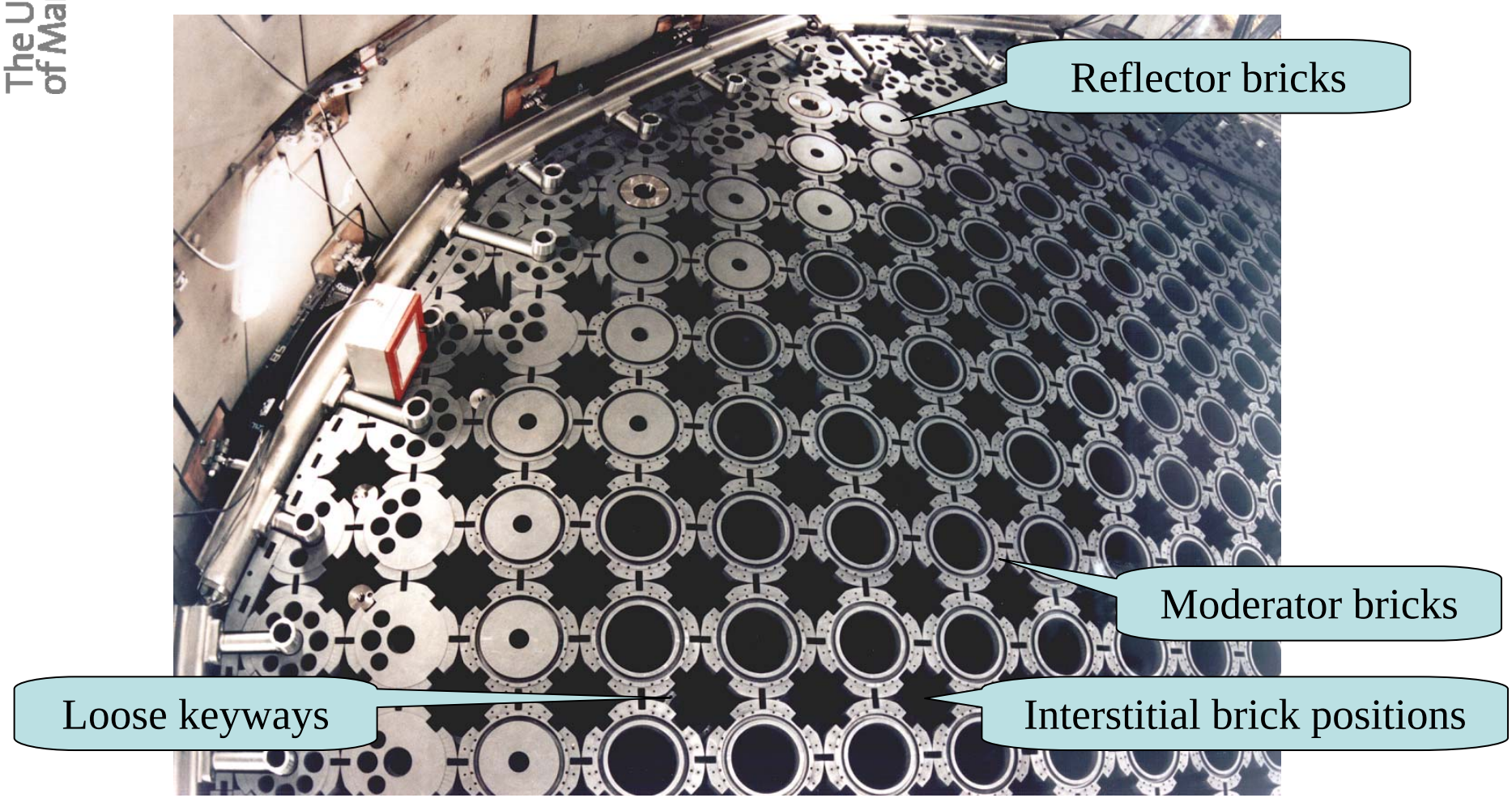
# AGR core Whole Core Modelling




Construction of AGR Core

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# AGR Graphite Brick Superelement

- In order to model arrays of AGR bricks supper elements have been developed
- The stiffness matrix for a brick is reduced to only include the nodes at the boundaries thus including the number of degrees of freedom in the finite element model reducing the size and time of assessments
- A special irradiated graphite superelement has been developed for use with the ABAQUS finite element code

QuickTime™ and a decompressor are needed to see this picture.

QuickTime™ and a decompressor are needed to see this picture.

# Superelement analysis of moderator brick with a crack

- Superelement for 1/8 brick combined with ABAQUS elements calling the UMAT

QuickTime™ and a
decompressor
are needed to see this picture.

# Superelement

- 10 x 10 fuel bricks model

QuickTime™ and a decompressor are needed to see this picture.

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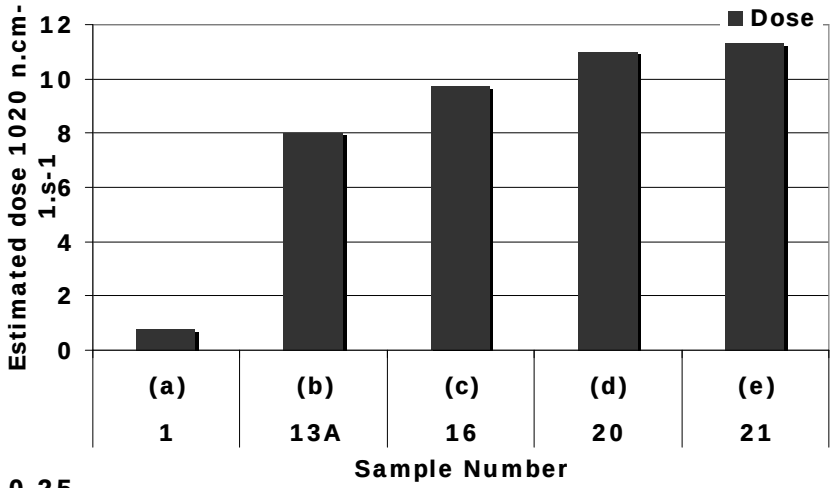
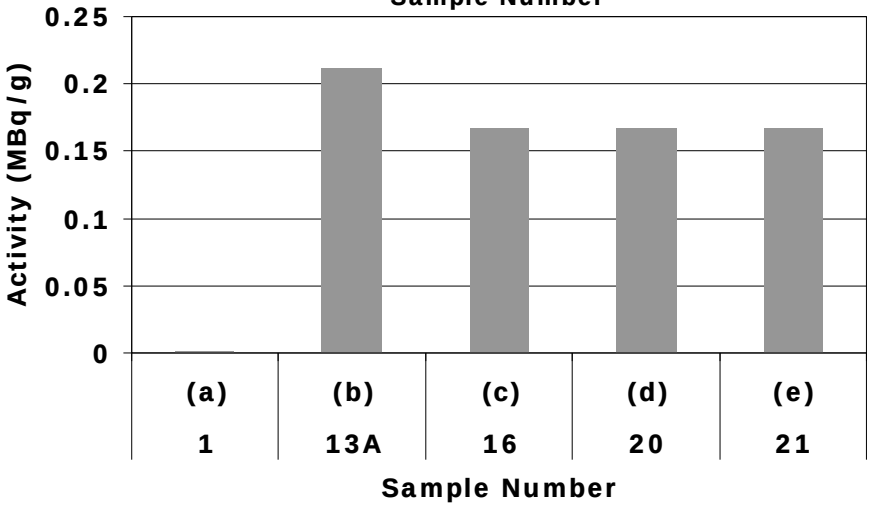
## Characterisation of irradiated graphite waste EC FP7 Carbowaste

- The UK graphite moderated reactors will have produced somewhere in the region of 90,000 tonnes of irradiated nuclear graphite after operation ceases.
- In order to make informed decisions of how best to dispose of this large volume of waste it is necessary to understand the character of the irradiated graphite waste and the effectiveness of the various proposed decontamination and immobilisation treatments.
- This work is funded by Carbowaste and NDA
- The objective is to use microstructural and radiochemical techniques in order to quantify the isotopic location and distribution within the graphite.
- This data will be used to compare with theoretically calculated isotopic inventory from trace elemental analysis.

CARBOWASTE

# BEPO Graphite Activity



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# Isotopic Inventory

- Isotopic Inventory is a result of:
  - Moderator - graphite plus the impurities within.
  - Components of the fuel.
  - Coolant
  - Core Structural Materials - Steel Impurities

| Element | Magnox | AGR |
|---|---|---|
| Li | 0.05 | 0.05 |
| Be | 0.02 | 0.02 |
| B | 0.1 | 0.5 |
| N | 10 | 10 |
| Na | 1.0 | 4.0 |
| Mg | 0.1 | 0.4 |
| Al | 1.0 | 4.0 |
| Si | 35 | 35 |
| S | 50 | 60 |
| Cl | 2.0 | 4.0 |
| Ca | 35 | 25 |
| Ti | 3 | 0.7 |
| V | 12 | 0.4 |
| Cr | 0.35 | 0.4 |
| Mn | 0.04 | 0.25 |
| Fe | 10 | 28 |
| Co | 0.02 | 0.70 |
| Ni | 1.0 | 6.0 |
| Zn | 0.13 | 1.0 |
| Sr | 0.4 | 0.4 |
| Mo | 0.1 | 2.5 |
| Ag | 0.001 | 0.001 |
| Cd | 0.04 | 0.07 |
| In | 0.05 | 0.06 |
| Sn | 0.05 | 1.0 |
| Ba | 1.5 | 0.5 |
| Sm | 0.04 | 0.05 |
| Eu | 0.004 | 0.005 |
| Gd | 0.005 | 0.01 |
| Dy | 0.008 | 0.006 |
| W | 0.12 | 0.15 |
| Pb | 0.12 | 0.8 |
| Bi | 0.08 | 0.05 |

**Figure 3 Graphite impurity Levels (ppm)***

| | | | |
|---|---|---|---|
| $^{3}H$ | $1.2 \times 10^{14}$ | $^{93}Mo$ | $8.5 \times 10^{8}$ |
| $^{10}Be$ | $7.1 \times 10^{10}$ | $^{93m}Nb$ | $5.5 \times 10^{8}$ |
| $^{14}C$ | $8.5 \times 10^{13}$ | $^{94}Nb$ | $1.0 \times 10^{5}$ |
| $^{36}Cl$ | $9.5 \times 10^{11}$ | $^{99}Tc$ | $1.7 \times 10^{8}$ |
| $^{41}Ca$ | $7.3 \times 10^{11}$ | $^{108m}Ag$ | $2.3 \times 10^{10}$ |
| $^{54}Mn$ | $2.7 \times 10^{8}$ | $^{113m}Cd$ | $1.0 \times 10^{10}$ |
| $^{55}Fe$ | $1.5 \times 10^{13}$ | $^{121m}Sn$ | $4.5 \times 10^{10}$ |
| $^{59}Ni$ | $9.3 \times 10^{10}$ | $^{133}Ba$ | $5.6 \times 10^{11}$ |
| $^{60}Co$ | $2.7 \times 10^{13}$ | $^{152}Eu$ | $2.2 \times 10^{11}$ |
| $^{63}Ni$ | $1.3 \times 10^{13}$ | $^{154}Eu$ | $5.2 \times 10^{12}$ |
| $^{65}Zn$ | $2.1 \times 10^{8}$ | $^{155}Eu$ | $1.6 \times 10^{12}$ |

**Figure 4 Activation Inventory (Bq) of reference Magnox Reactor after 40 years reactor operation followed by 10 years decay.**

**White et al. Assessment of Management modes for graphite from reactor decommissioning. CEC 1984.*

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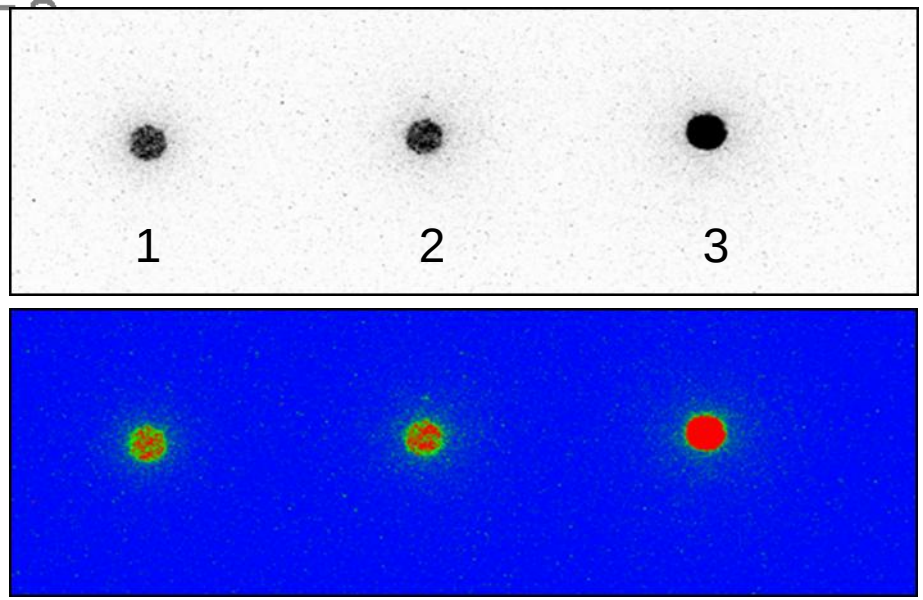
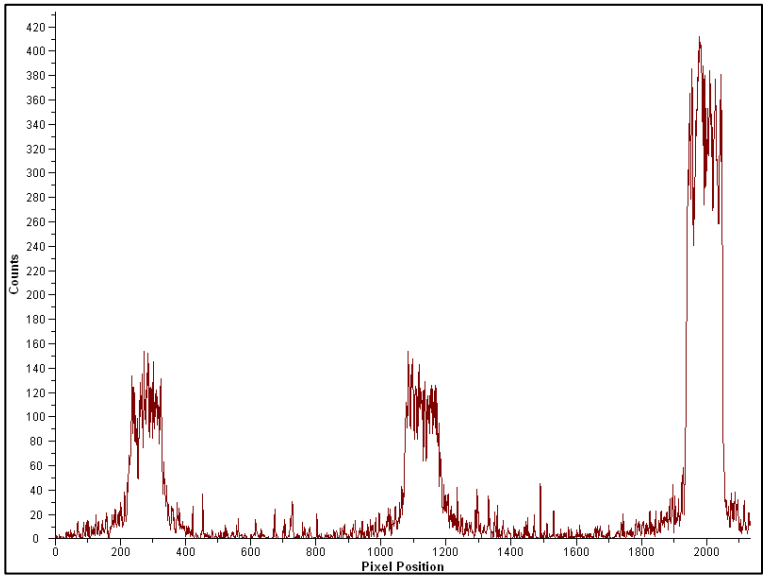
# Autoradiography

- Autoradiography is the visual distribution pattern of radiation.
- Autoradiography determine β and γ radiation, not α due to it being stopped by the photographic film which is the recording medium used for this technique.
- Autoradiography differs from the pulse-counting techniques in several ways. Each phosphorous crystal in the photographic emulsion is an independent detector.

# Autoradiography: Low energy detection




- Low energy tritium detection autoradiography (detects all radioactivity above 0.018MeV) results – 3 hour exposure time.
- Grey scales shows different radioactivity intensities.
- The coloured image shows the background in blue, medium intensity in green and high intensity areas in red.

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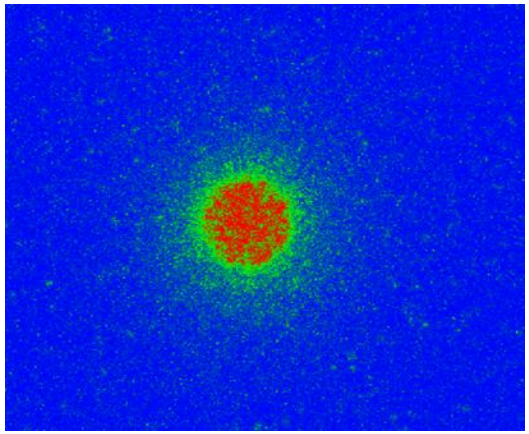
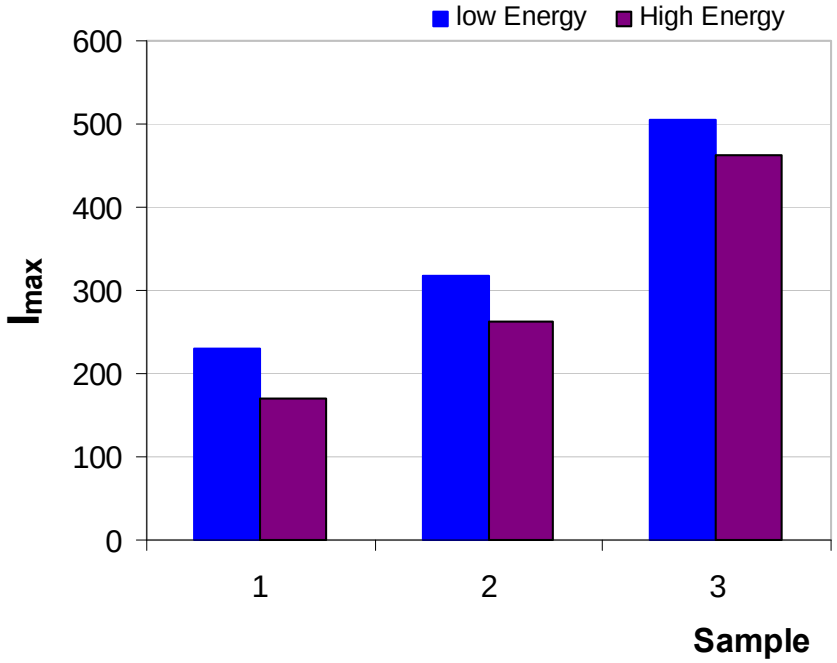
# Autoradiography: Comparison



- These preliminary tests show the isotopic inventory is not evenly distributed throughout the graphite matrix.

- Further analysis of intensity shows the isotopic difference between low and high energy films, contributed from tritium present within the graphite.



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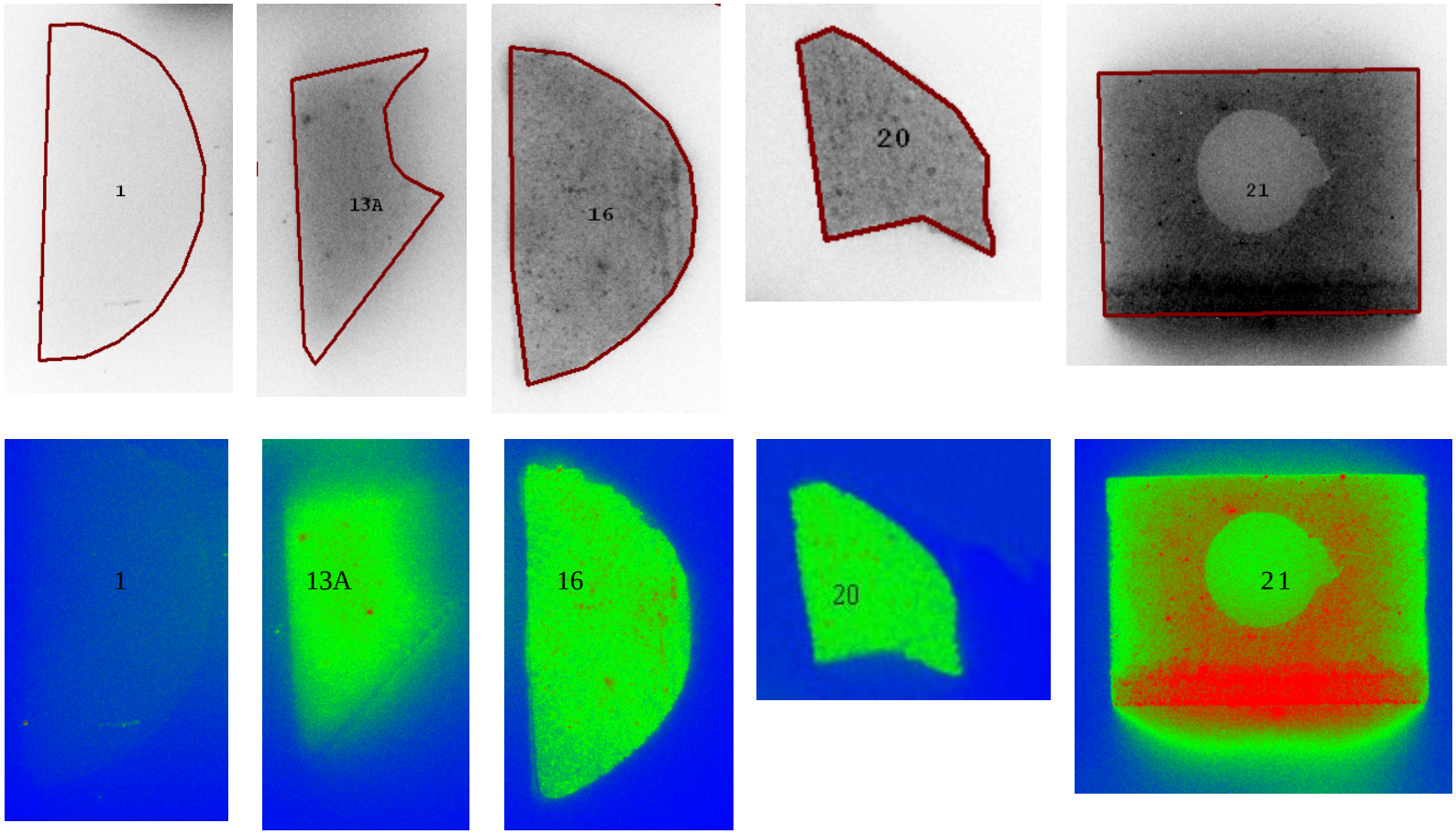
# Autoradiography: All BEPO Samples

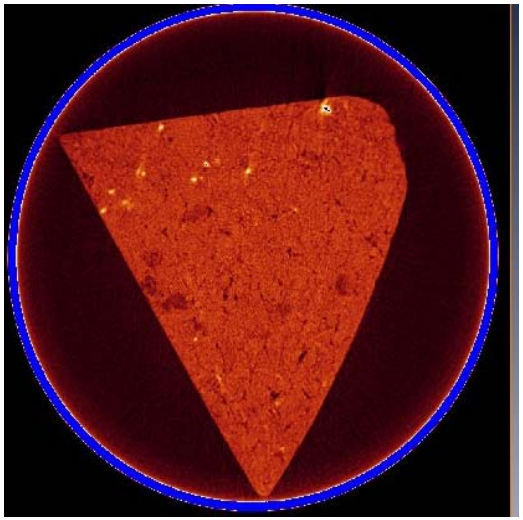


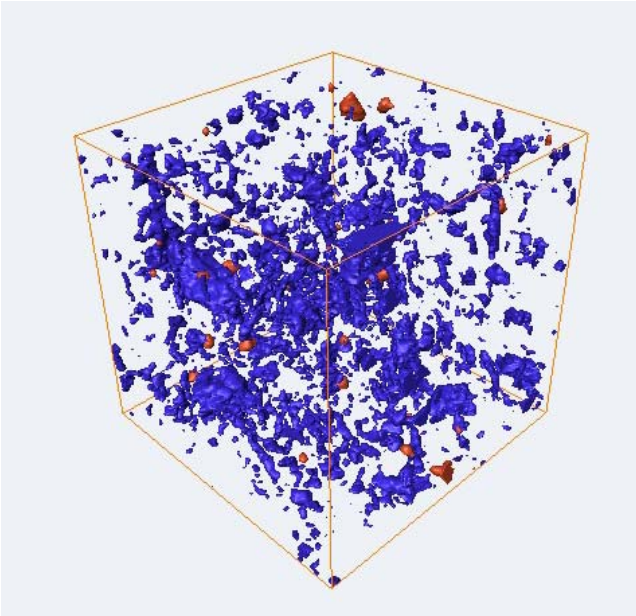
# X-ray Tomography irradiated BEPO 16

- 2D images show slices within the graphite matrix. Several high attenuation spots are visible within the BEPO graphite matrix.

- 3D images show the porosity distribution.

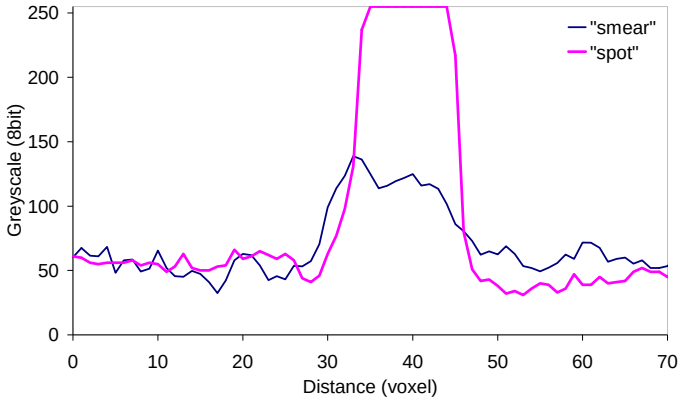
- The blue is the internal porosity and the red is the high attenuation spots.

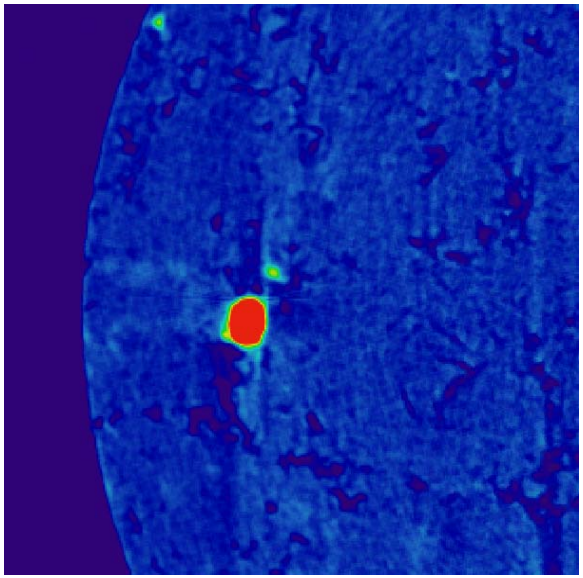




# EDX of high attenuation “spot”

- Bright areas in CT reconstruction
  - found in many samples



“spot” (J12)

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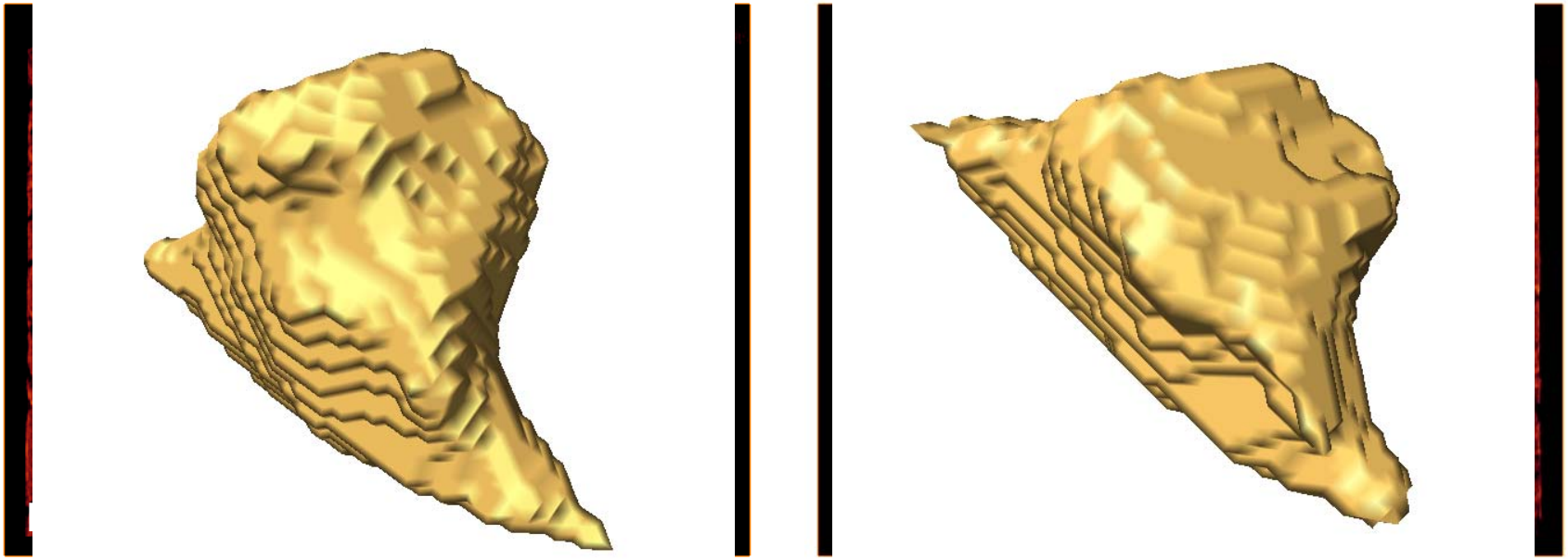
# EDX of high attenuation “spot”



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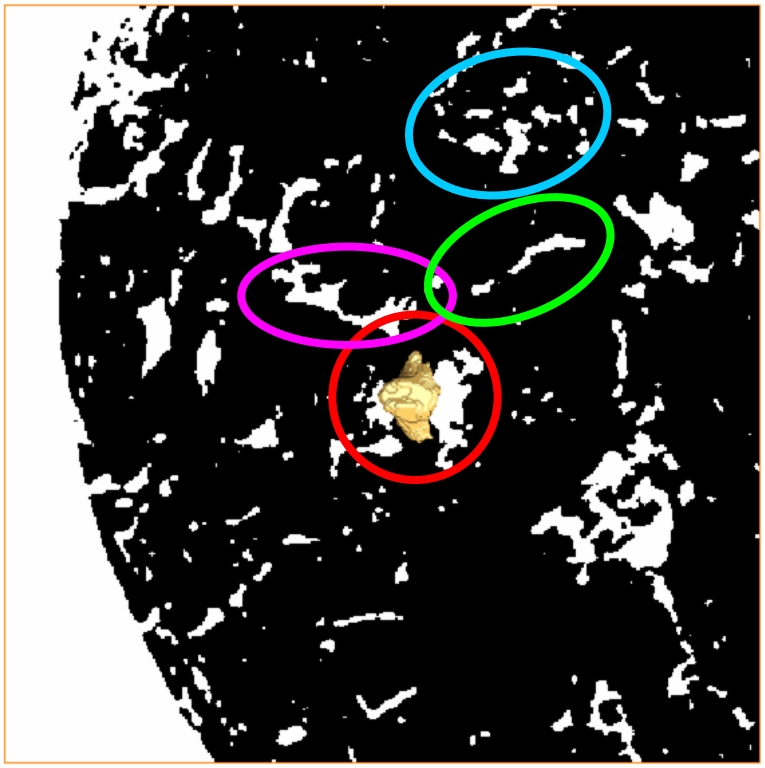
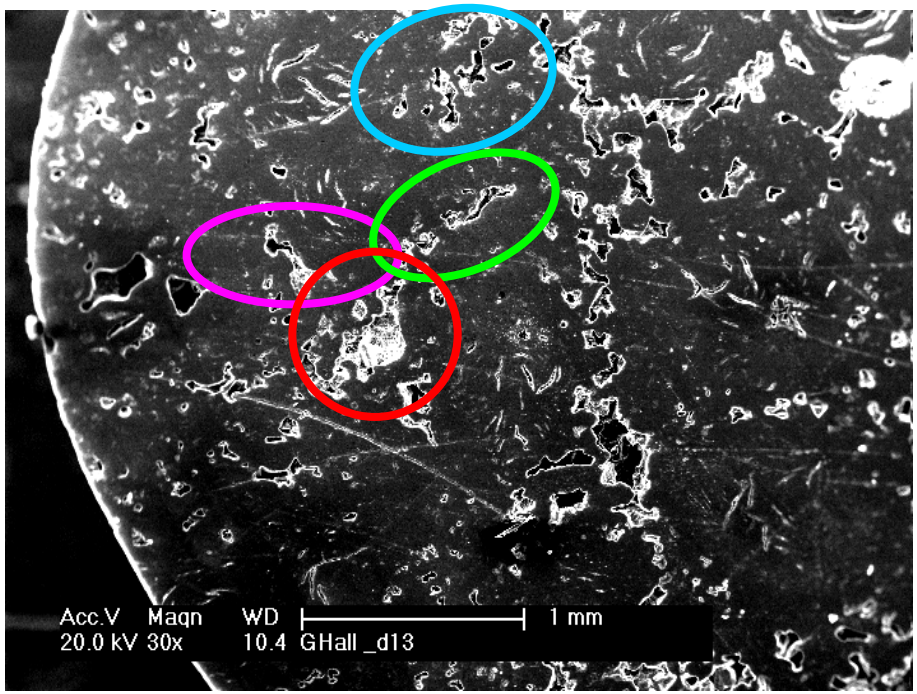
# EDX of high attenuation “spot”



tomography




SEM

*(SEM and EDX by Dr W. Weaver and Dr A Jones)*

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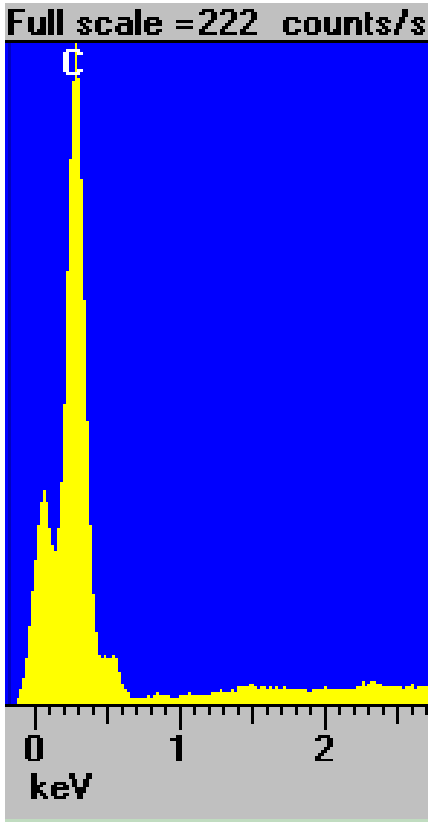
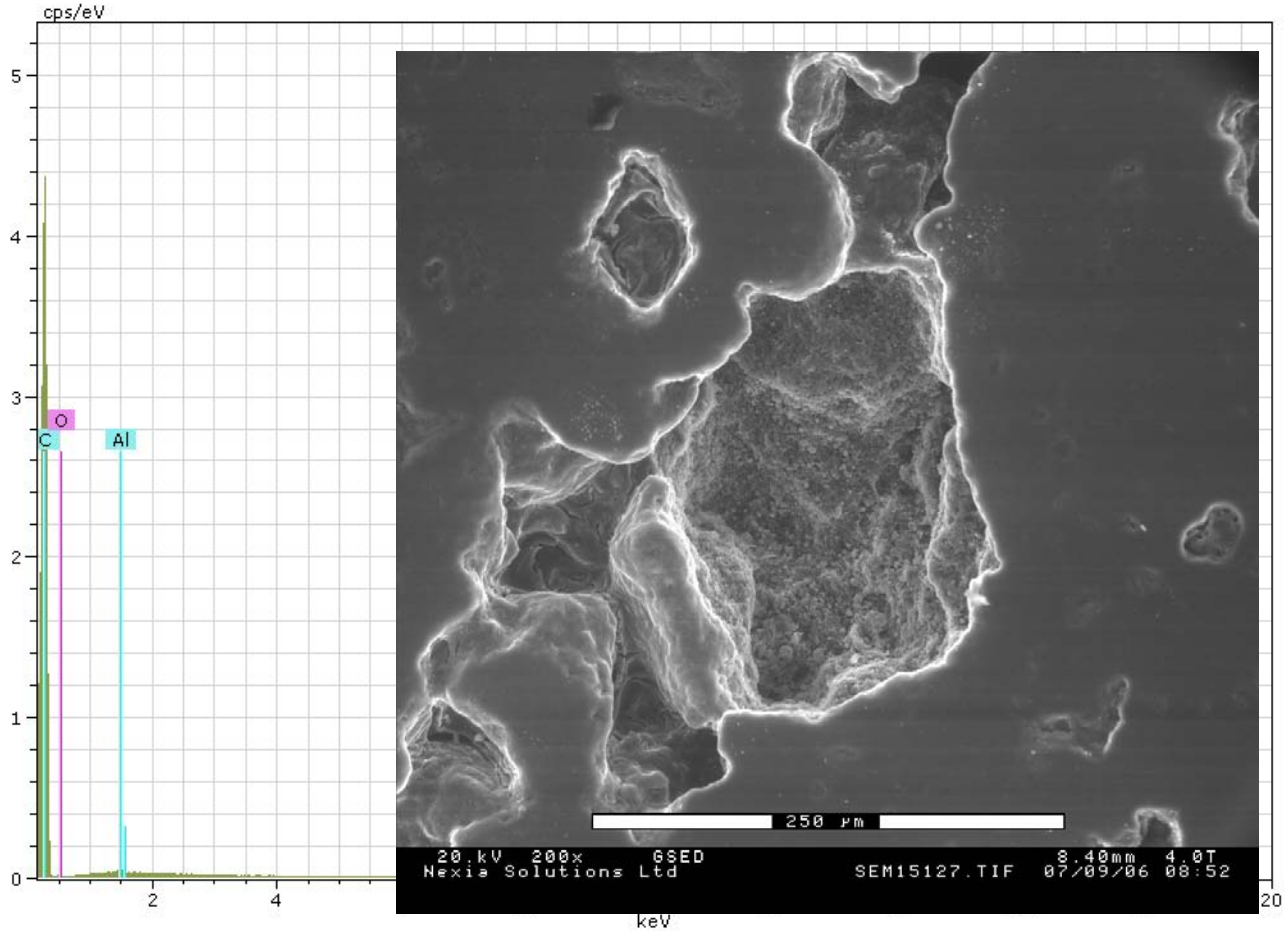
# EDX of high attenuation “spot”





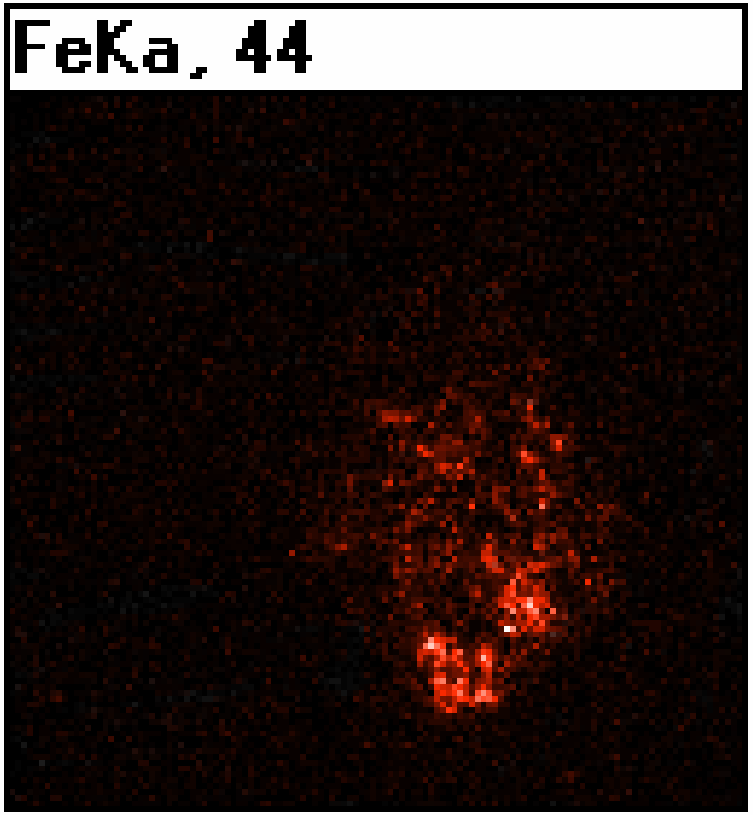


spectrograph of high attenuation “spot”

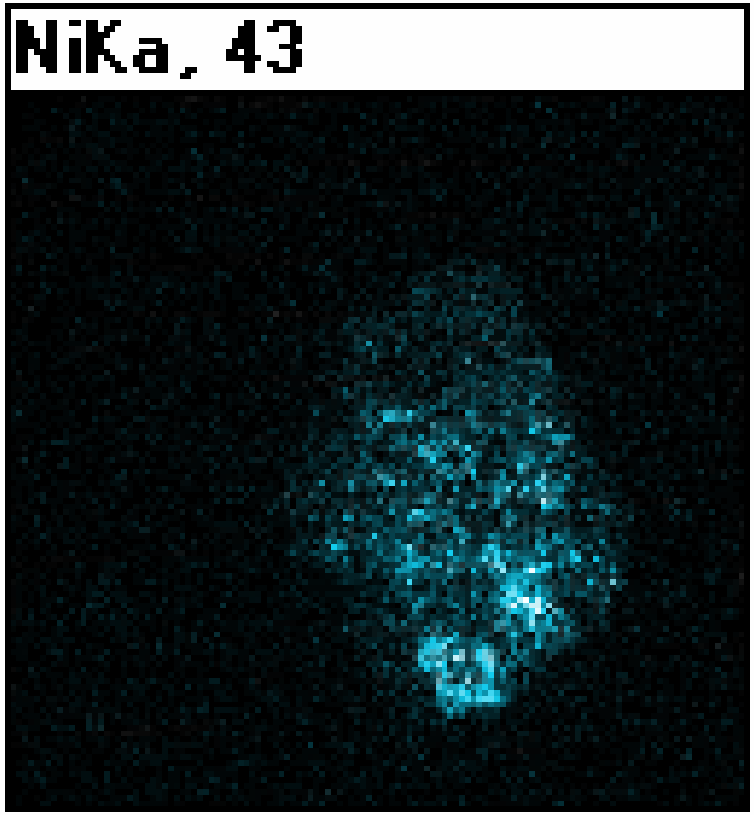
spectrograph of high attenuation “spot”

SEM of high attenuation “spot”

# EDX of high attenuation “spot”




secondary electron image




aluminium

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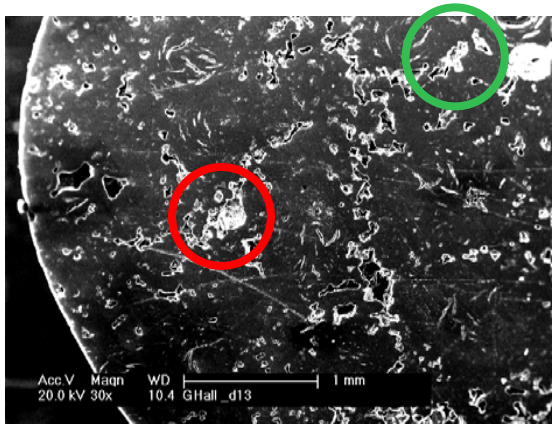
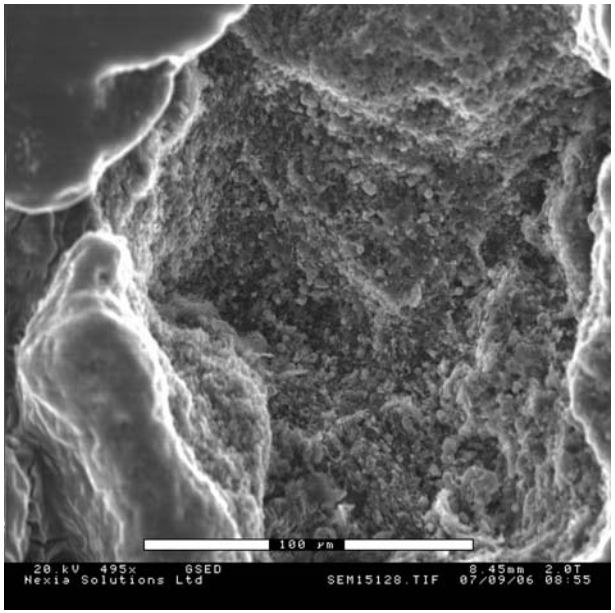
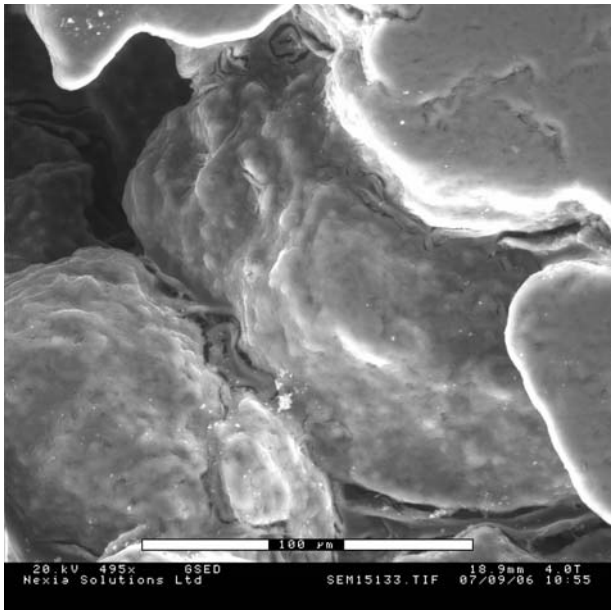
# EDX of high attenuation “spot”




high attenuation pore




non-high attenuation pore

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# Conclusions

- A significant amount of research is aimed at the continued safe operation of the UK AGRs and remaining Magnox reactors, including the possibility of life extension
- The European Framework Programmes FP5, FP6, FP7 continue with RAPHAEL and CARBOWASTE
- A growing area of European research effort is related to the decommissioning and waste disposal of irradiated graphite waste from graphite moderated reactors (including operational waste) in the UK, France, Lithuania, Italy, Spain and Germany

**Acknowledgement**

**Research discussed in this presentation was funded by the HSE(ND), EPSRC, British Energy, Magnox, European Commission and the NDA**