NATIONAL NUCLEAR LABORATORY

Chemical mapping of irradiation-induced defects

Simon Dumbill

Talk Outline

Introduction to NNL capabilities

Chemical mapping – why are we doing this?

EDS techniques
- Mapping vs linescanning

EELS techniques
- Core loss vs low-loss

Data analysis

Irradiated Materials Studies at NNL

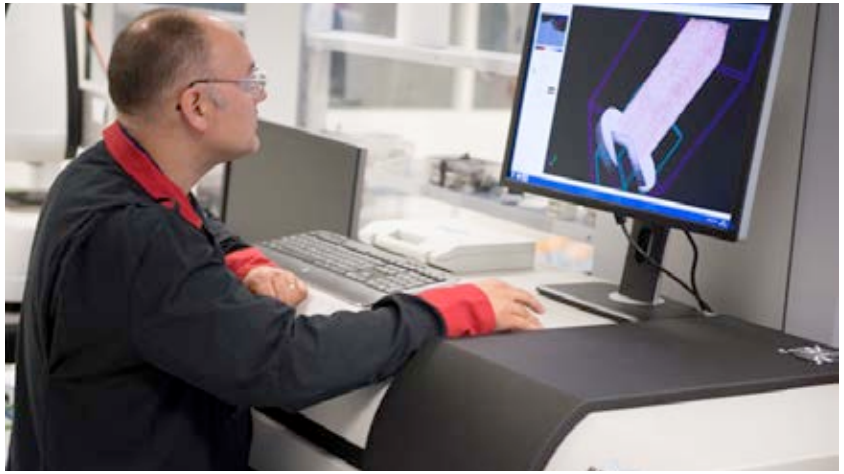
- High active facility at Windscale Laboratory
- - incl Royce-funded Raman/Hv/optical microscope
- Medium and low active facilities at Central Laboratory
- Low active facility at Preston

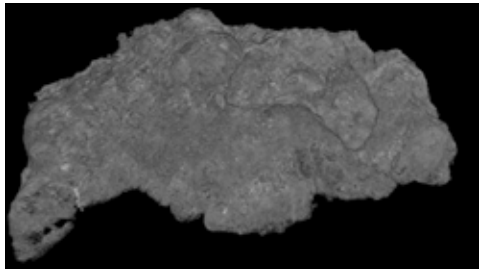
- Active facilities in Central Lab
  - Fumehoods
  - Gloveboxes
  - Electron microscopes for active materials
  - XRD
  - Raman (Royce funded)
  - Chemical analysis
  - Radiochemistry

- Electron optics group experience covers:
  - Nuclear graphite
  - Zirconium alloys (LWR cladding)
  - Steel (AGR cladding, pressure vessel)
  - Carbon deposit flakes
  - Non irradiated and irradiated fuels
  - Pond sludge
  - Glass (waste-form)
  - Nanoparticles

Bruker 1172 X-ray CT scanner

- X-ray tomography of macroscopic active samples
- Highly automated
- Max size 50 mm in diameter – but highly dependent on material
- Non destructive
- 20 – 100 kV, ~ 0.65 µm peak resolution
- Typically used for 3D-tomography of uranium foil in cement, Magnox simulant sludge, carbonaceous deposits





Fuel-Active Gallium FIB-SEM at Central Laboratory

- I 0.9 nm resolution @ 15 kV, SEM
- 50 V – 30 kV beam deceleration
- SE, BSE, rBSE
- 50 mm^2 SDD EDX and EBSD detector with TKD
- 65 nA Ga ion beam (~ 5 nm resolution ion imaging)
- 2-line GIS system (Pt, O_2)
- 'Cryo'-stage

- Installed in 2013
- Active in 2018

End of life in 2025!

FEI part of Thermo Fisher Scientific

NNUF National Nuclear User Facility

Technical contact:
Dr Adam Qaisar
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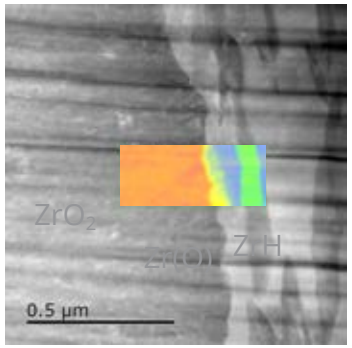
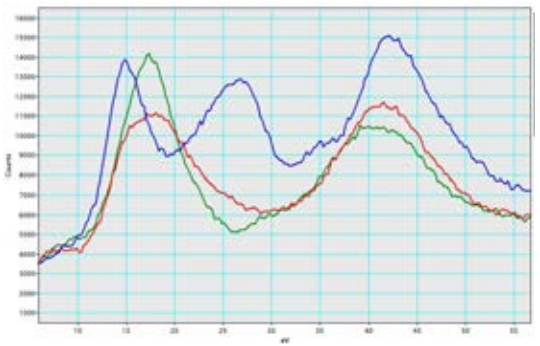
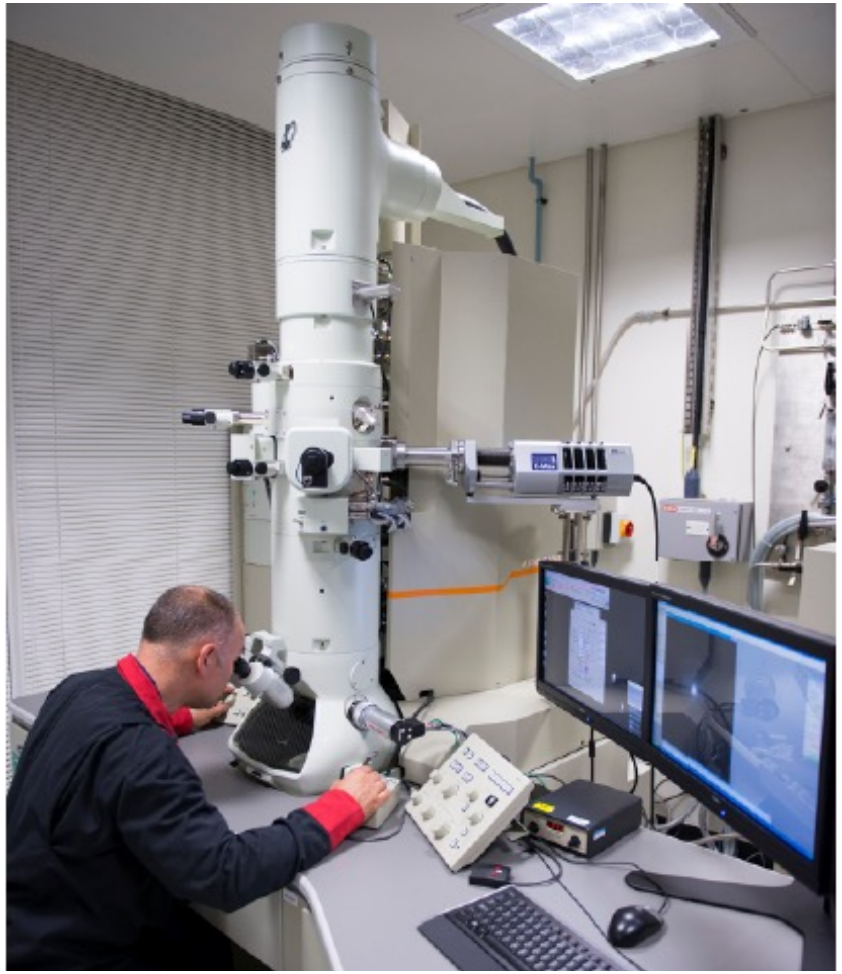
JEOL 2100 Transmission Electron Microscope

- LaB_6 electron source
- 80-200 kV
- TEM resolution ~ 0.2 nm @ 200 kV
  STEM resolution ~ 2 nm @ 200 kV
- TEM, electron diffraction and STEM
- Variety of BF, ADF and HAADF detectors

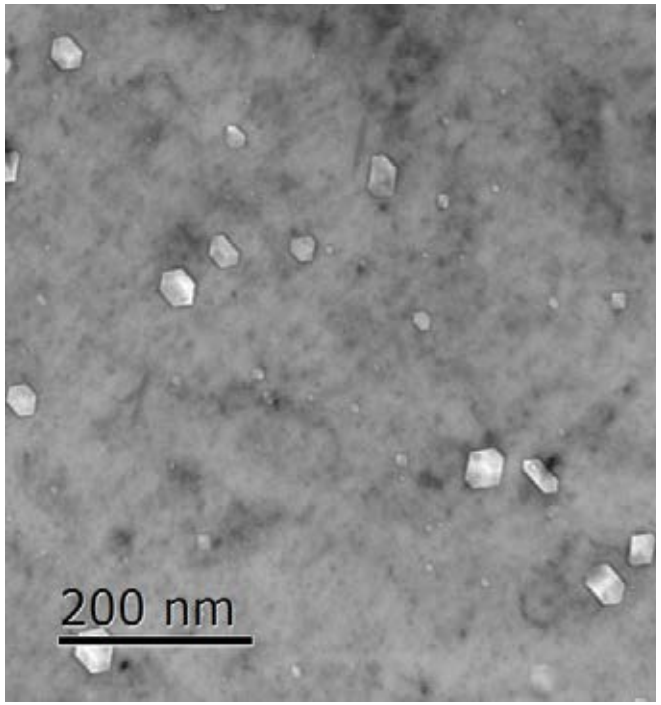
- Oxford Ultim Max 100mm^2 EDX detector
- Gatan Quantum 695ER GIF (EELS, EFTEM)
- EELS and EDX spectrum mapping

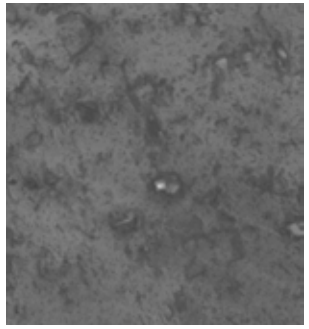


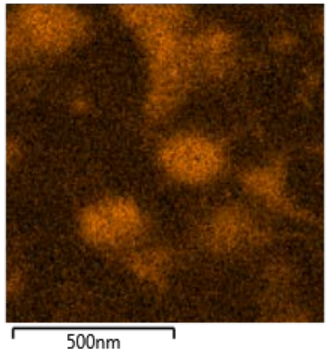


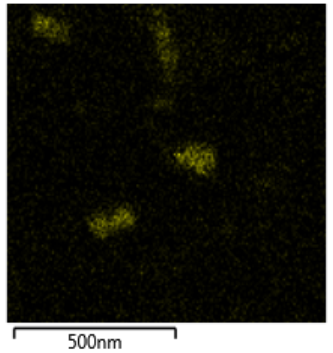


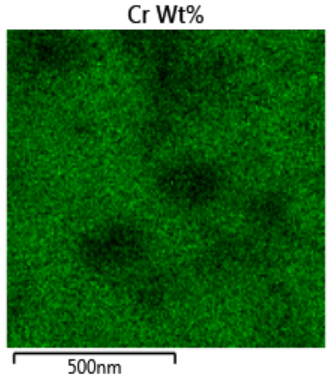
(S)TEM characterisation of ex-reactor 20-25Nb fuel cladding

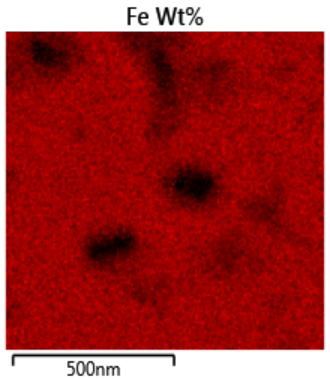


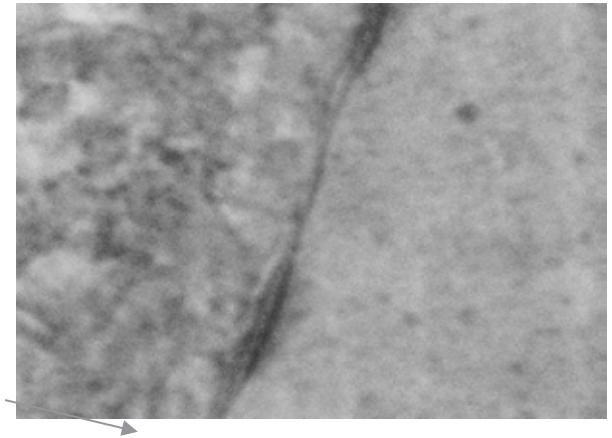


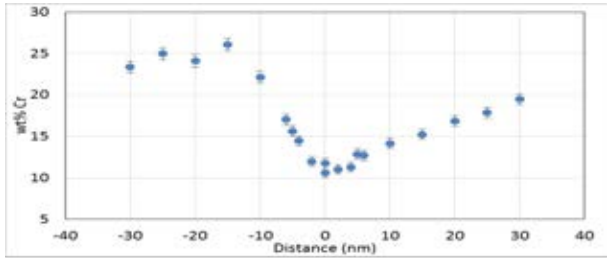


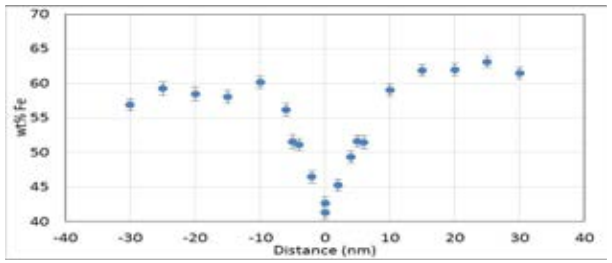


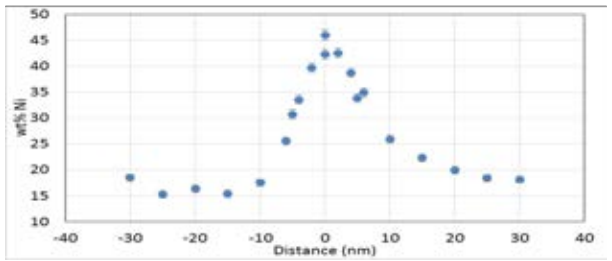












- STEM was used to characterise effect of radiation induced segregation (RIS) on grain boundary and matrix composition
- EDX over matrix reveals areas as low ~ 10 % Cr with enhancement in Ni/Si and formation of Ni_3Si near voids
- Void size was characterised from TEM BF images

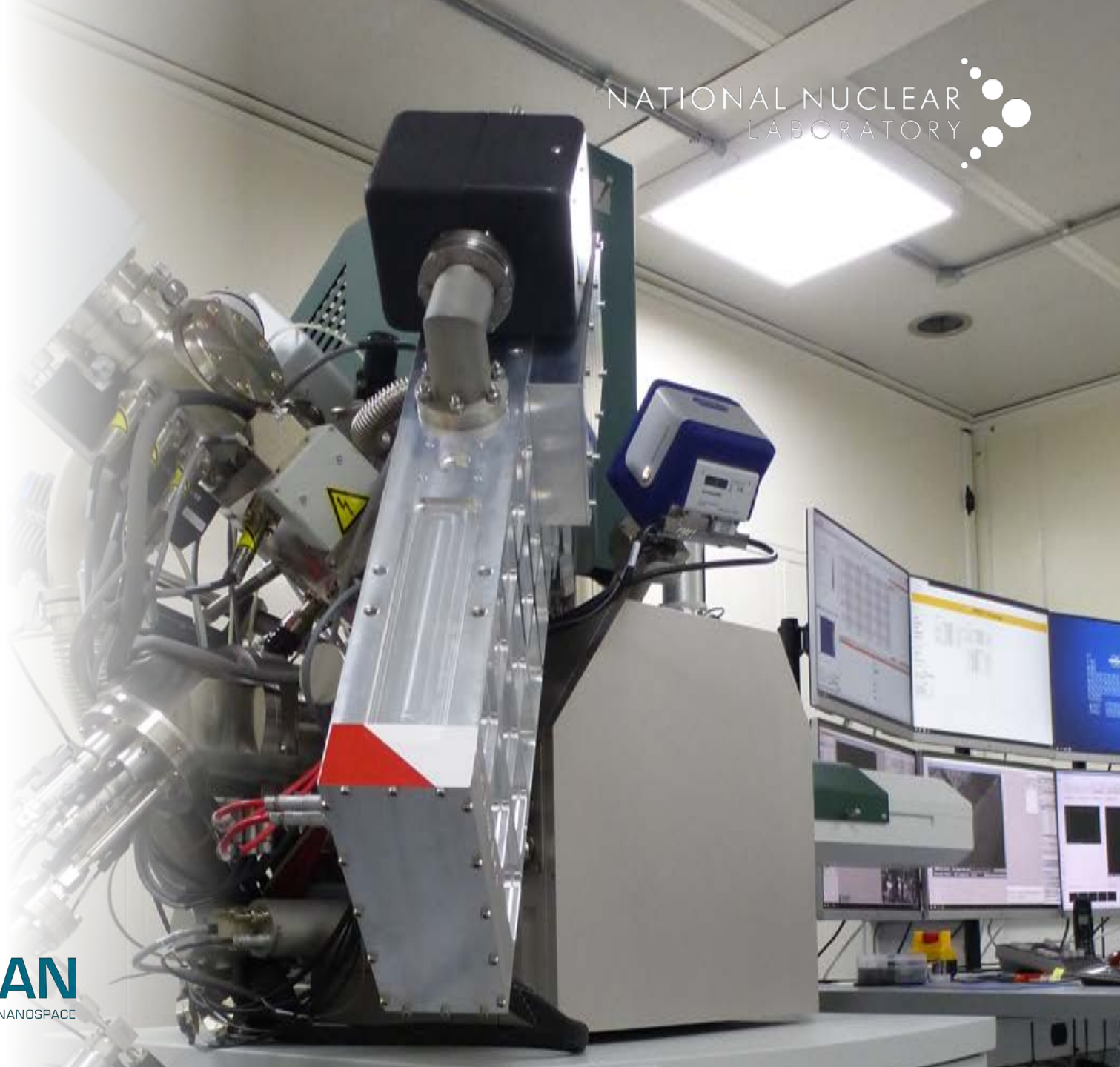
Fuel-Active Plasma-FIB-SEM with ToF-SIMS at Central Laboratory

Tescan XEIA3 PFIB-SEM

- 0.7 nm resolution @ 15 kV, SEM
- Beam deceleration
- Immersion optics
- In beam: SE, BSE, low-energy BSE
- rBSE & rSTEM
- Low vacuum mode
- 1 pA to 1 µA Xe ion beam current, <15 nm resolution
- 5-line GIS system: Pt, C, XeF_2, O2-bleed, H_2O etch enhance
- Hexapod rocking stage
- OmniProbe OP400

Analytics

- Bruker 100 mm^2 EDS
- Bruker FlatQUAD 60 mm^2 1.1 Sr low kV EDS
- Bruker EBSD with TKD
- H-TOF SIMS <60 nm lateral resolution, 3 nm depth, <1.5 ppm det. lim.



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HENRY ROYCE INSTITUTE

TESCAN
PERFORMANCE IN NANOSPACE

NATIONAL NUCLEAR LABORATORY

Aberration corrected FEG-TEM and EELS at Central Laboratory

- FEG module installed
- First electrons end of March

JEOL ARM-200F

- 200 kV cold FEG electron source
- Cs-corrected STEM probe
- High brightness source for best analytical performance

Analytics

- Oxford Instruments 100mm^2 SDD EDS
- Gatan GIF Quantum 965ER with DualEELS and EFTEM capabilities

Supporting equipment

- Tescan XEIA3 PFIB (Xe)
- FEI Helios 600i FIB (Ga)
- Struers electropolishing
- Gatan ion mill (PIPSII)

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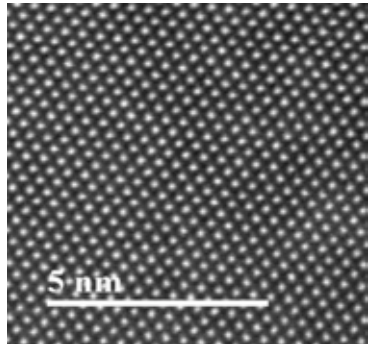
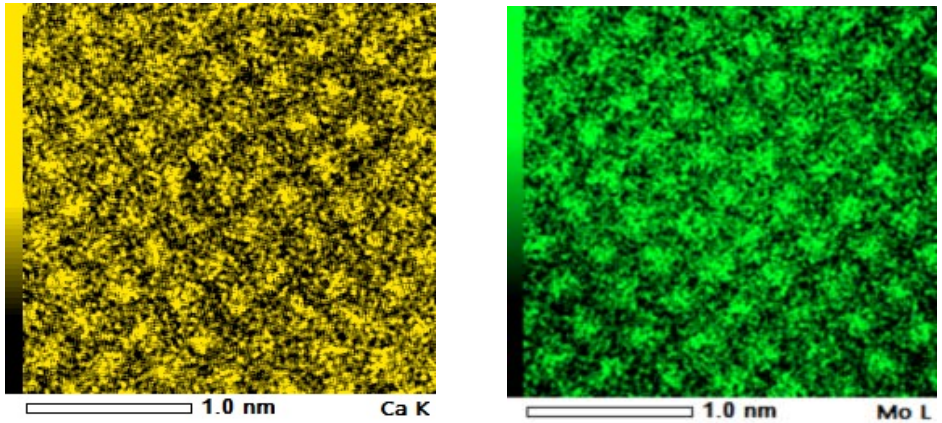
JEOL

FEG-TEM Capabilities

- Atomic resolution element mapping

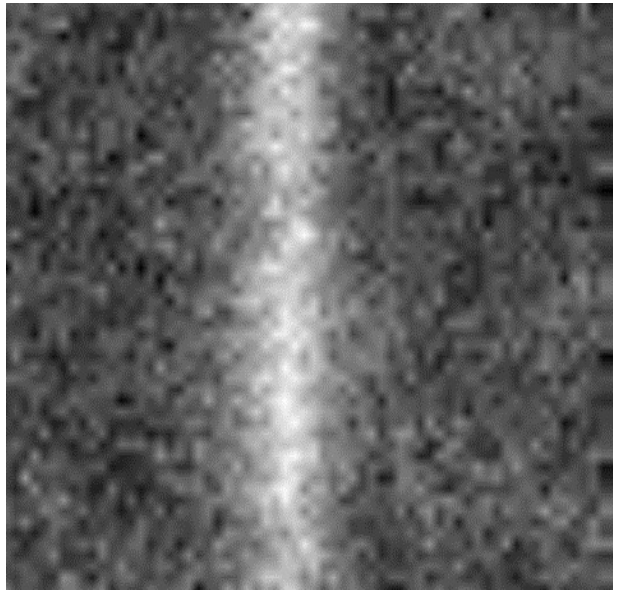


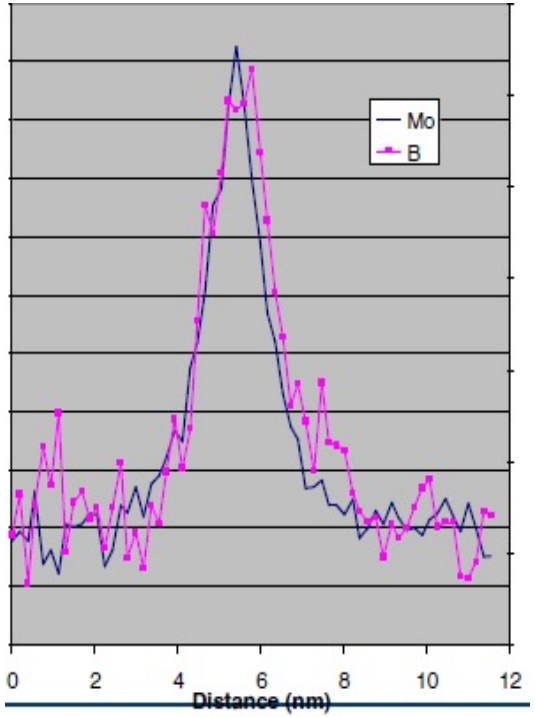


Lattice image and atomic resolution chemical analysis of Ca and Mo

- High throughput grain boundary and matrix chemical mapping

  e.g. grain boundary in 316 steel
  Analysis time 3-4 minutes





Irradiation-damage microstructures

The annihilation of point defects produced by irradiation occurs either by mutual recombination, or by elimination on point defect sinks. Such sinks are dislocations, second phases, voids/bubbles or grain boundaries.

Differences in diffusion rate or solute drag results in compositional change at the sinks. A lot of modelling has been done to attempt to predict levels of grain boundary segregation.

The chemical changes in the region of the point defect sinks occur over a range of a *few tens of nanometres* at most. The changes in composition can result in precipitation or even in matrix instability. Also, segments of grain boundary can bow out and cause exaggerated enrichment/depletion profiles

Characterisation Techniques

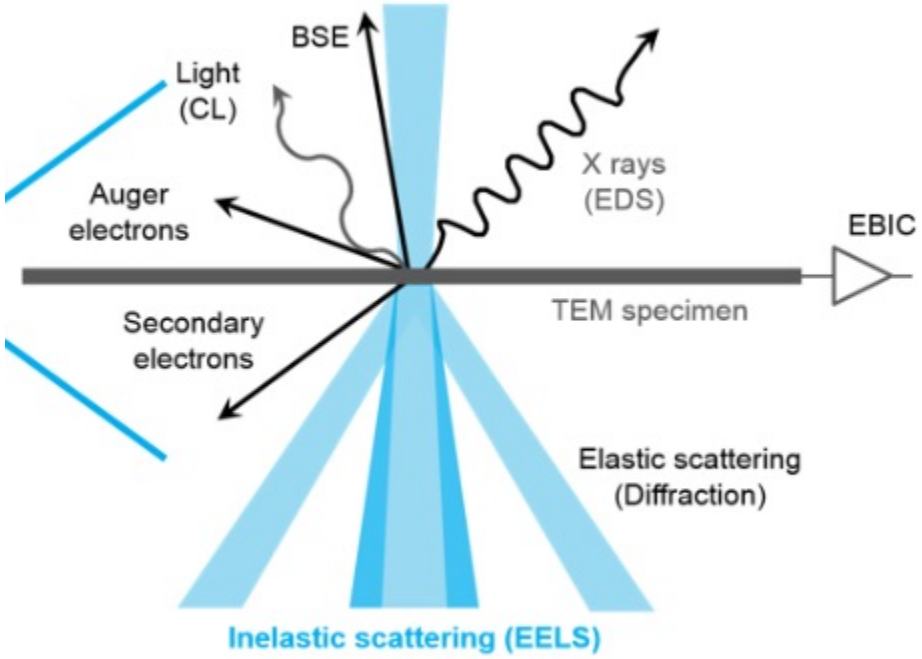
To equip you for the long run, learning microscopy is surprisingly similar to playing an instrument so I'm taking the 'jazz' approach …

- **Imitate**
  - **Find good examples and repeat them in your situation**
- **Assimilate**
  - **Hone these techniques and develop expertise**
- **Innovate**
  - **Improve the technique or bring something new in**

The fine details of what's required to apply any characterisation technique are often best taught by the equipment supplier's trainer or your in-house guru

So, the rest of this session will focus on some good examples – and some problems….

EDS data acquisition



Nice-to-haves

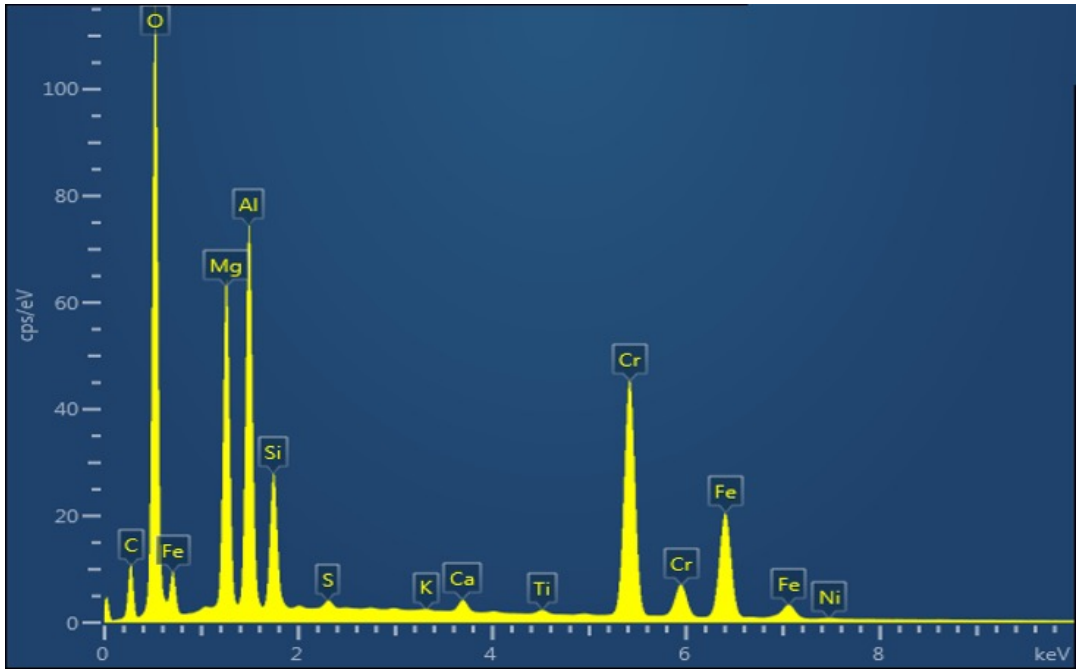
- FEG, aberration corrector
- High-solid angle EDS detector (>1 Sr)

Requirements:

- Grain boundaries must be vertical (aim for projected width <2nm)
- Sample thickness ideally 50-80nm – but depends on analytical requirements. Too thin = not enough counts. Too thick = superposition of features, beam spreading, loss of spatial resolution.
- Sample cleanliness. Plasma cleaning is vital on electropolished samples and highly advised even on FIB sections.
- Minimise contribution from sample radioactivity

Trade-offs

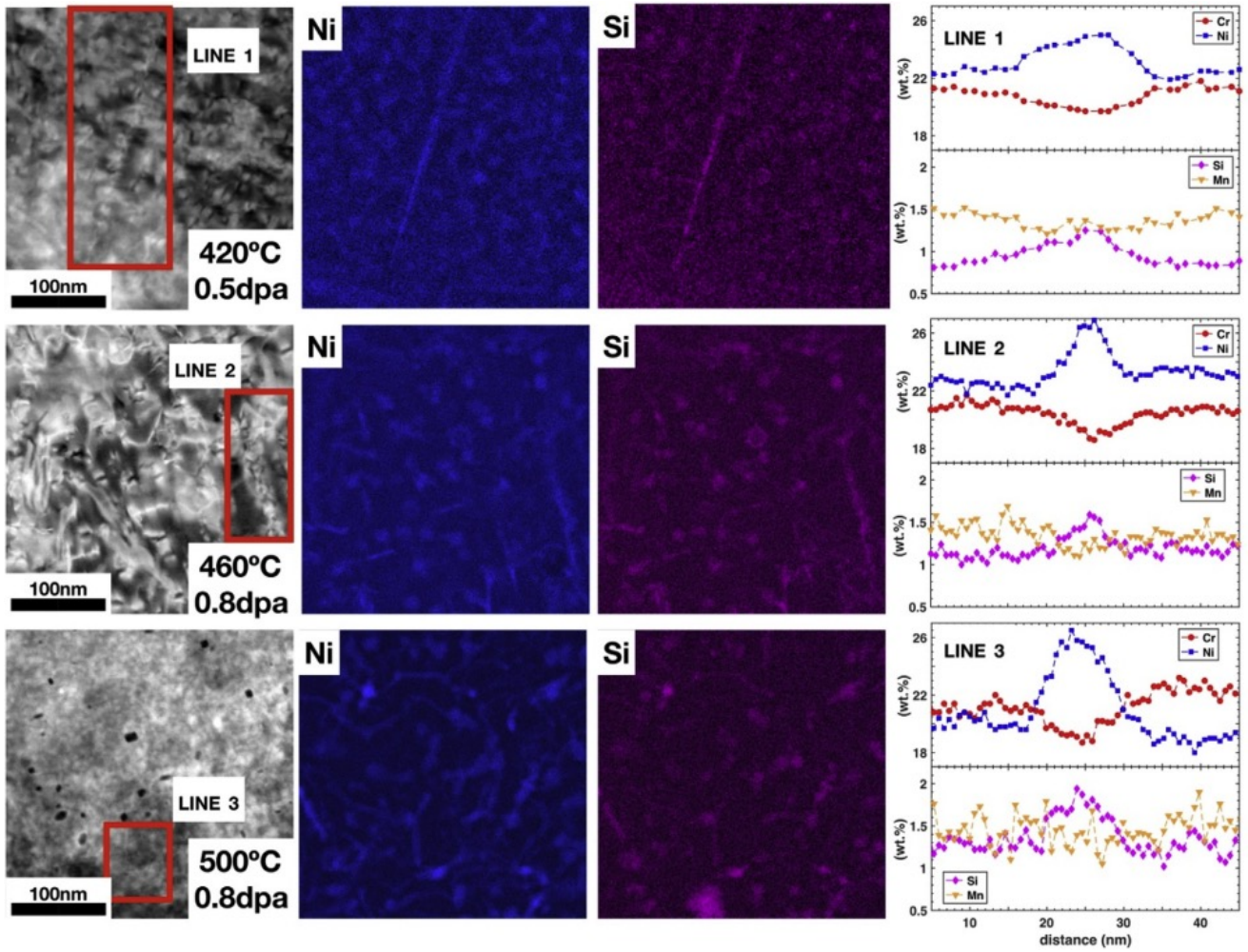
- Maps vs linescans - what data quality do we want?



Not protectively marked

Example: 20-25Nb AGR fuel cladding

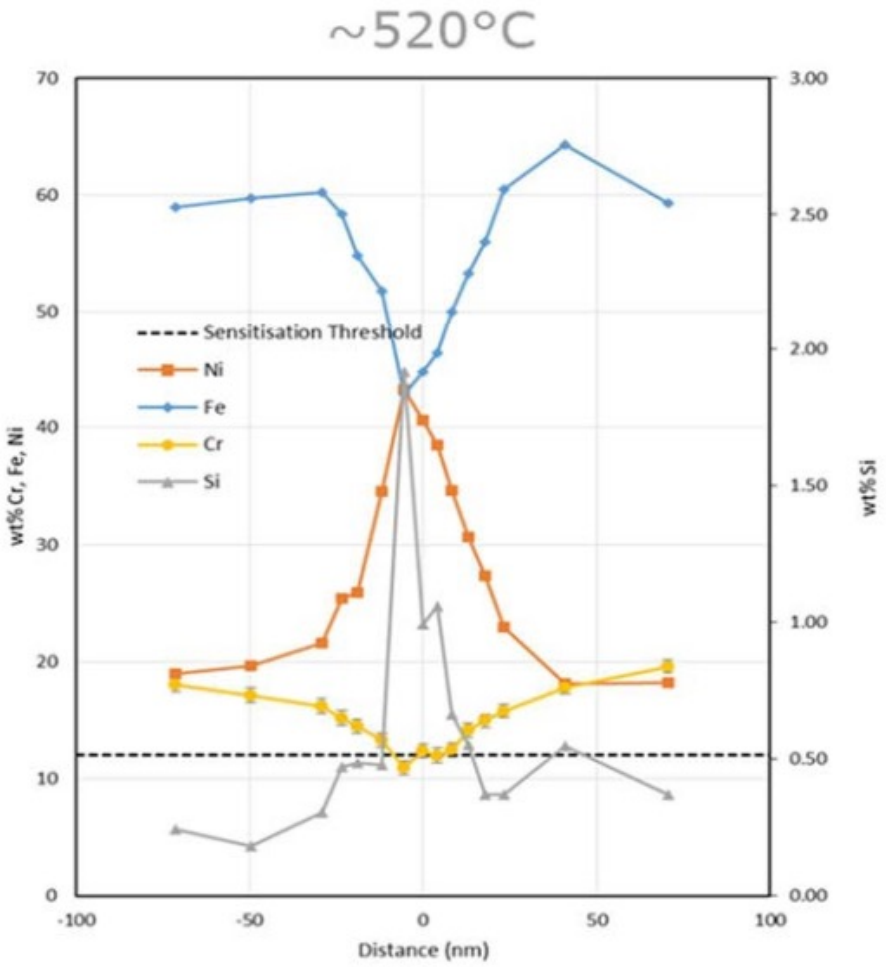
Ion irradiations at DCF (ref 3)



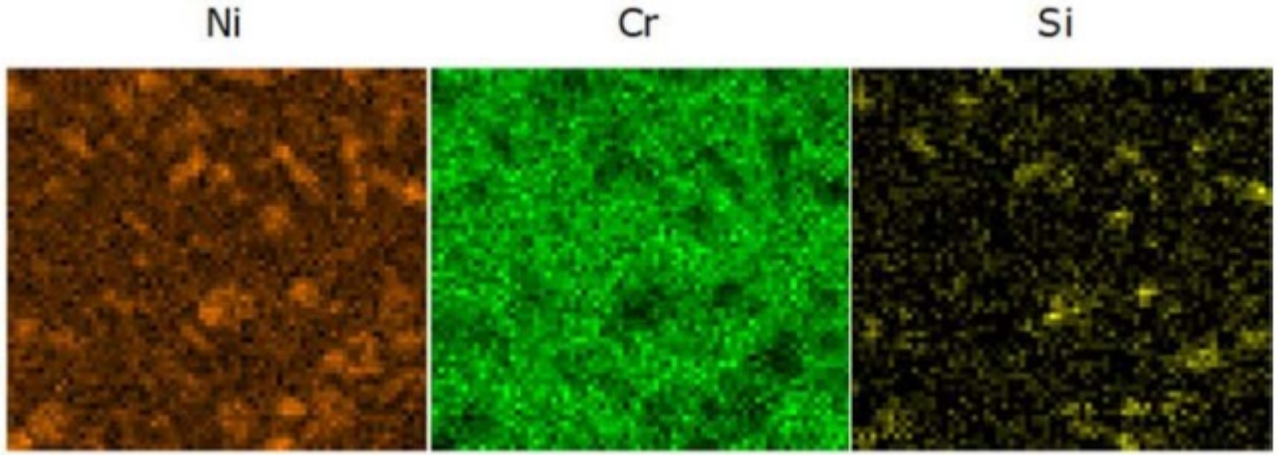
- Segregation at grain boundaries and at intragranular sinks
- Line profiles extracted from maps
- 30 min acquisition, 700pA

Example: 20-25Nb AGR fuel cladding contd.

Neutron irradiated cladding (ref 4)



- Segregation at grain boundaries and at intragranular sinks.
- Very dramatic changes at grain boundaries are possible – down to ~8wt% Cr.
- Note also the different widths of the Ni and Si profiles – precipitation as well as RIS?
- Ni and Si enriched at dislocation loops, sometimes forms detectable Ni_3Si



Data Quality

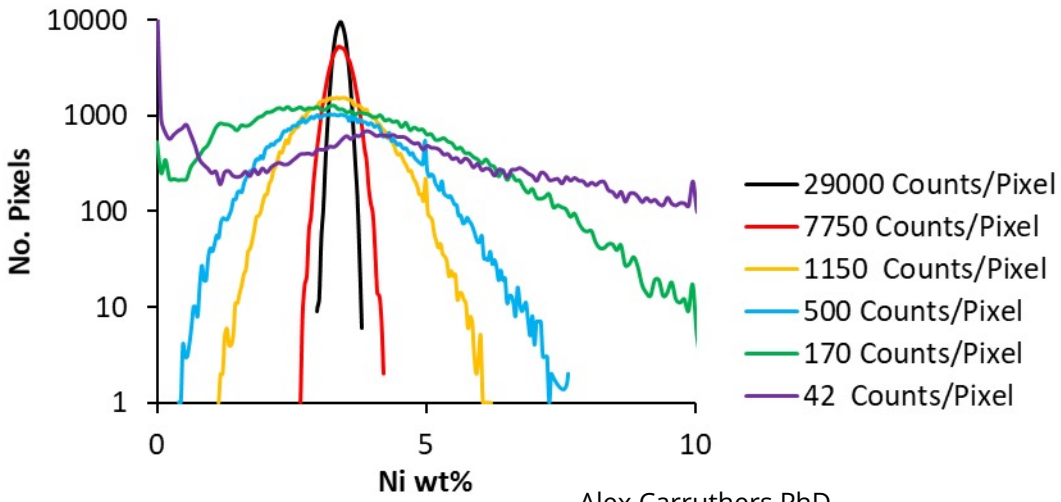
Choices

Map resolution		pix	Total acquisition time (sec)	msec/pix	Output Count rate (cps)	Total X-ray counts per pix
128	128	16384	2400	146	8000	1172

Do we want illustrative data - or quantitative?

Maps can tell a story even with remarkably few counts in them

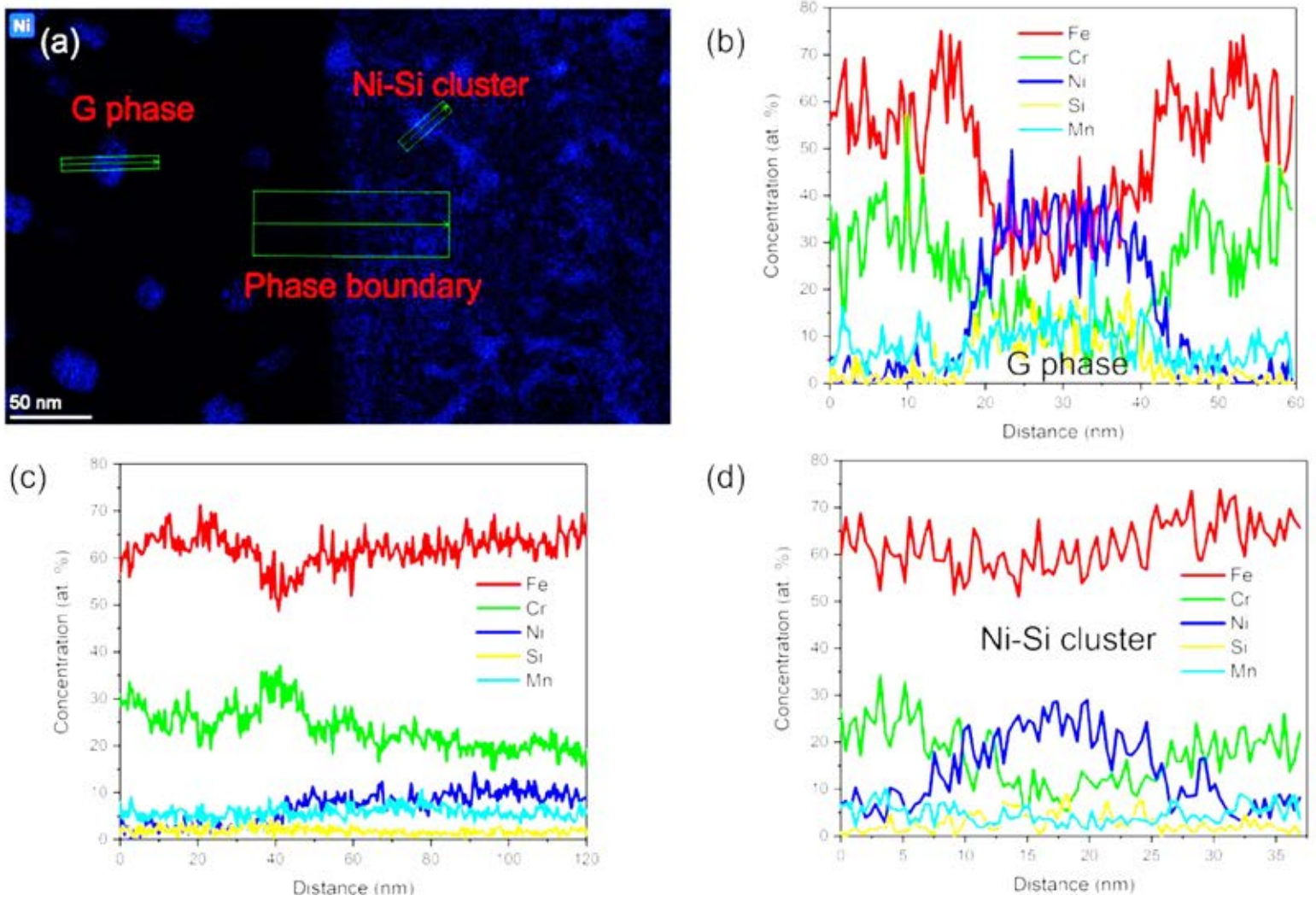
The choices made about the data acquisition obviously affect the data quality



Alex Carruthers PhD thesis

Example of linescan extracted from map data

- From Li et al https://doi.org/10.1016/j.jnucmat.2023.154287



Major elements are ±5 to 10%

Large integration window for gb – is the boundary well-enough aligned for this?

Proton irradiated 308/304 weld

EDS point measurements

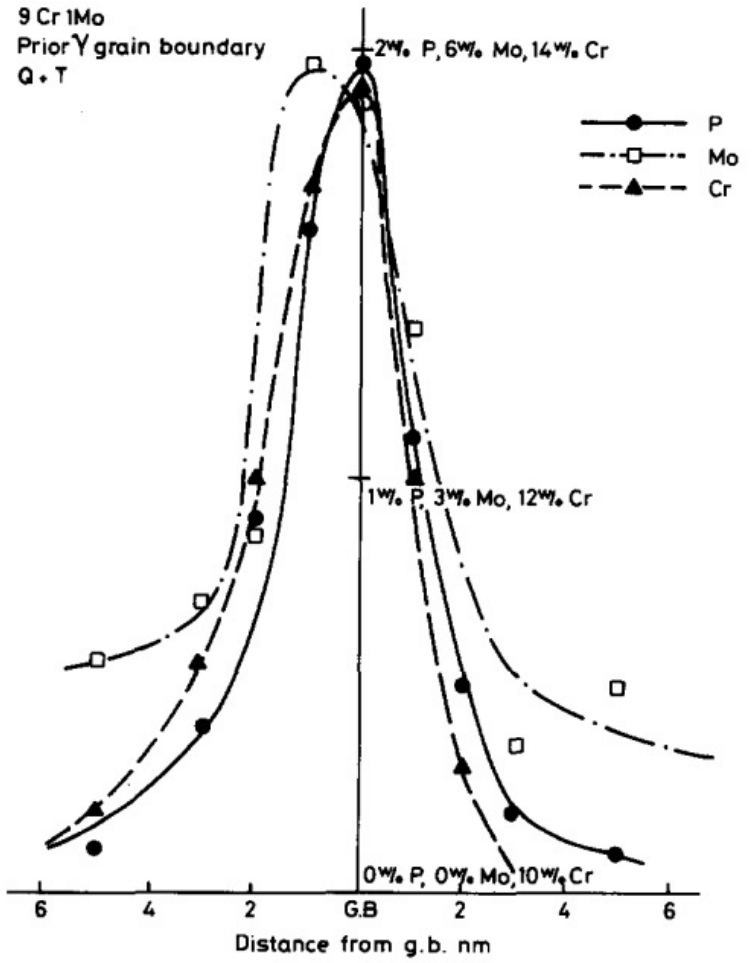


Fig. 1. EDX profiles of chemical composition near a prior austenite grain boundary in a 9wt%Cr–1wt%Mo ferritic steel. Note that the vertical scales are different for the three segregated elements, P, Mo and Cr, and the respective standard errors are 0.26, 0.66 and 0.44 wt%.

- Example from 1989, FEG-STEM, ~1nm probe size, ~700pA, 0.15Sr EDS detector
- Phosphorus segregation ~1.9 +/- 0.26 wt% equivalent to 0.4 monolayers
- 100 second acquisition time per point. Total time ~ 20 minutes (3 minutes with 1Sr detector)
- Acquisition strategy should depend on your needs for the data
- Ref 1

EDS Mapping

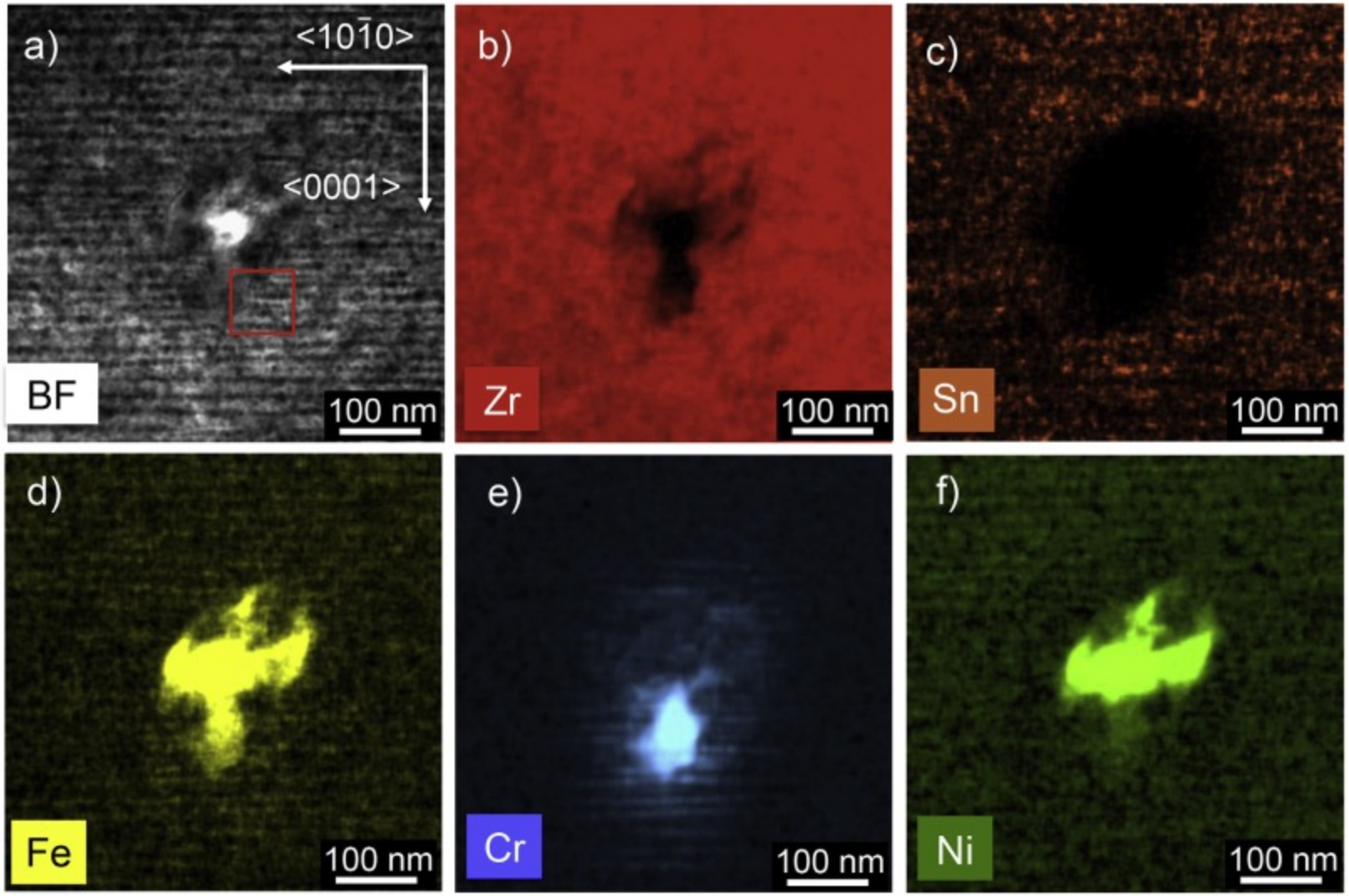
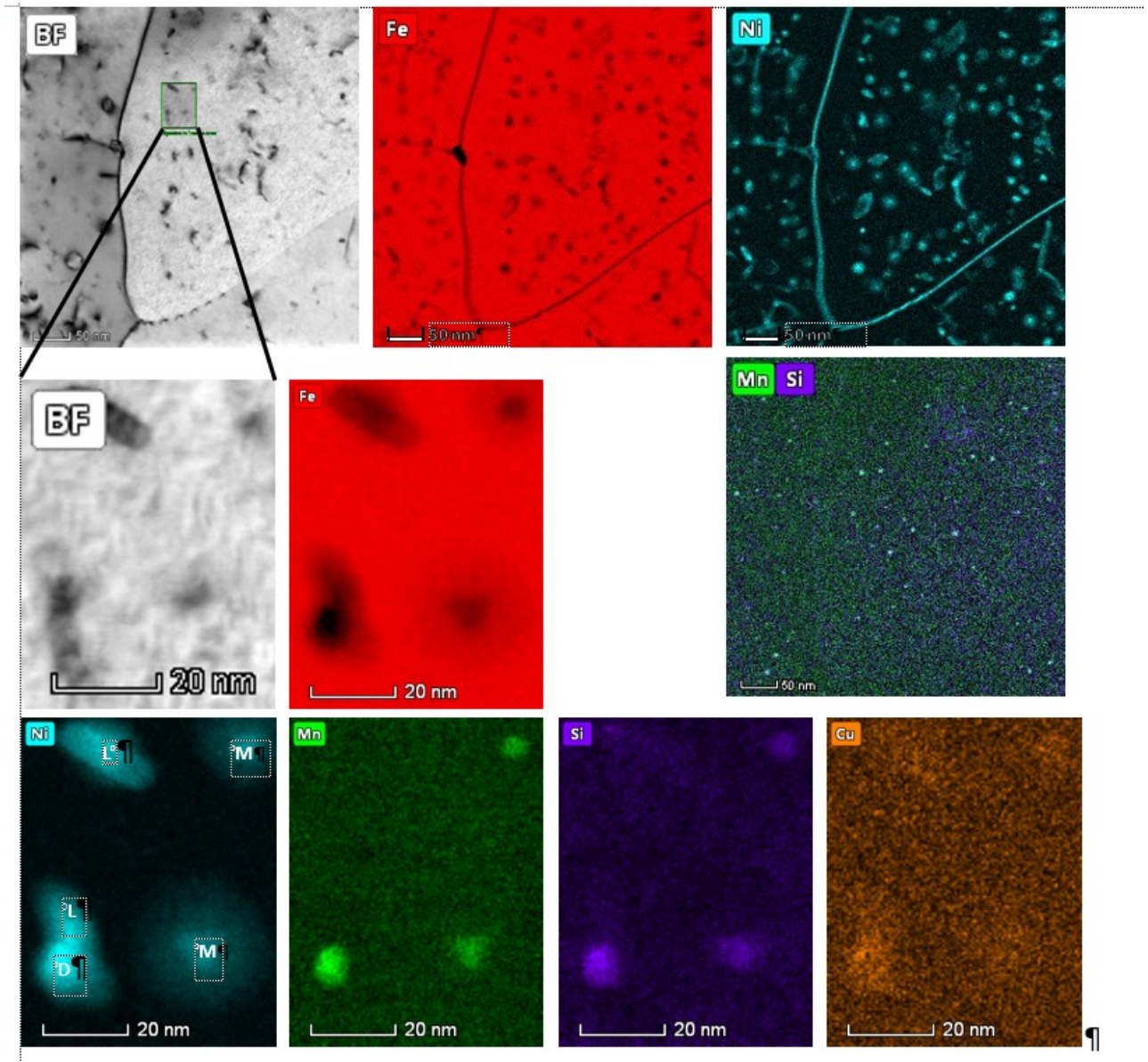


Fig. 7. The zone axis <11$\bar{2}$0> BF STEM image and Zr, Sn, Fe, Cr and Ni chemical maps are displayed in a)-f), receptively for an dissolving SPP with both Fe-Cr and Fe-Ni SPP re
irradiated in a BWR clad to a fluence of 14.7 × 10^{25} n m^{-2} ~24.5 dpa. The red box in a) indicates the region for higher magnification chemical mapping in Fig. 8. (For interpretat

A good example

Ref 7

Mapping example from irradiated A508 Gr4N RPV steel



Proton irradiated at 370°C
Strong segregation of Ni to grain boundaries, multi-element precipitates and dislocation loops

Ref 13

EELS data acquisition

Nice-to-haves

- FEG (for STEM-EELS acquisition), EFTEM

Additional Requirements over EDS:

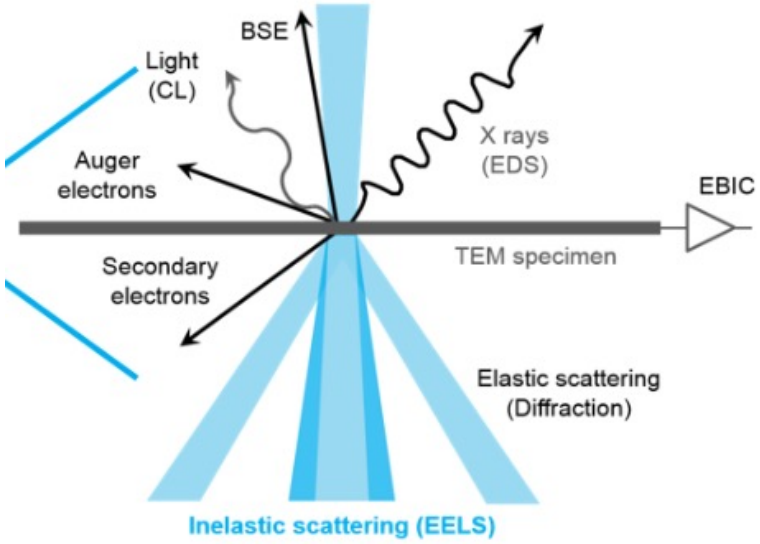
- Sample thickness ideally 30-60nm – but depends on analytical requirements. Too thin = not enough counts. Too thick = multiple scattering, superposition of features, beam spreading, loss of spatial resolution.
- Sample cleanliness. Plasma cleaning is vital on electropolished samples and highly advised even on FIB sections.

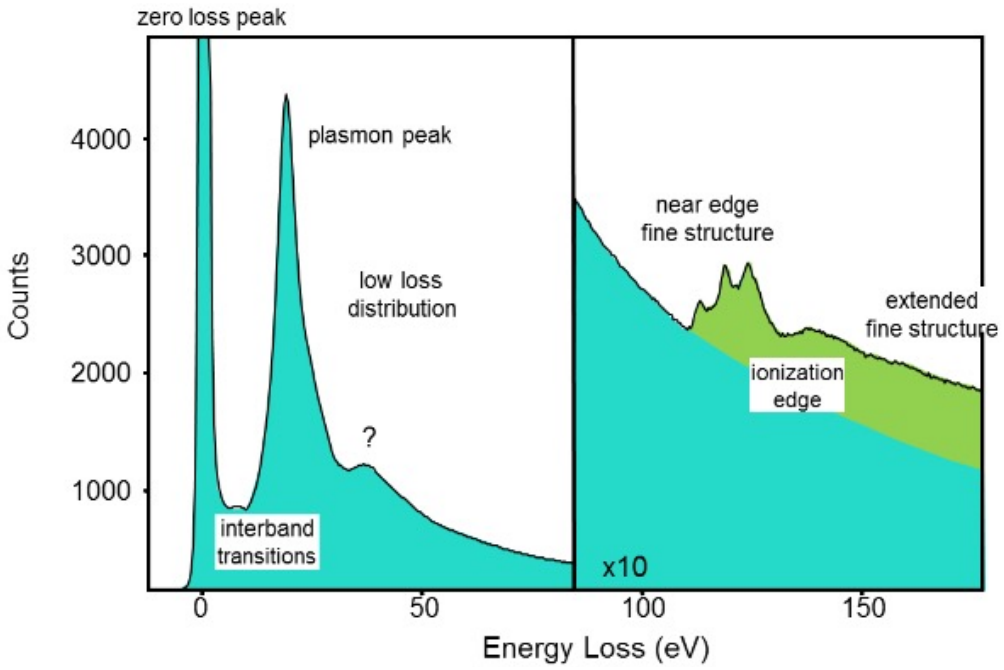
Advantages

- Light element sensitivity
- Can map crystal structures using plasmon mapping
- Sensitive to chemical state
- Insensitive to radiation from sample

Disadvantages

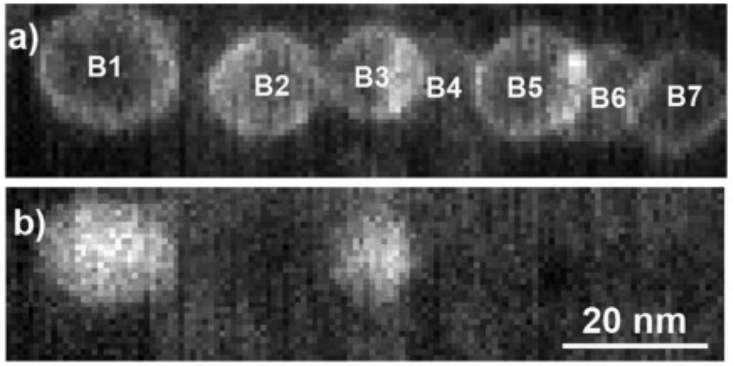
- Quantification is more difficult than EDS
- May require multiple data acquisition runs (different energy ranges

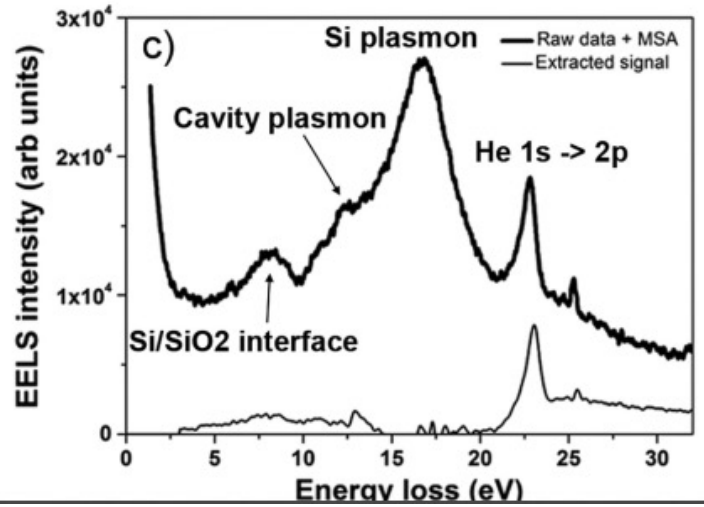




EELS example – He bubbles (1)

Bubbles detected using surface plasmons and He identified from ionization edge





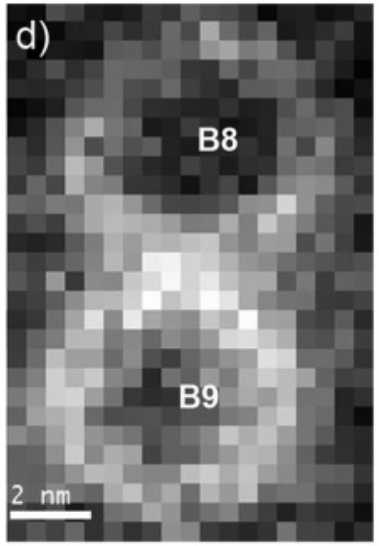
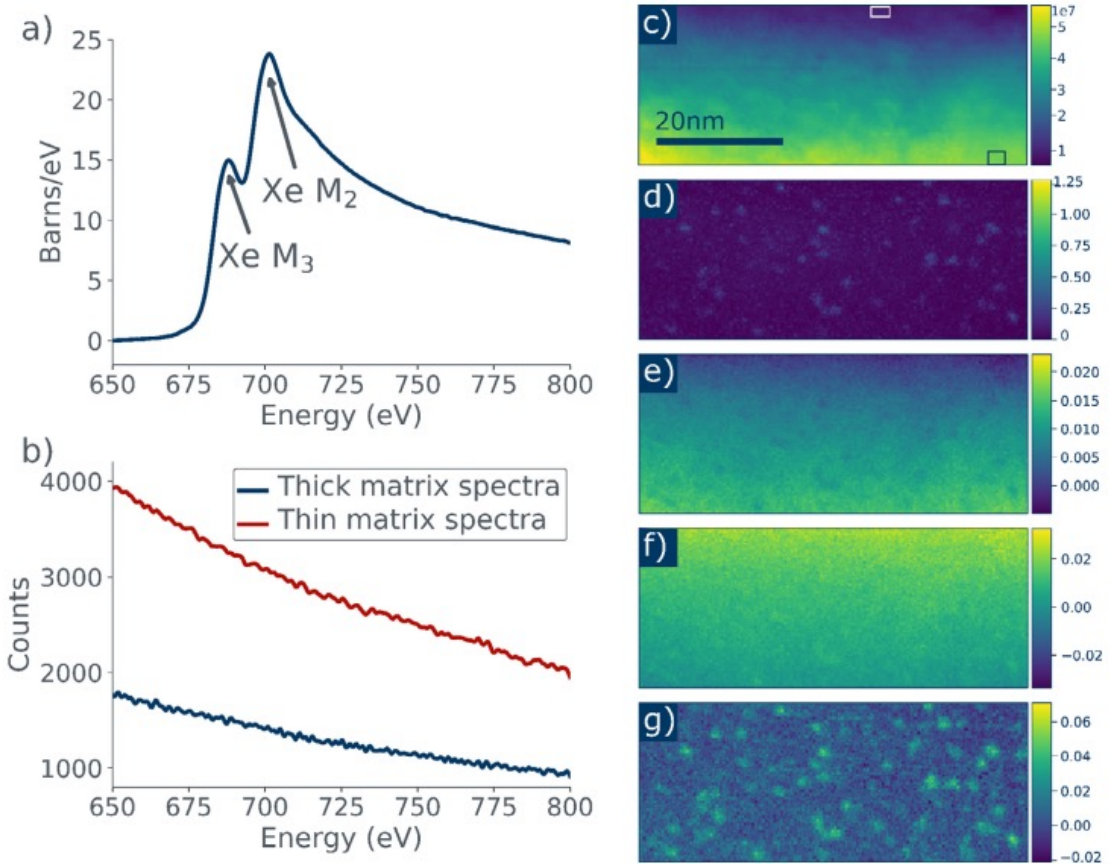


FIG. 2. Helium cavities in silicon. (a) Energy-filtered image in the cavity-plasmon energy range (12.3–13.3 eV) extracted from the spectrum image revealing a string of seven cavities. (b) Helium chemical map on the same area as (a) showing that only the two cavities labelled B_1 and B_3 contain helium. (c) EELS spectra extracted in the middle of B_1 in black (the data are realigned and treated with Multivariate Statistical Analysis[31]) and the corresponding extraction of the helium-K-edge in light black. The small peak at 26 eV is an artefact of the CCD camera due to the intensity of the zero-loss peak. (d) Energy-filtered image in the cavity-plasmon energy range (13.2–14.2 eV) extracted from the spectrum image recorded on two tiny bubbles.

- Ref 6

EELS example – Xe bubbles in Zr4



- MLLS fitting used to deconvolute thickness effects from HAADF image
- Allowed calculation of Xe density in each bubble
- Results showed most bubbles are gas not solid.

- Ref 8

EELS phase mapping

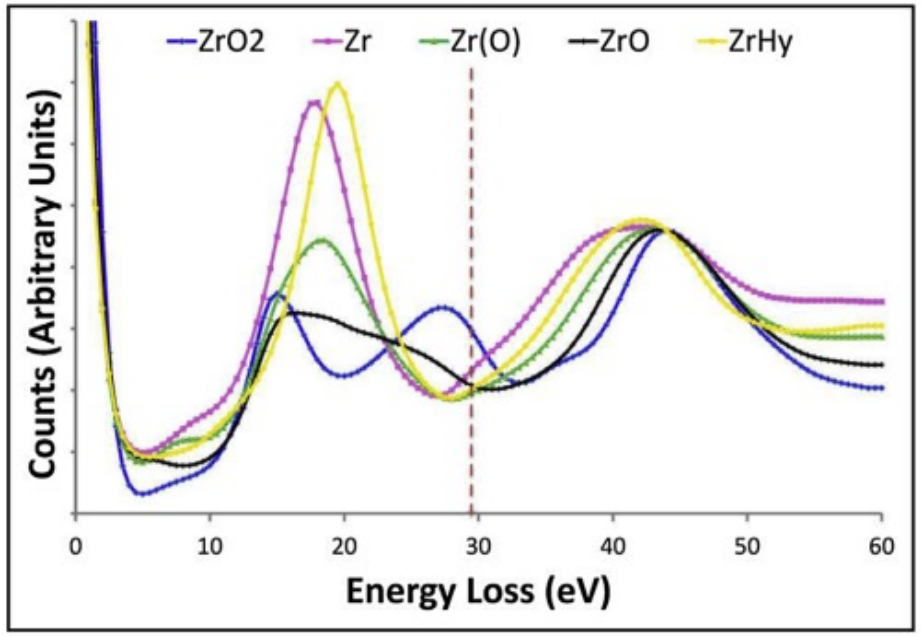
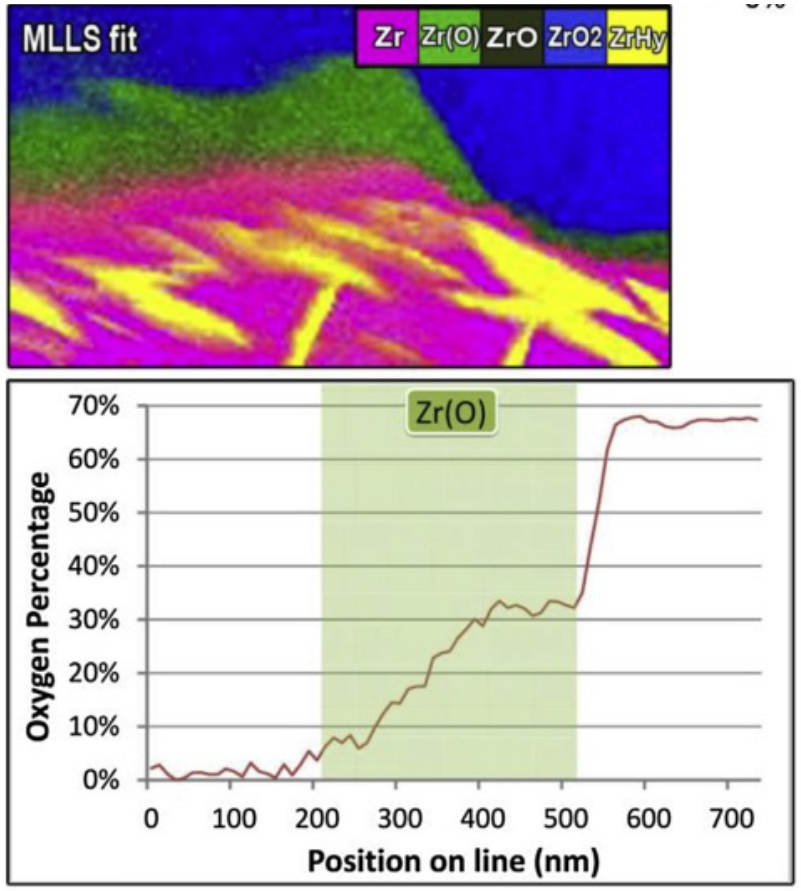


Fig. 1. Representative low loss spectra for each phase in the oxidised material, recorded for a Zircaloy-4 sample corroded in pressurised water reactor (PWR) conditions at 350 °C.



MLLS fitting reveals the distribution of phases near the oxide-metal interface in oxidizing zirconium.

Hydrides are likely due to FIB thinning – and can be avoided by use of cryo-FIB.

EELS – EFTEM Core loss mapping

- Ref 12
- Thickness map locates radiation-induced voids
- Elemental maps show precipitation

- Note:
- Very weak nickel edge
- Single-range EELS acquisition so no silicon data

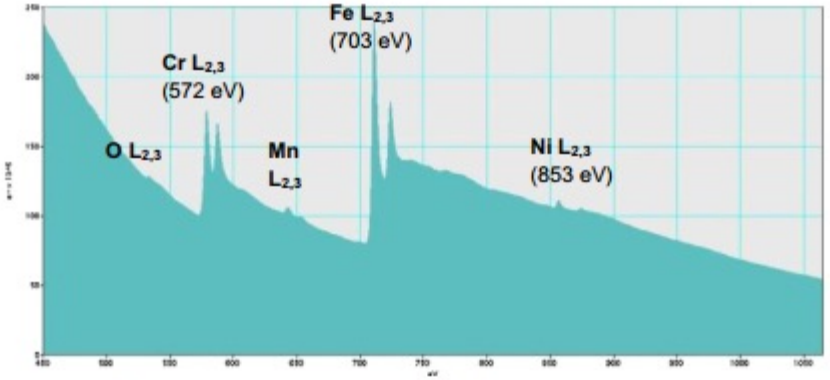
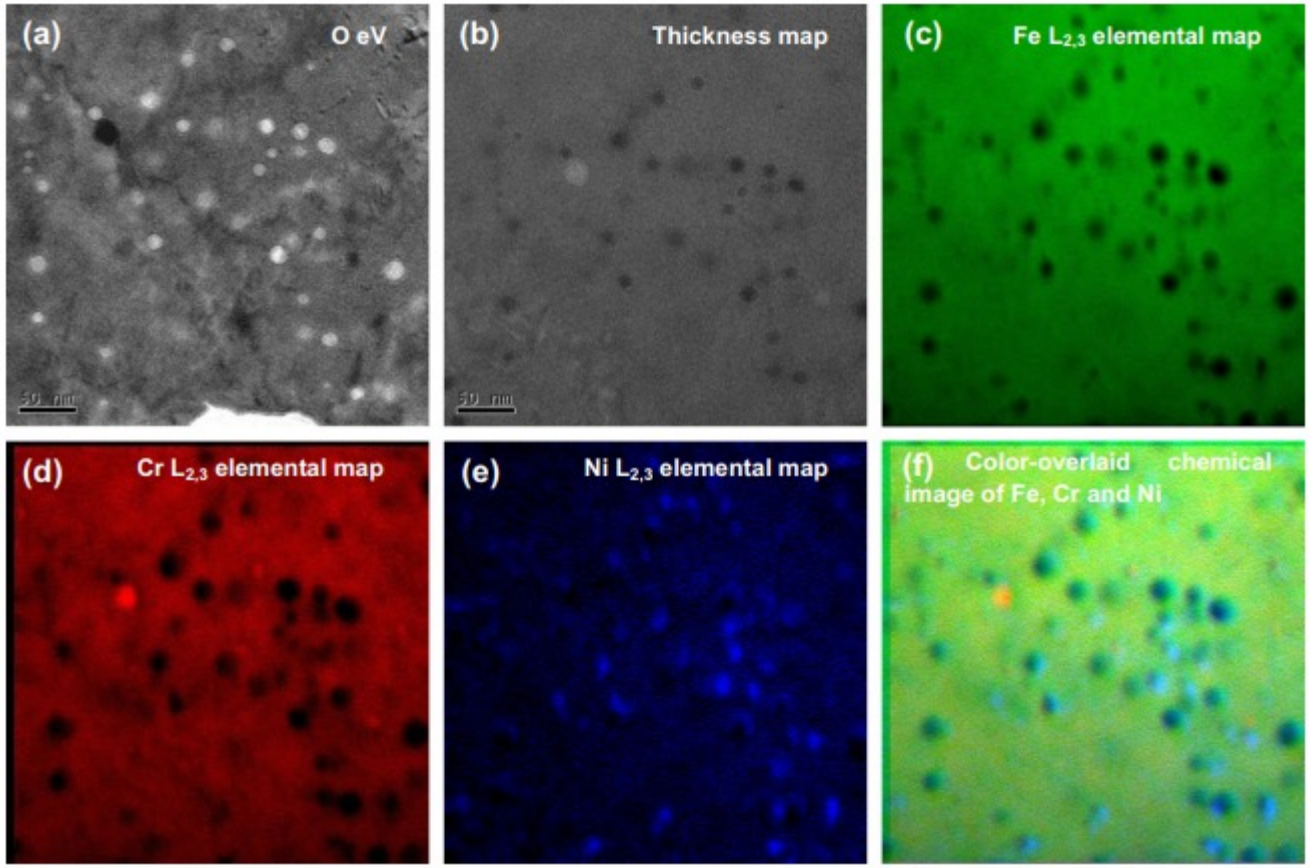


Fig. 7. EEL spectrum obtained in 304L after irradiation at 390 °C up to 36 dpa.



Not protectively marked

EFTEM example

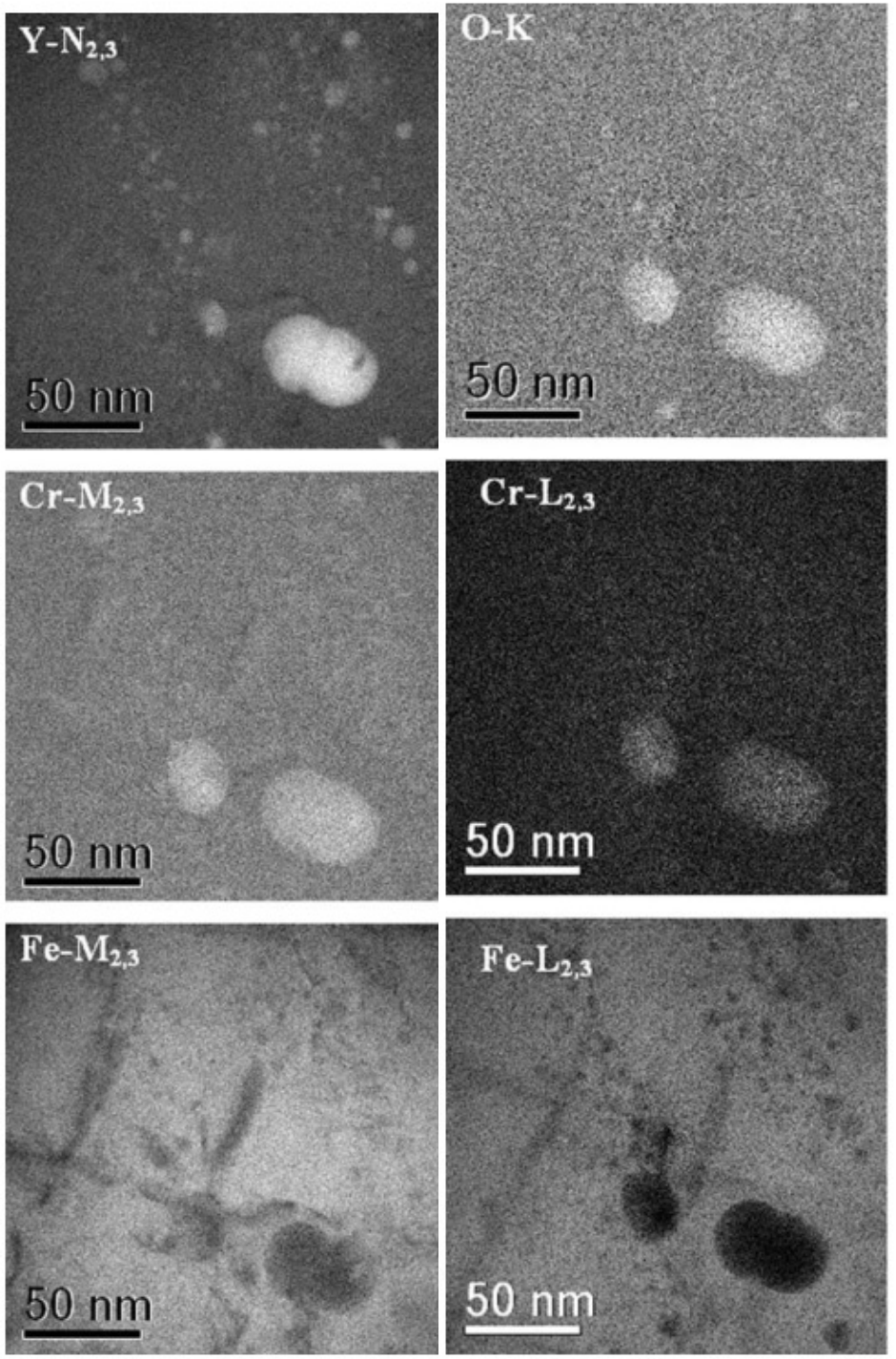
Fe-12Cr +0.4wt%Y_2O_3

Image-Cs corrected JEOL 2200MCO

The correction is important in achieving the resolution shown here

$(Y,Cr)_2O_3$ precipitates down to 5-10nm diameter are detected

Ref 10



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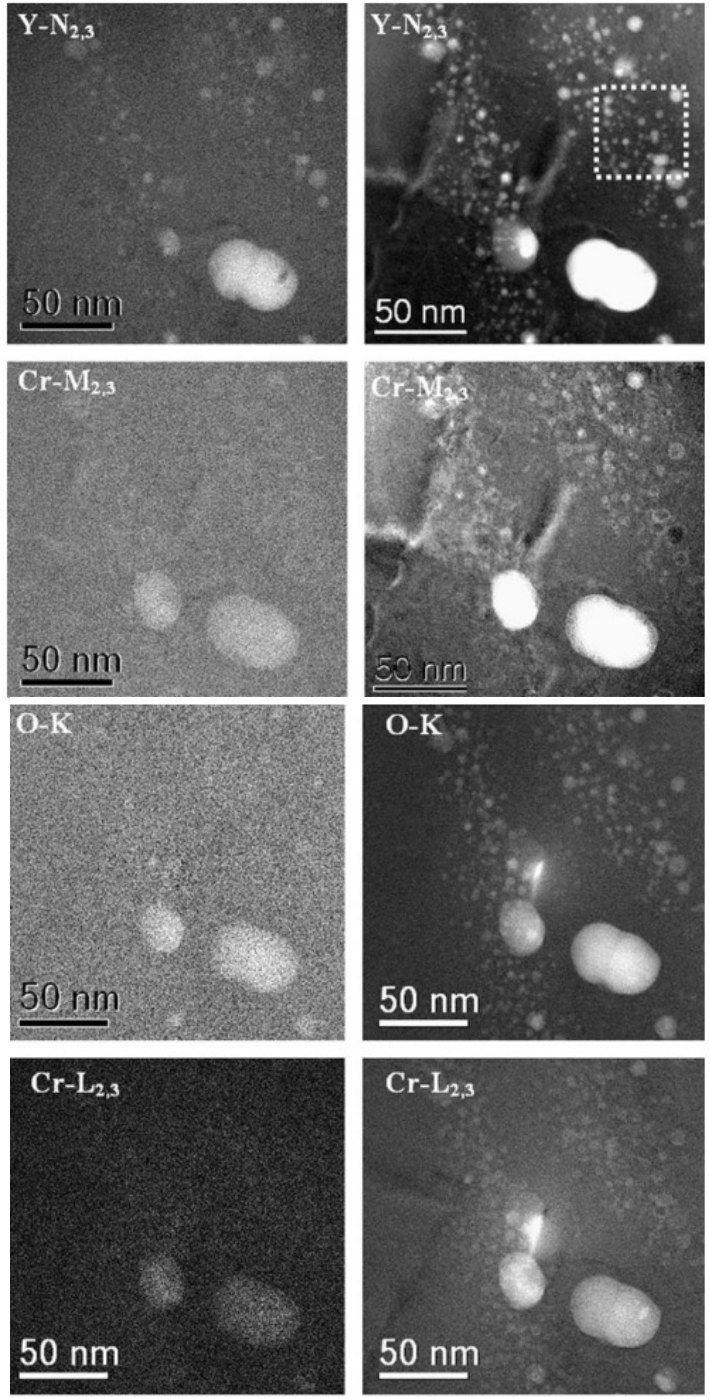
Data Processing

Counting statistics are always an issue (EDX and EELS) and the problem of overlapping signals can add considerable difficulty to the interpretation of data.

MSA or PCA are statistical analysis approaches that can help.

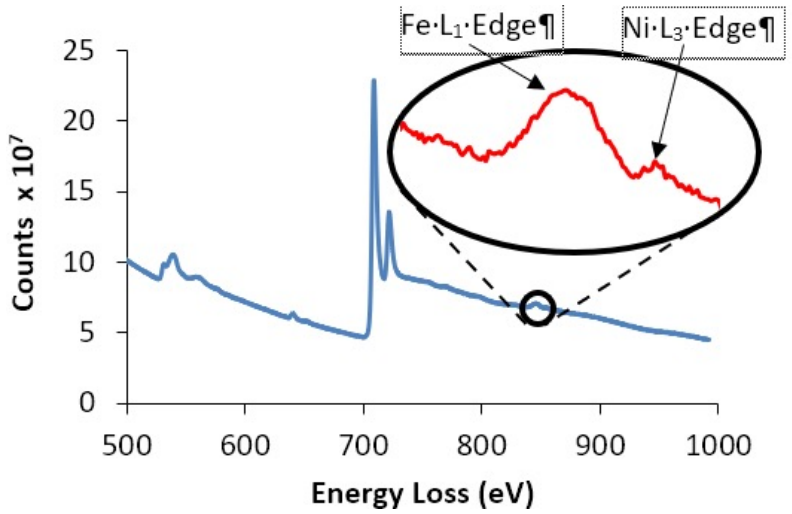
Plugins available for DM, Hyperspy and ImageJ

This example from Ref 10 shows the considerable enhancement in clarity of maps of small $(Y,Cr)_2O_3$ precipitates in a Fe-Cr alloy. (Note that the use of image Cs correction in this work considerably improves the resolution attainable).

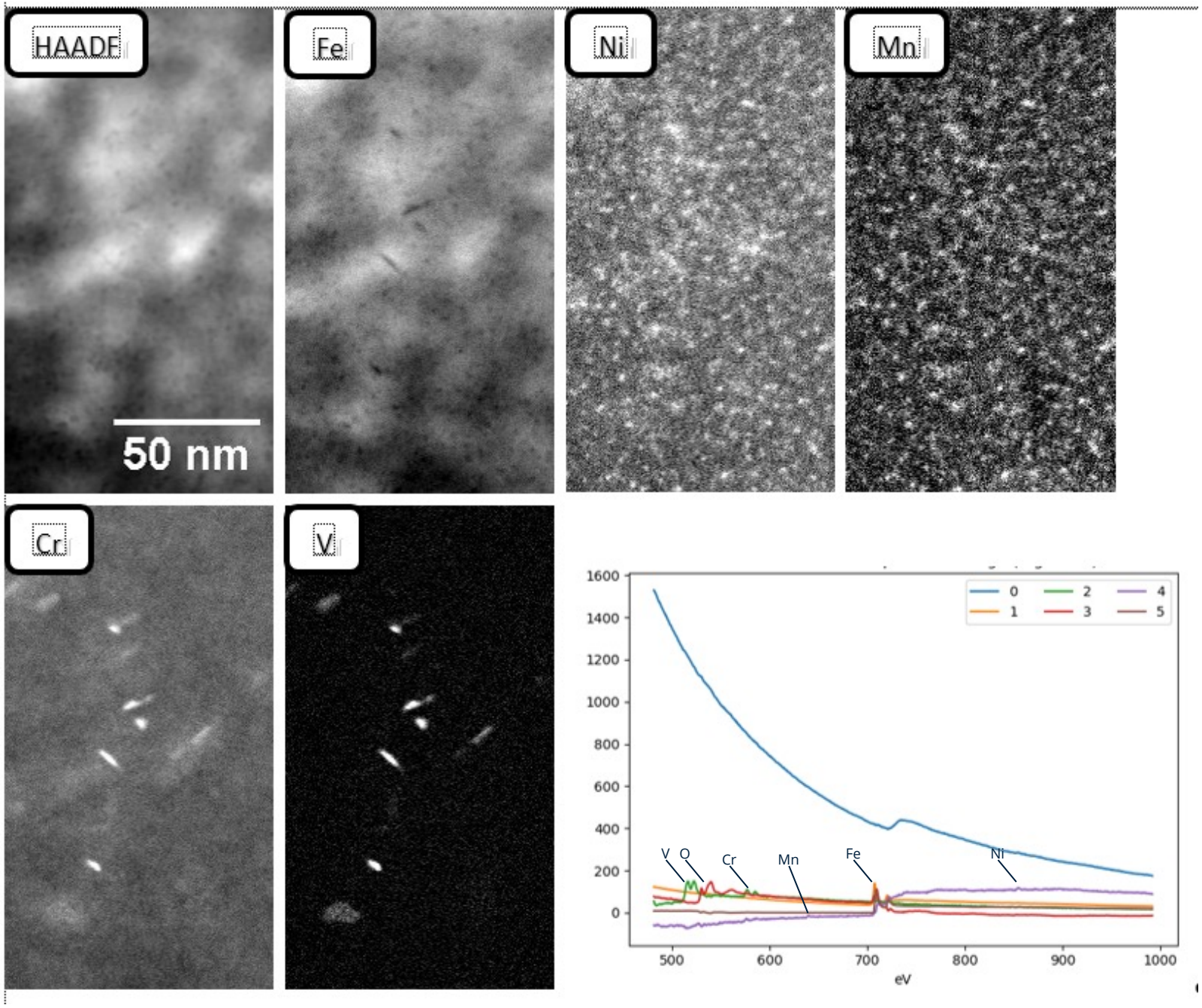


Data Processing contd.

Background fitting in EELS can be difficult due to overlapping edges or plasmons.
Statistical analysis methods can be used to overcome this problem



Ref 13



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Thank you

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