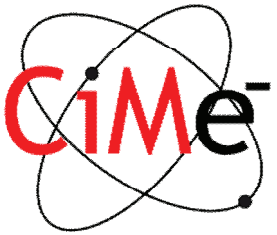
Microanalyse en 3D par MEB-FIB

Limitations, Potentiel et Perspectives



Pierre Burdet

Marco Cantoni

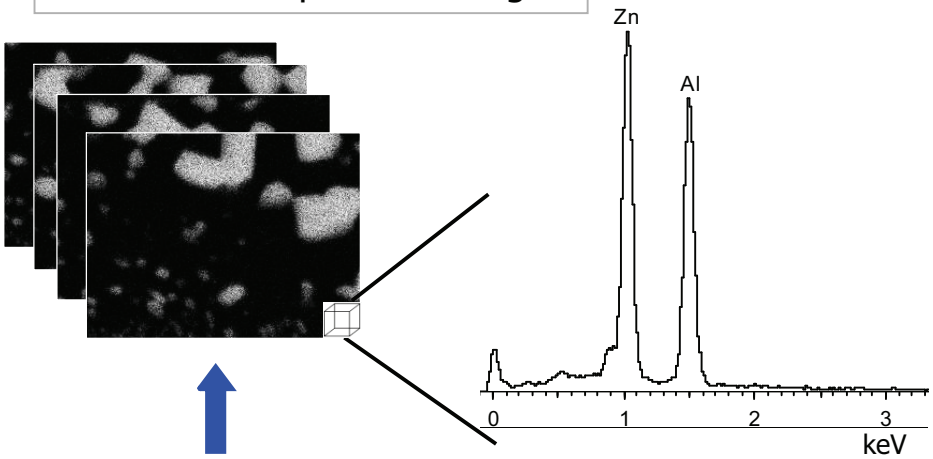
Outline

- Introduction
  - 3D EDX by FIB/SEM
- Limits
  - Spatial resolution
  - Acquisition time
  - Acquisition geometry
- Applications
  - Potential : NiTi and stainless steel welding by laser
  - Perspective : Algorithm for enhanced quantification on Al-Zn
- Conclusions

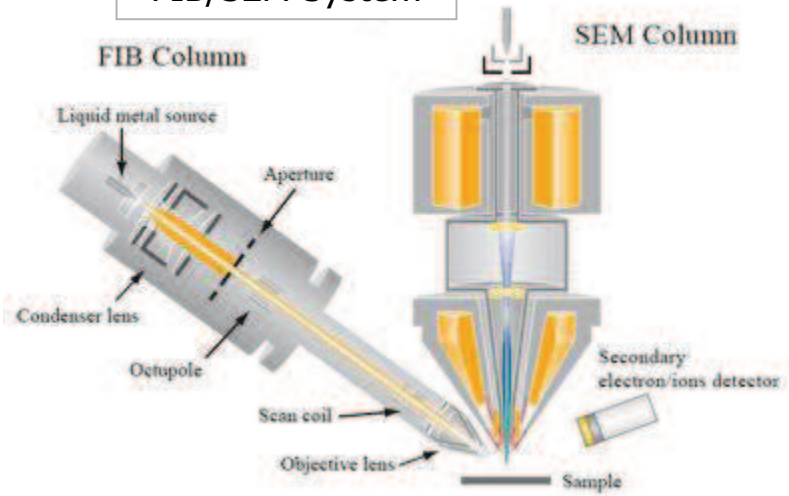
Introduction: 3D EDX by FIB/SEM

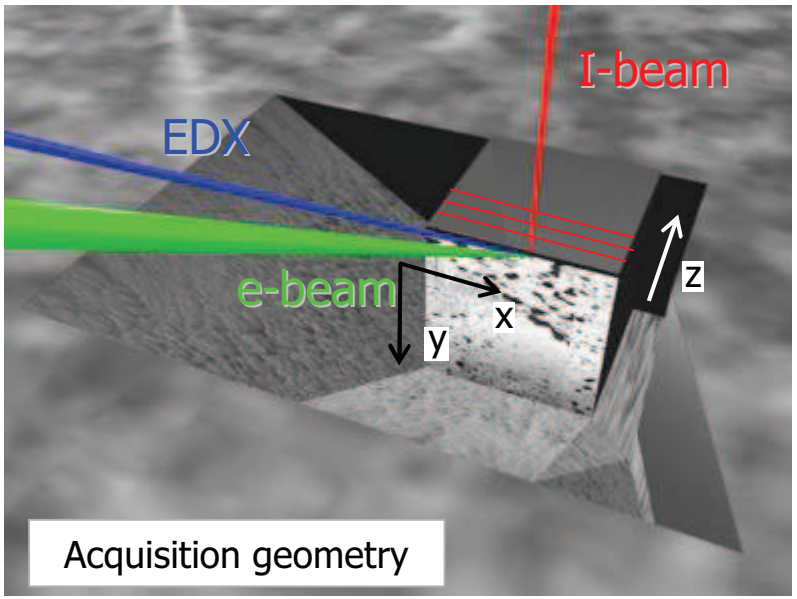
- FIB/SEM (54°)
  - Surface tilt 36°
  - Azimuth 90° and TOA 27° (Zeiss FIB/SEM)
- 3D Acquisition
  - Serial sectioning
  - Serial EDX mapping

Stack of EDX spectrum images



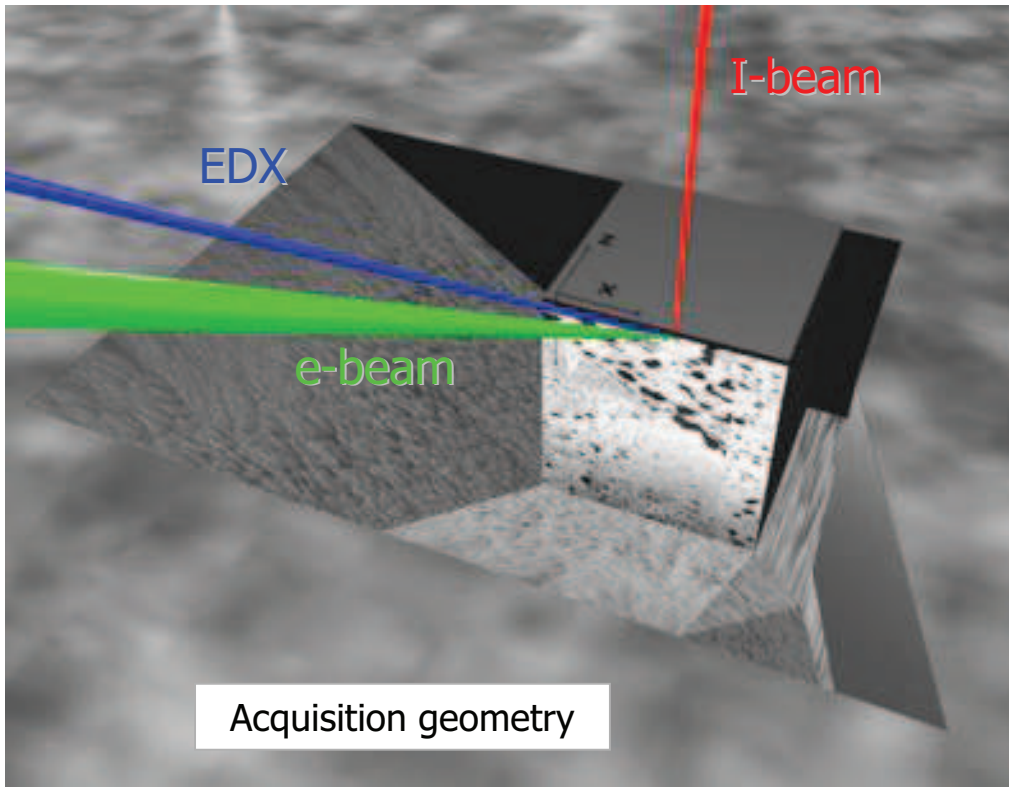
FIB/SEM System





Introduction: 3D EDX by FIB/SEM

- EDX mapping 2D vs. 3D
  - Sequential acquisition
    - Time consuming
    - Drift
  - Acquisition geometry
    - Surface tilted 36°
    - Trenches



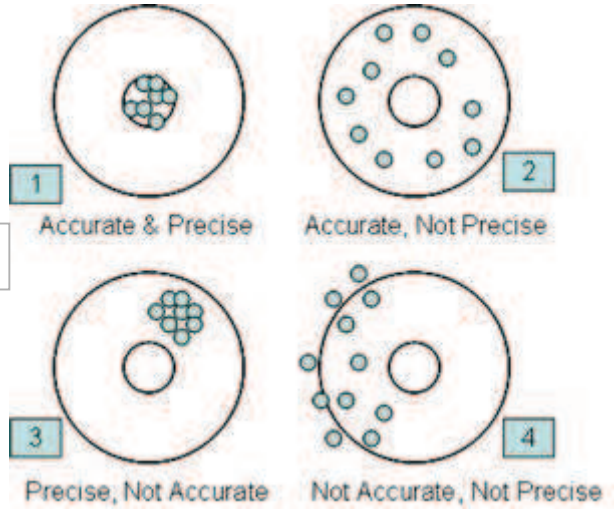
Limits: Overview

Resolution → - E_0
- Materials

Volume → - Time total
- Time per sequence (milling imaging)

Analyze → Precision → - Time per pixel
- Detector acquisition rate

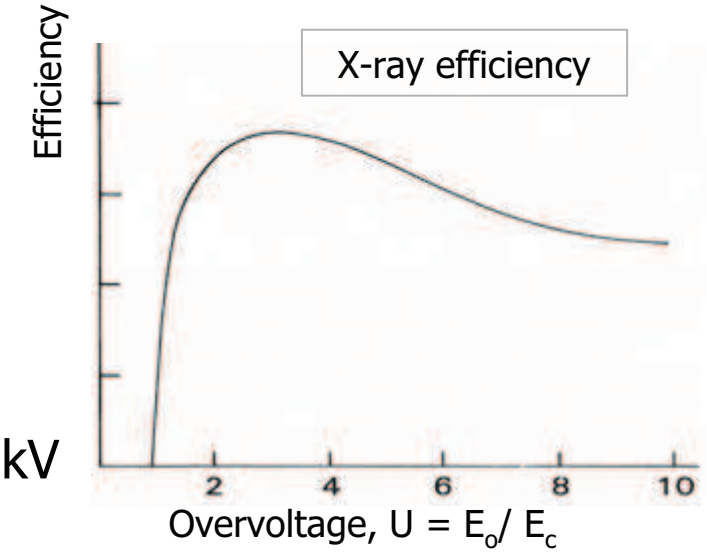
Analyze → Accuracy → - Quantification
-Acquisition geometry (Parasite X-rays)
-Microvolume

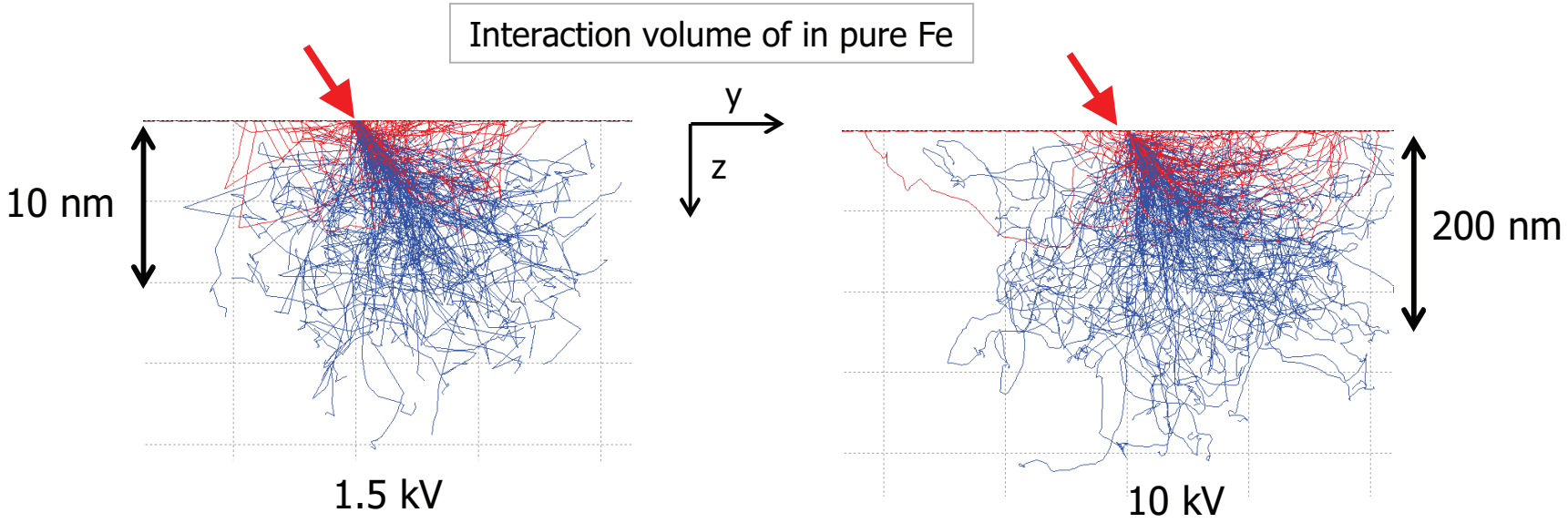


Accuracy vs. precision

Limits: Spatial resolution

- Electron beam energy (E_0)
  - Interaction volume size
  - SEM (SE or BSE): Low E_0
  - EDX: high E_0
    - High enough to excite X-rays
    - Fe Kα (6.4 keV) → minimum of 10 kV

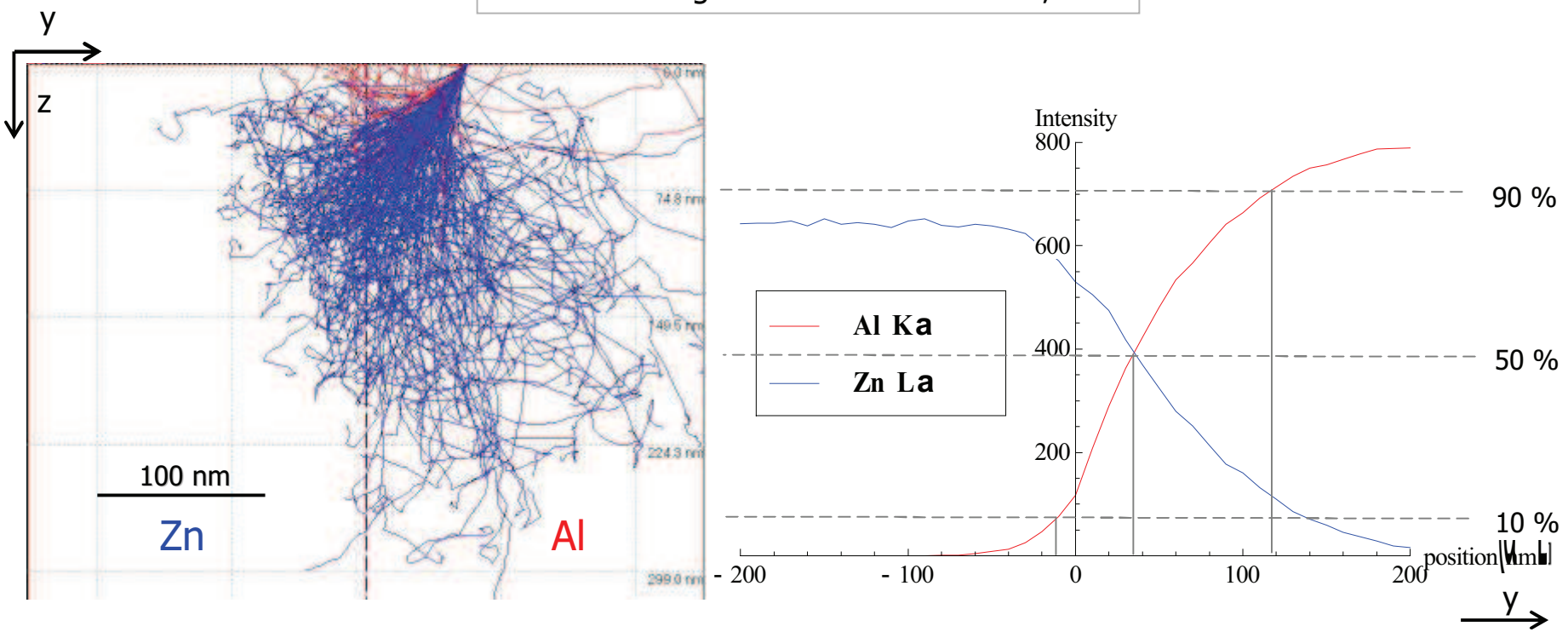




Limits: Spatial resolution

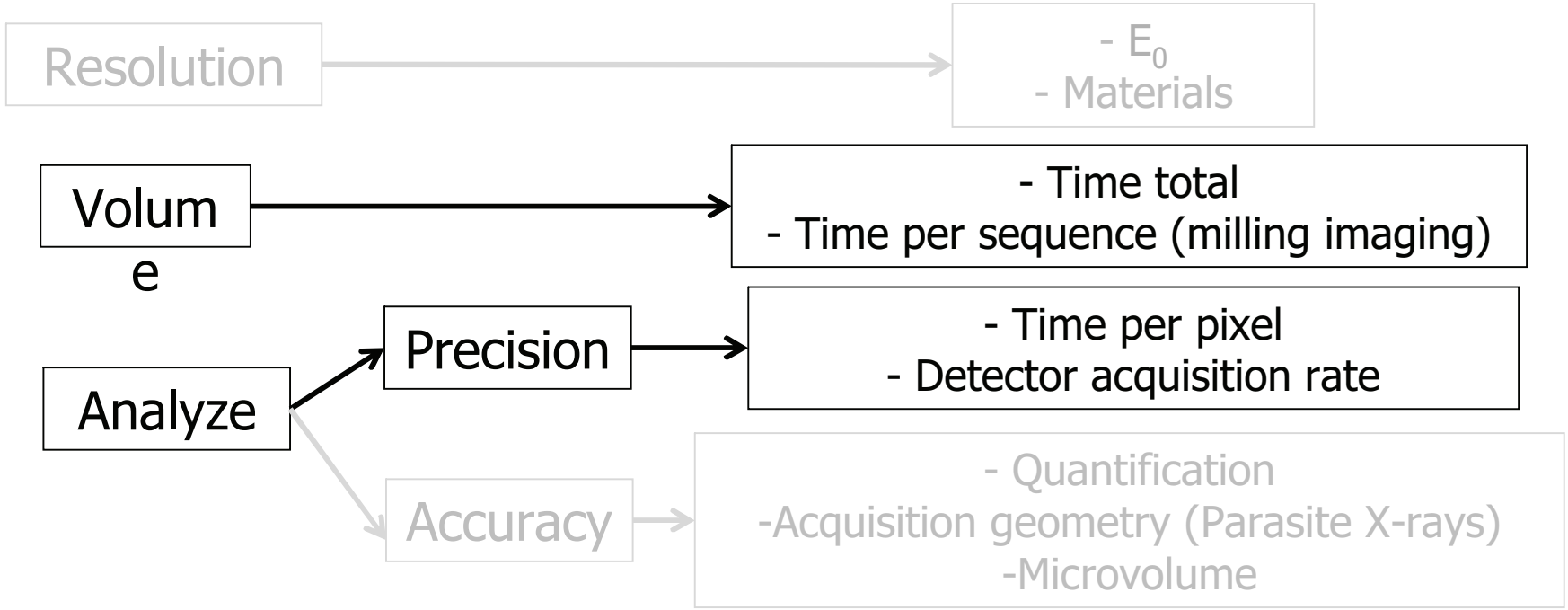
- Generated X-ray distribution
  - Spread along beam axes: z and y (tilt 36°)
  - Impact on resolution and delocalisation
    - Depending on materials and interface geometry

Linescan trough Al-Zn interface at 5kV, 36°



Limits: Acquisition time

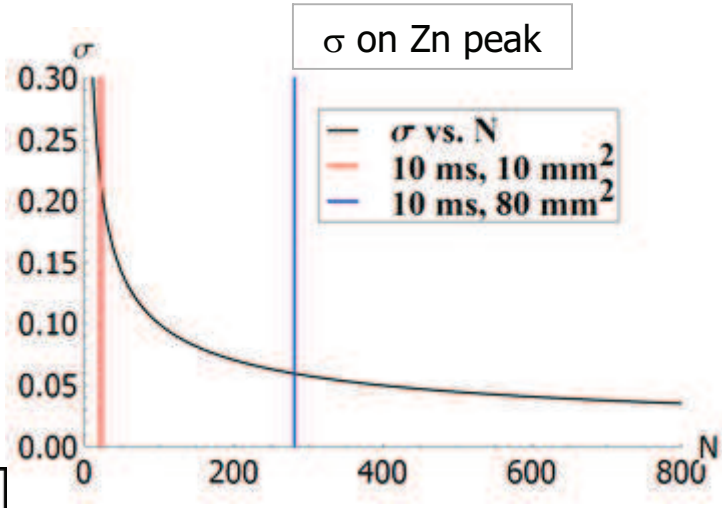
– Total time available
  - ~ 24 hours
– For significant volume (no. of slices)
  - Several EDX maps per hours (FIB milling fast)
  - → Some tens of milliseconds per spectrum



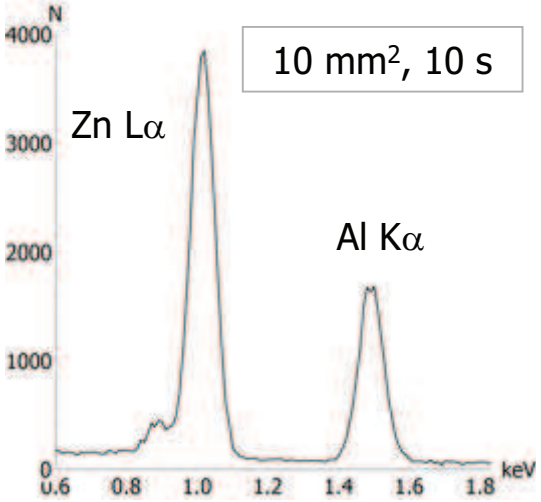
Limits: Acquisition time

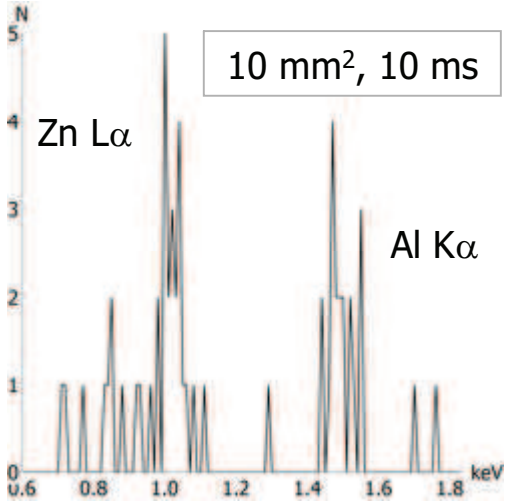
- Detector acquisition rate
  - SiLi vs. SDD
  - Active surface (10 mm^2 → 80 mm^2)
- Analyses
  - Limited by counting statistics
  - σ follows Poisson law

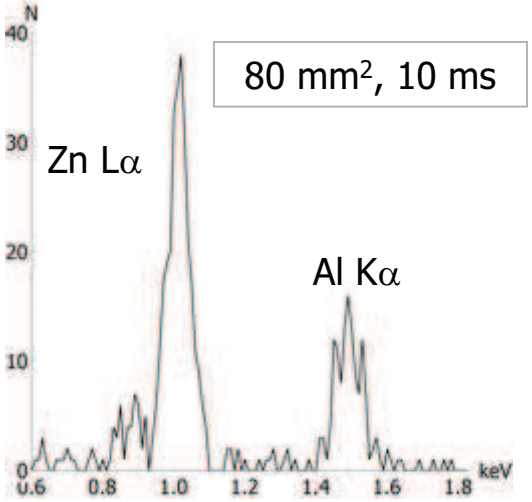
$$\sigma \propto \frac{1}{\sqrt{N}}$$



Spectrum at 5 kV, 1 nA, SDD

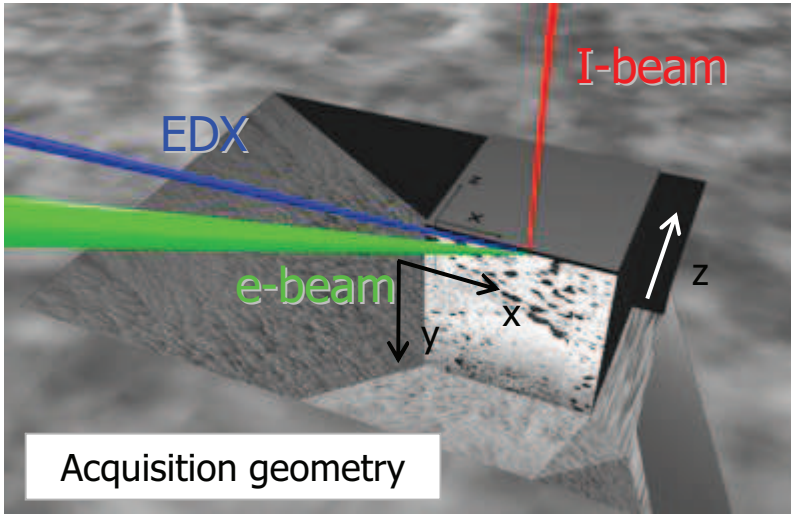






Limits: Acquisition geometry

– Trenches
  - Shadowing of detector
  - Parasite X-rays



Resolution → - E_0 - Materials

Volume → - Time total - Time per sequence (milling imaging)

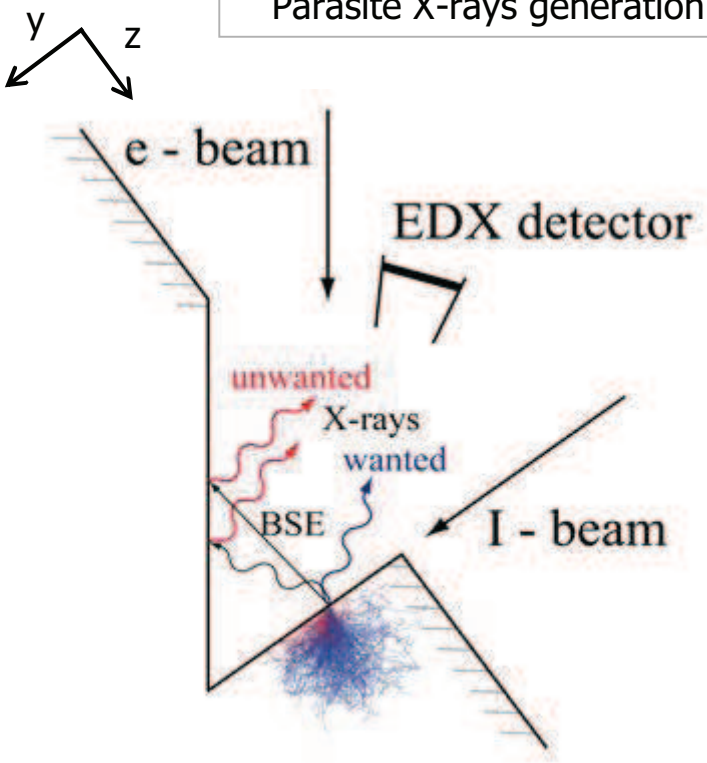
Analyze → Precision → - Time per pixel - Detector acquisition rate

Analyze → Accuracy → - Quantification -Acquisition geometry (Parasite X-rays) -Microvolume

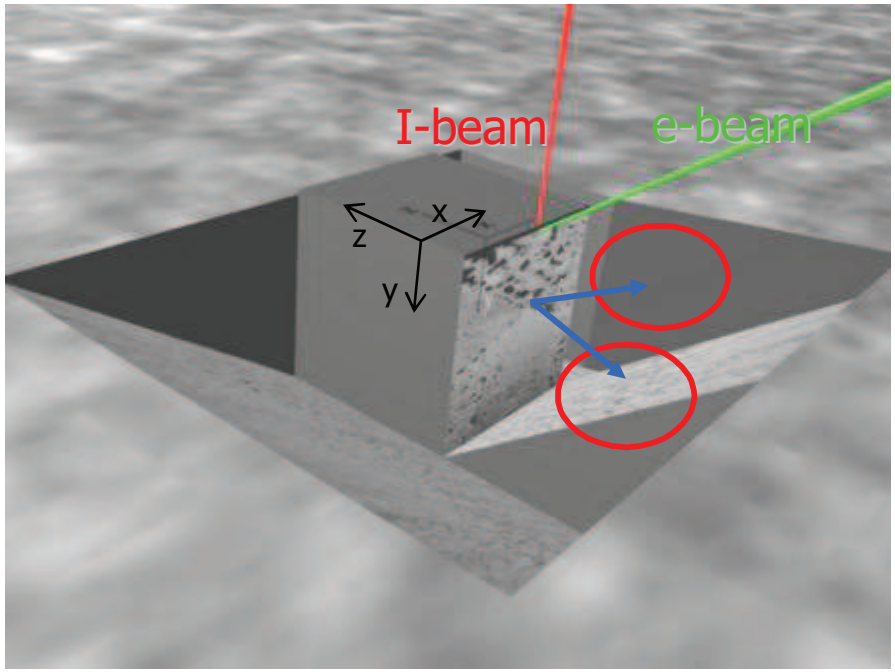
Limits: Acquisition geometry

– Parasite X-rays generated by
  - BSE hitting the surrounding
  - X-rays hitting the surrounding (Fluorescence)

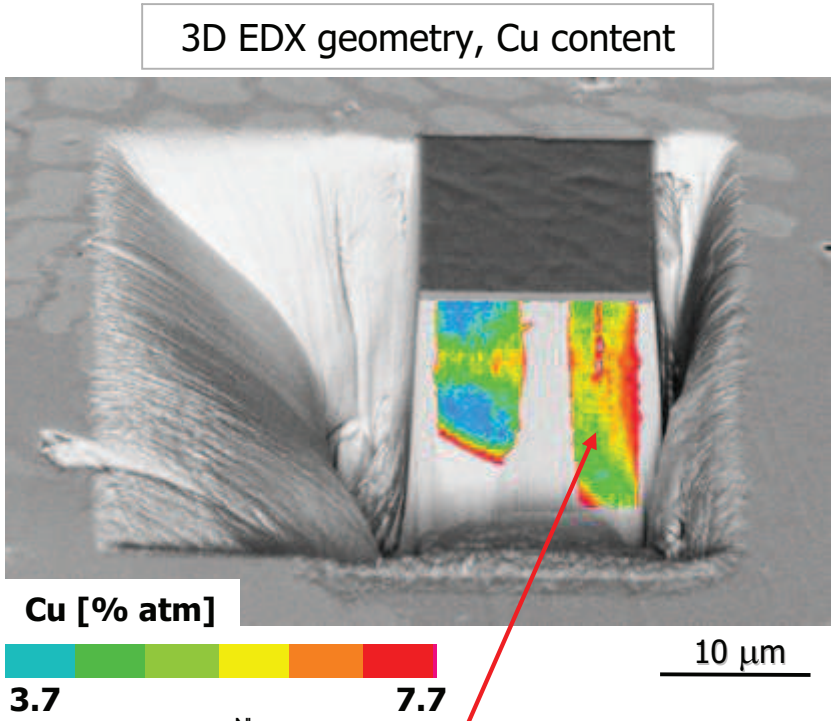
Parasite X-rays generation



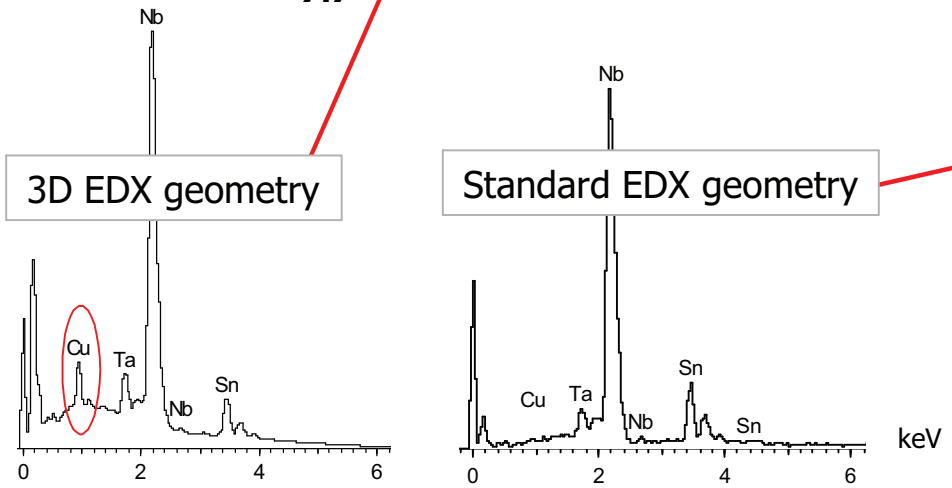
Detector's "view"

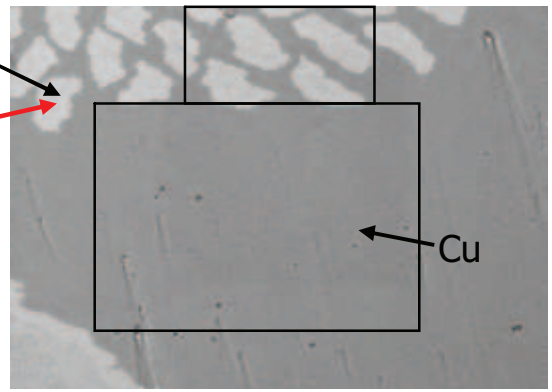


Limits: Acquisition geometry



- Highlight parasite X-ray
  - Trenches of copper
  - Face with wires of Nb_3Sn
- Parasite signal of Cu
  - Up to 7% atm (at 7 kV)
  - Up to 20% atm (at 20kV)
  - Depends on position



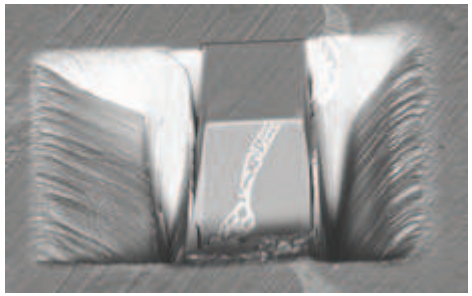


Limits: Acquisition geometry

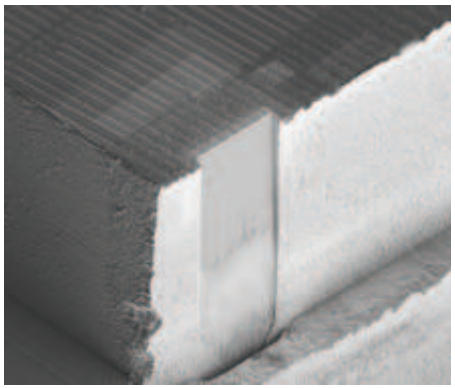
– Solutions
  - Move the wall facing detector further away
    – Mean 4 % atm of Cu for 7kV (5.5 % for normal geometry)
  - VOI at the corner of the sample
  - Remove VOI out of surrounding : Block lift-out

Small trench

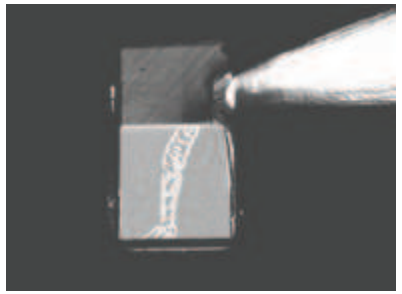
Wider trench



VOI at the corner



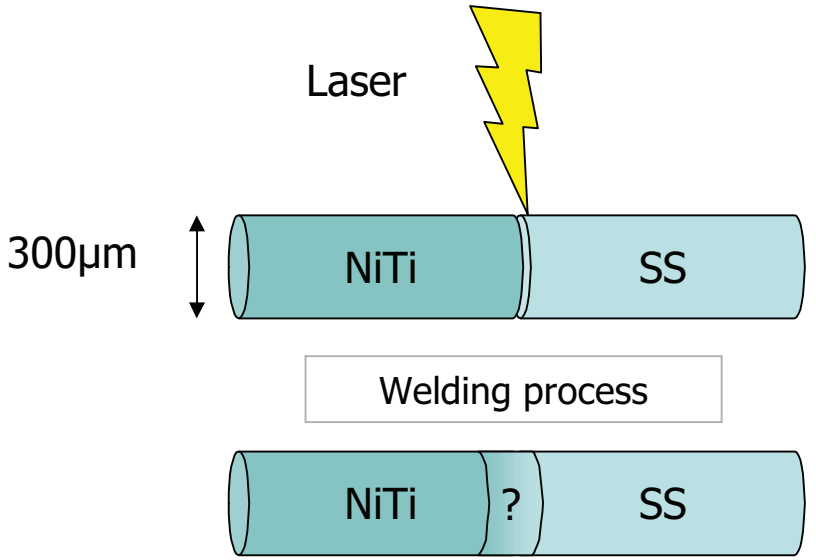
Block lift-out

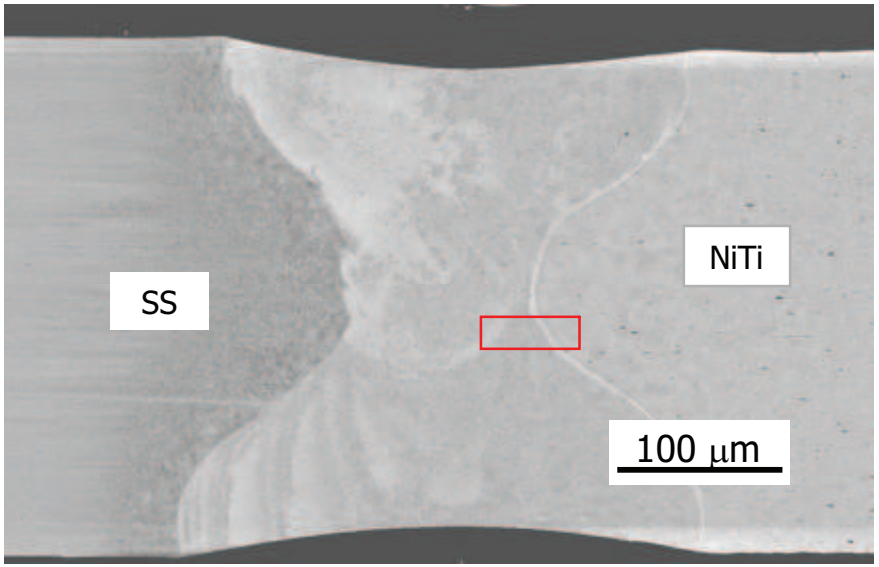


M. Schaffer and J. Wagner, Microchimica Acta 161:3-4 , pp. 421—425 (2008)

NiTi - steel welding

- Potential
  - NiTi – stainless steel welding
    - Biomedical application
  - Complex microstructure
    - Intermetallic phases
  - Fracture location
    - In weld close to NiTi



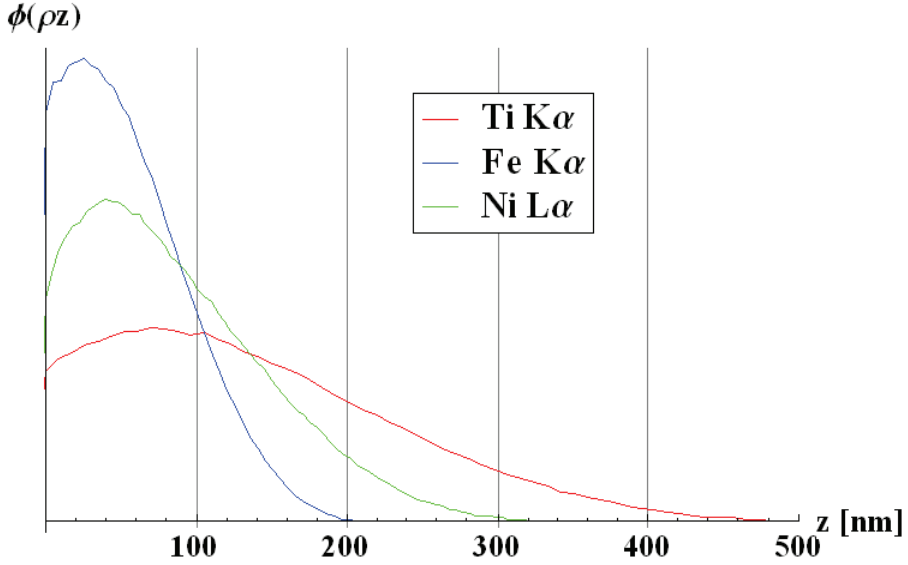


Longitudinal cut through welded wires

NiTi - steel welding: Acquisition

- FIB/SEM
  - Zeiss Nvision 40
  - EDX: Oxford X-Max 80mm^2
- Acquisition
  - E_0: 10 kV
- EDX map
  - Voxel: 100 x 100 x 100 nm
  - 30 ms per spectrum
- SE image
  - Voxel: 12.5 x 12.5 x 12.5 nm

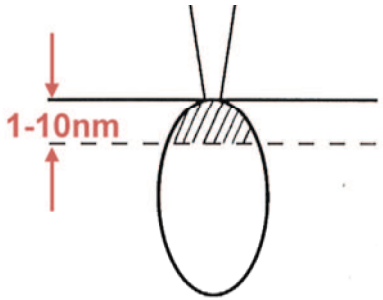
X-ray depth distribution at 10kV



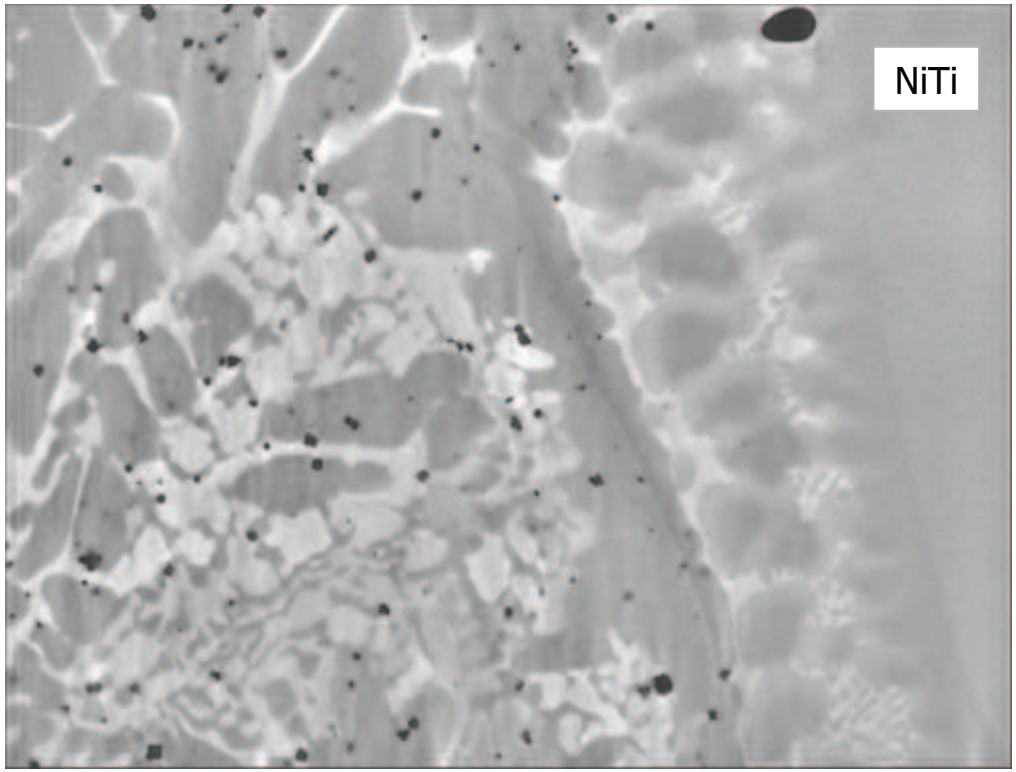
NiTi - steel welding: SE image

– SE (Secondary e^-) image
  - Contrast: phase (no direct interpretation)
  - Resolution: < 10 nm

SE escape depth

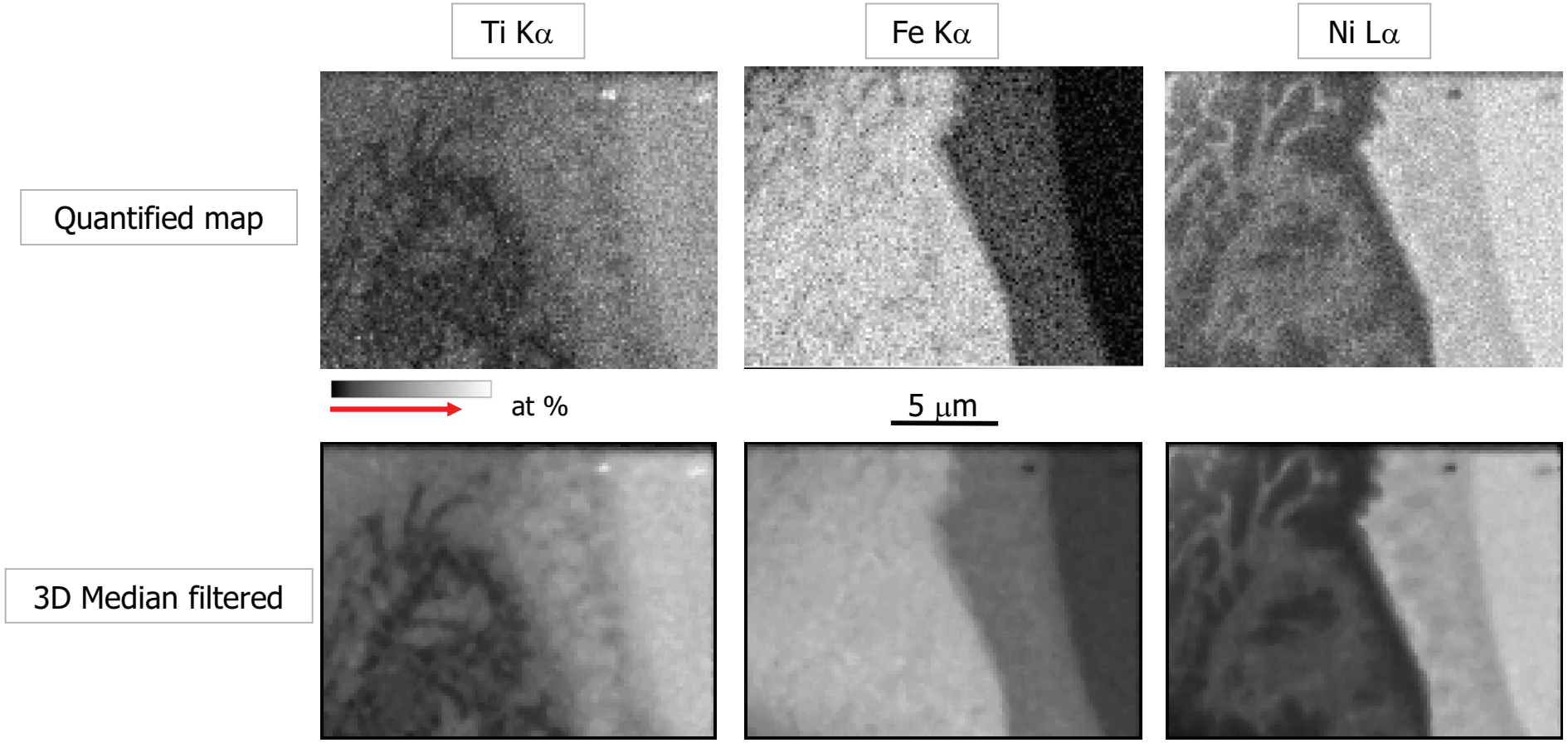


10 kV SE image



NiTi - steel welding: EDX map

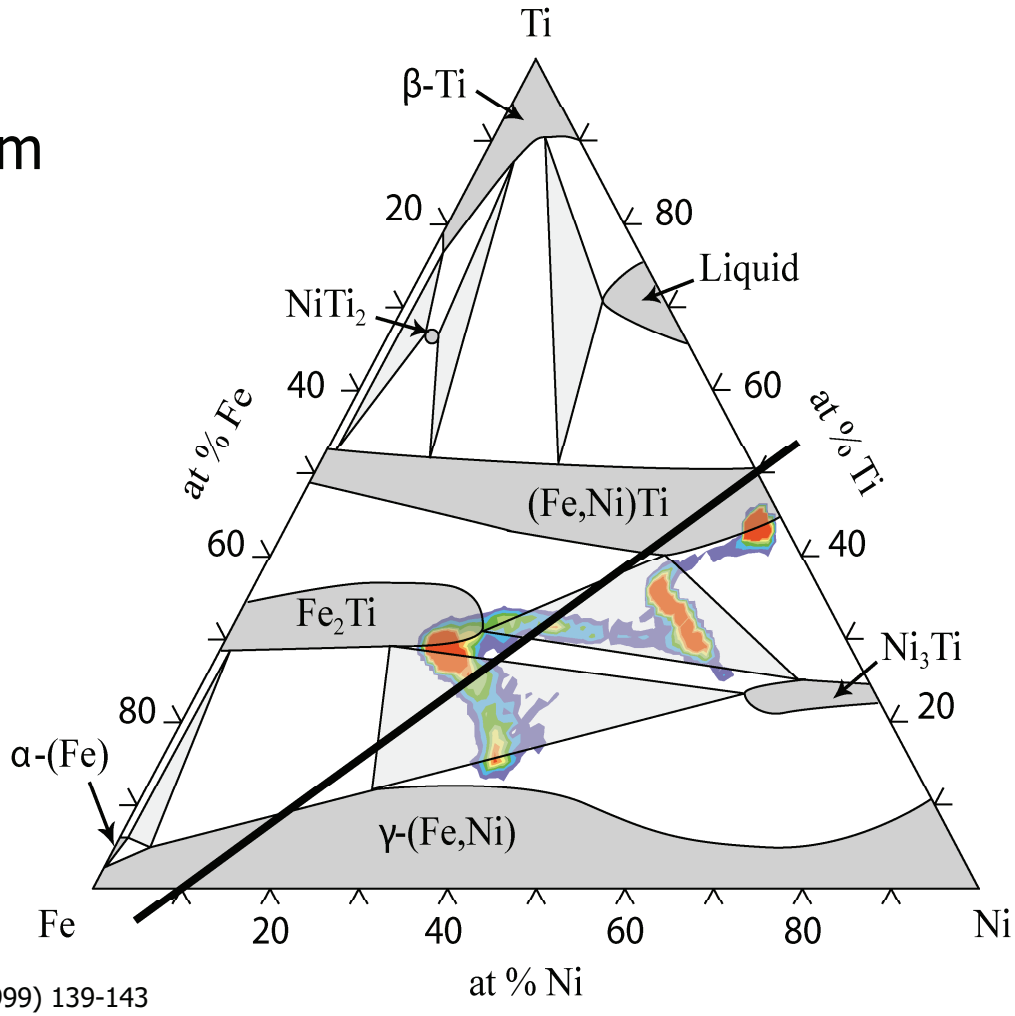
– EDX maps processing
  - Quantification ($\phi(\rho z)$)
  - 3D Median filter



NiTi - steel welding: Ternary diagram

- Prior study
  - 1 hour EDX map
- Composition frequency
  - Vs. ternary phase diagram
  - Following intermetallics

Ternary phase diagram vs. composition frequency



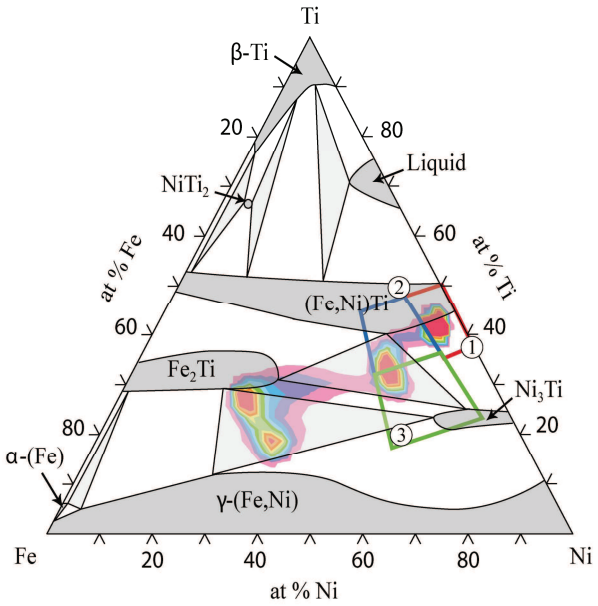
N. L. Abramycheva, V. Mosko, *Univ. Ser.* 2: Khimiya **40** (1999) 139-143

NiTi - steel welding: Segmentation

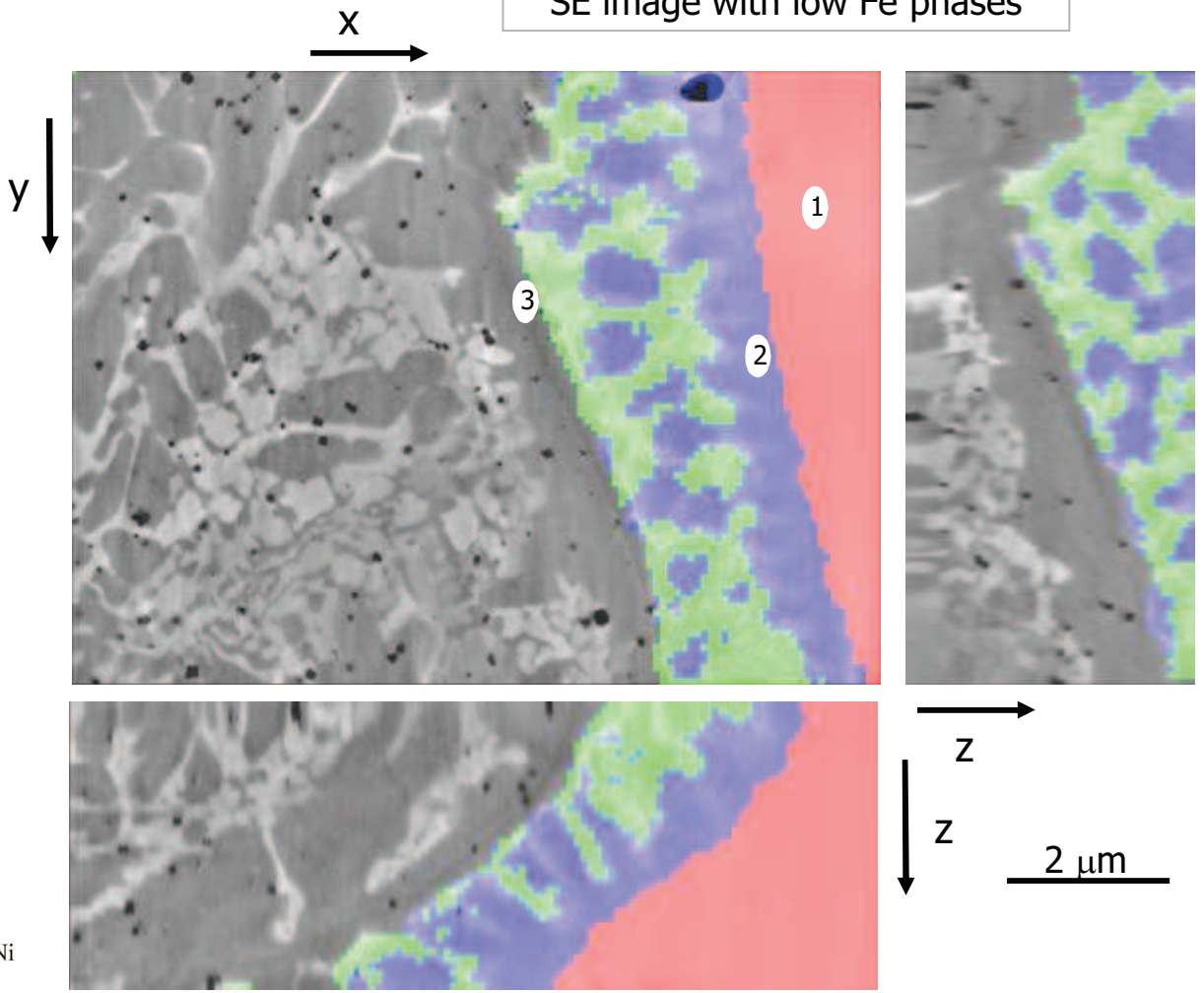
– Segmentation based on ternary diagram

- Red 1: NiTi
- Blue 2: (Fe,Ni)Ti
- Green 3: Ni_3Ti

Ternary diagram



SE image with low Fe phases

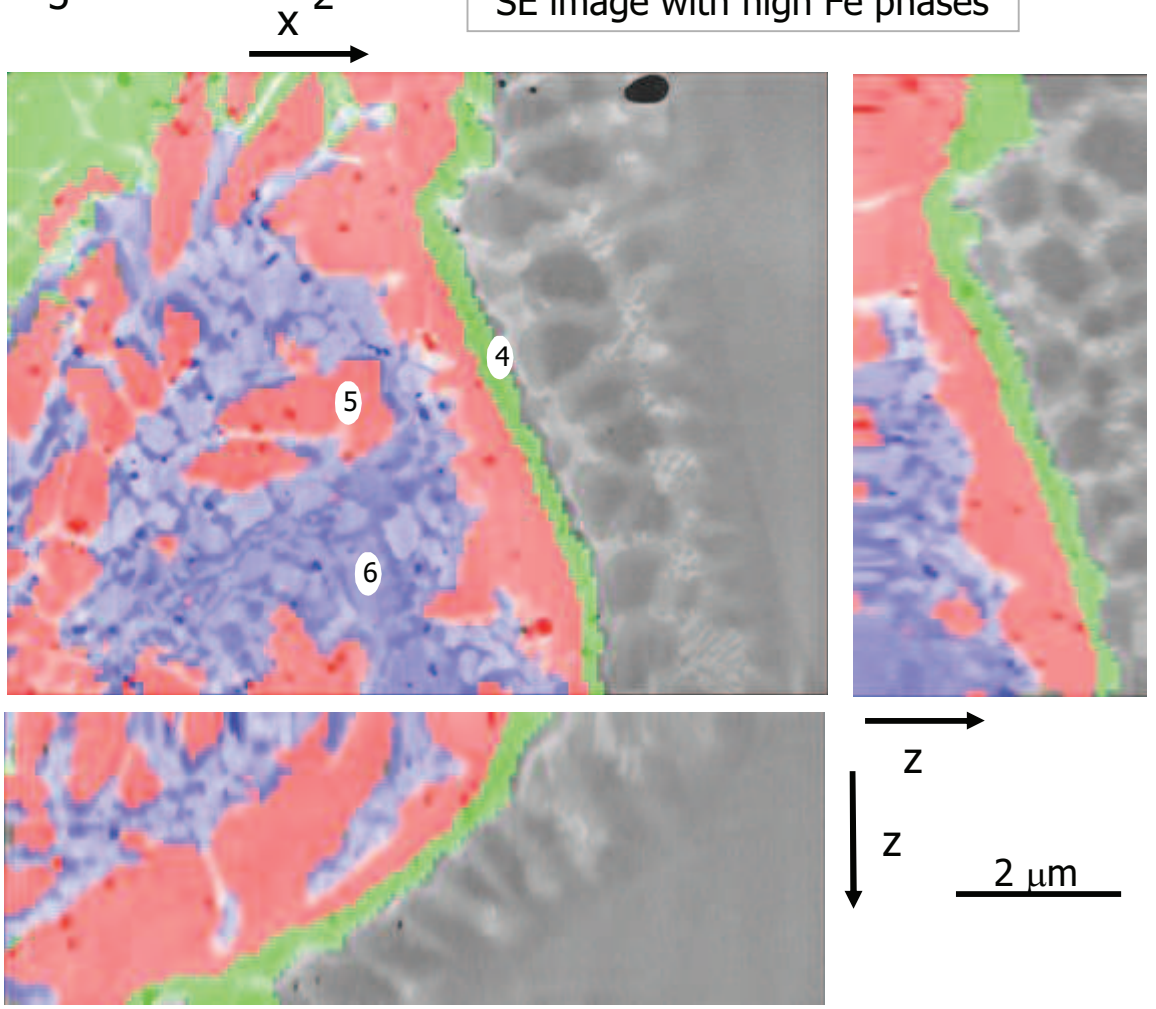


NiTi - steel welding: Segmentation

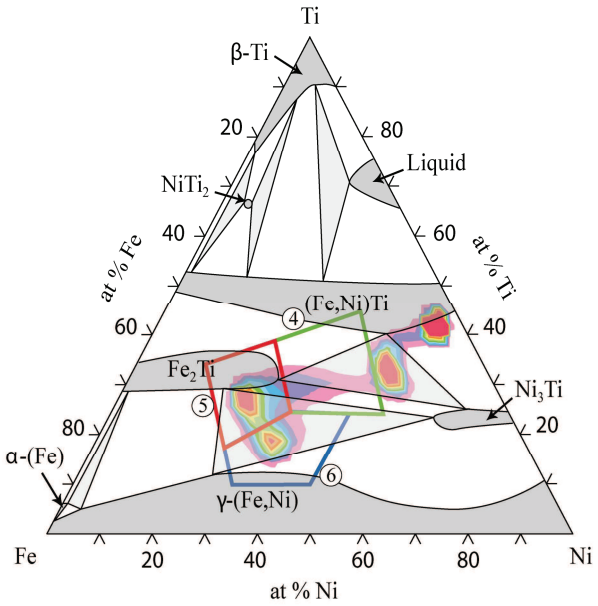
– Segmentation based on ternary diagram

- Green 4: Between Ni_3Ti and Fe_2Ti
- Red 5: Fe_2Ti
- Blue 6: γ-(FeNi)

SE image with high Fe phases



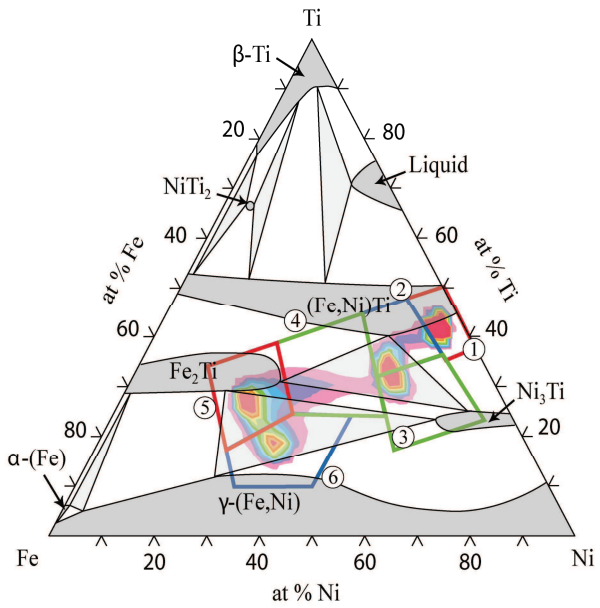
Ternary diagram

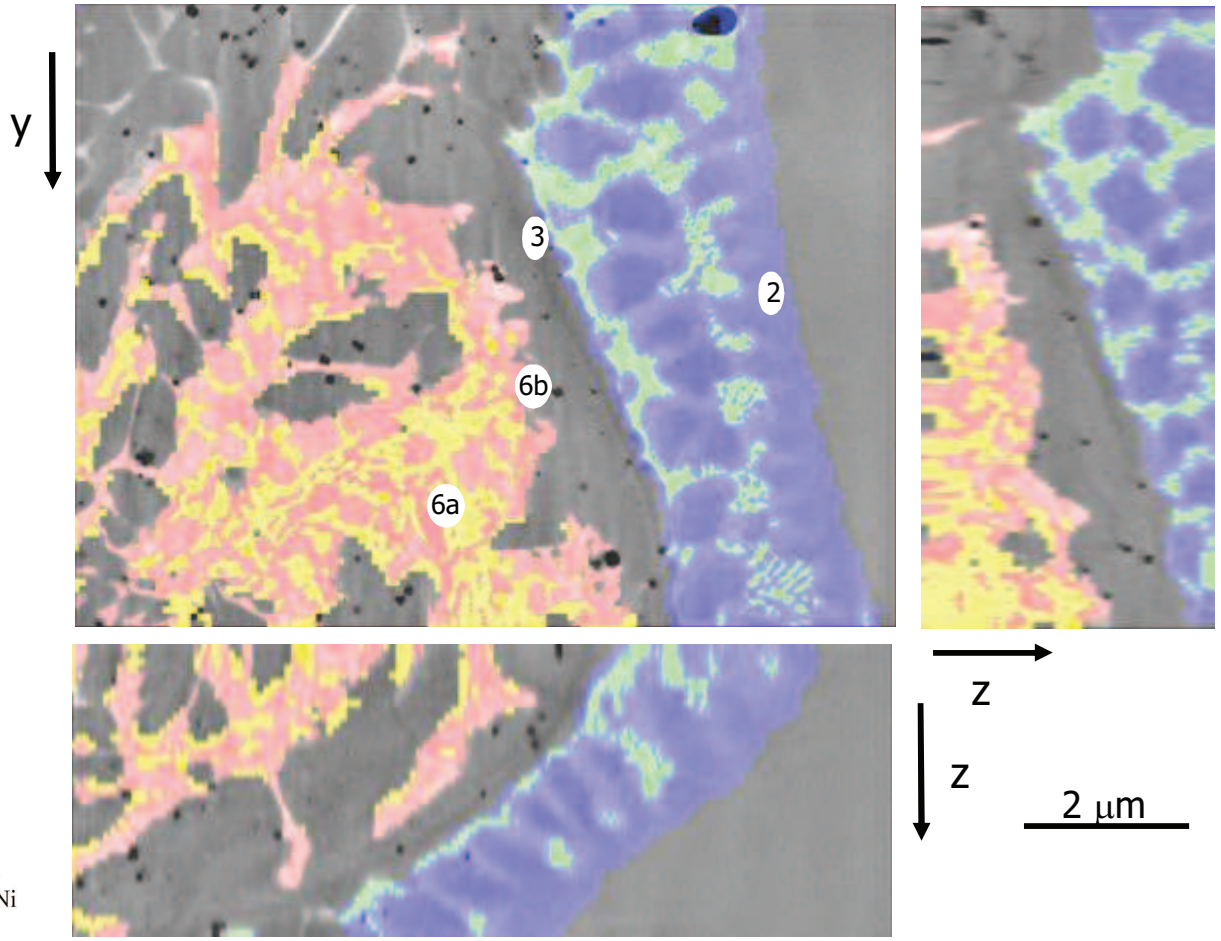


NiTi - steel welding: Segmentation

– Small microstructure
  - EDX phases used as mask
  - Threshold on SE contrast

Ternary diagram

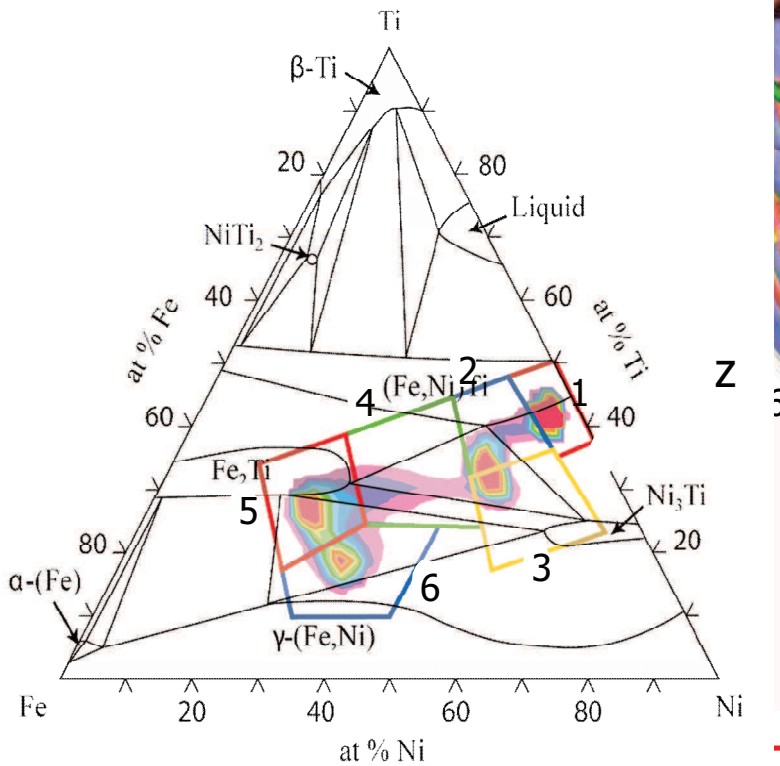


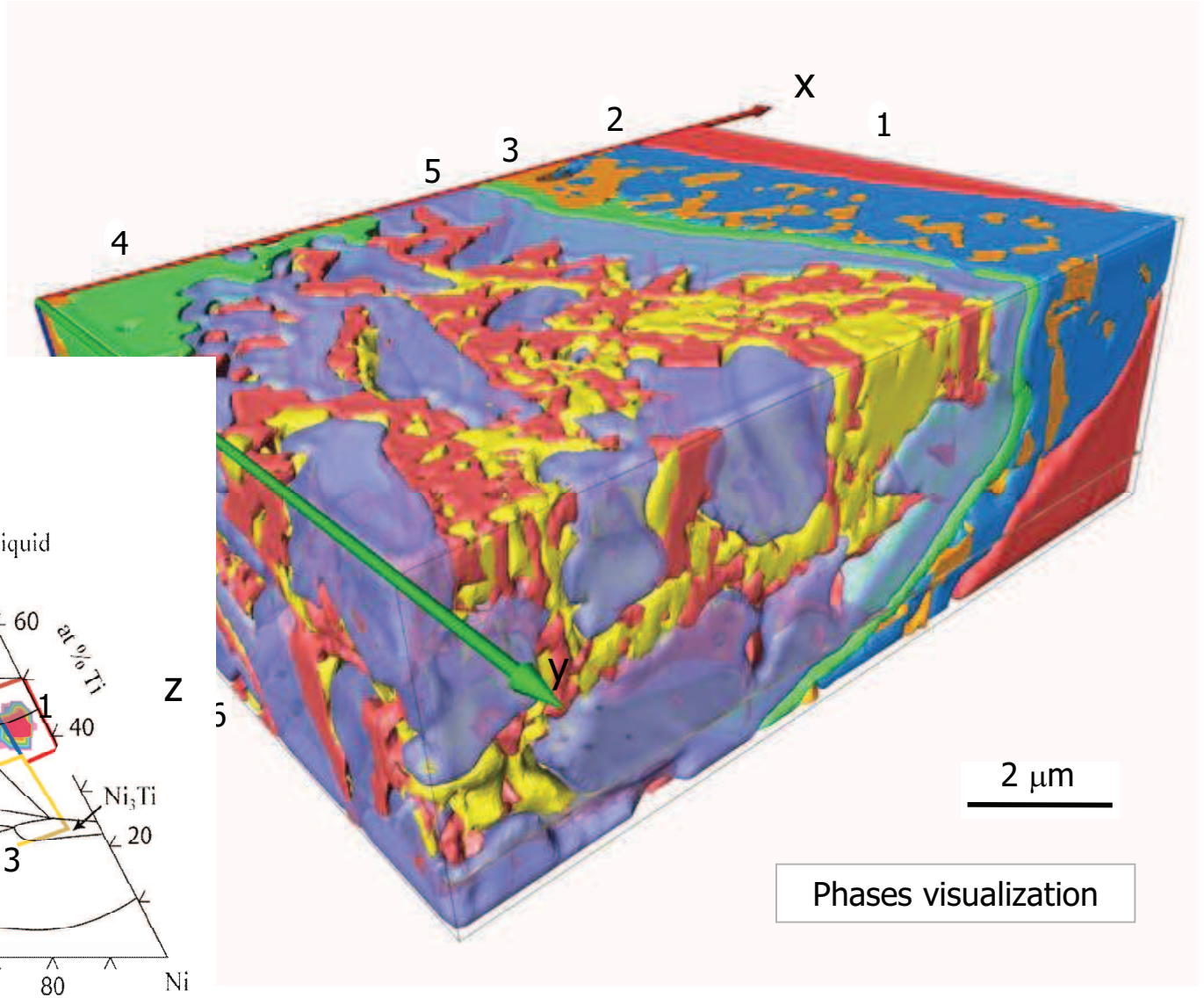


NiTi - steel welding: Visualization

– Visualization

Ternary diagram

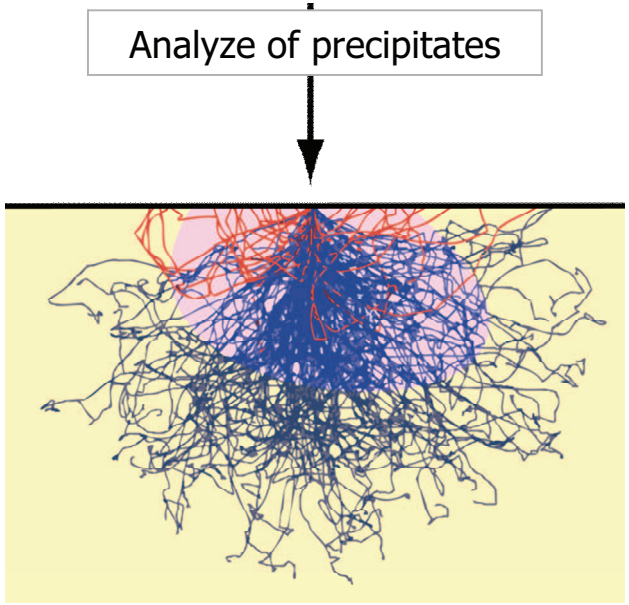


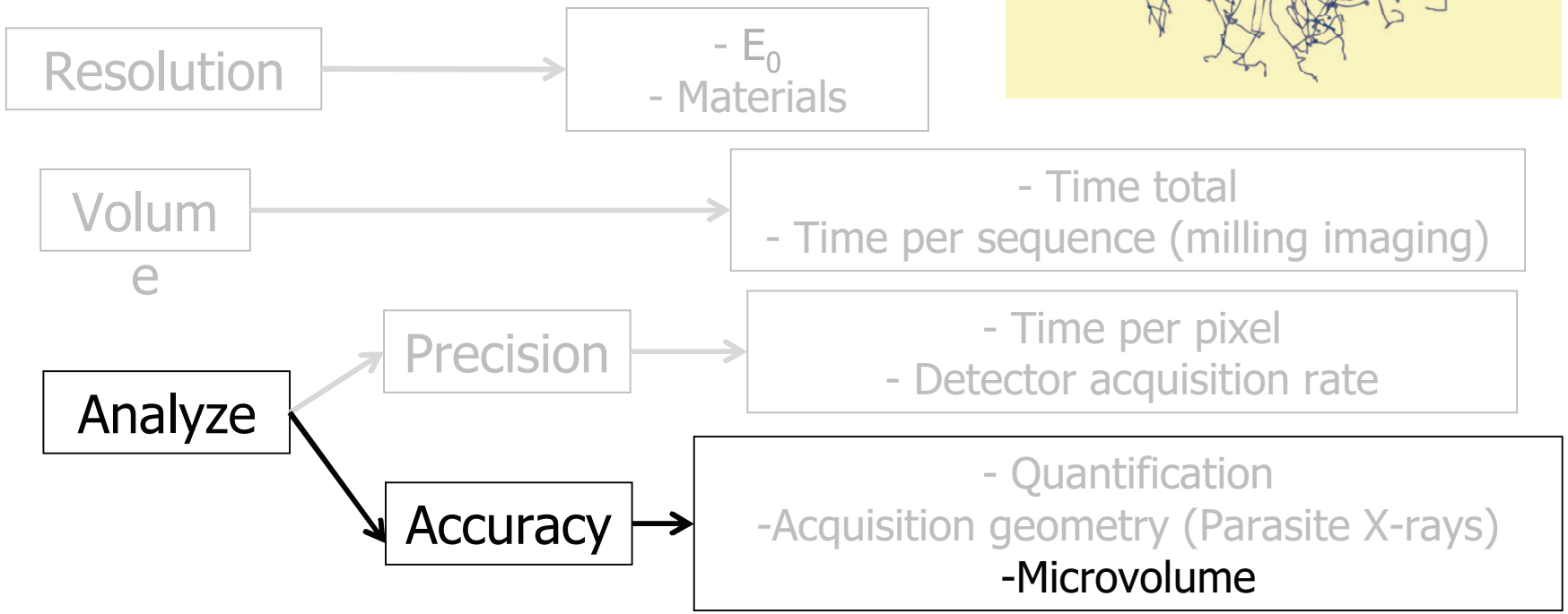


Phases visualization

Enhanced quantification

- Perspective
  - Inhomogeneous microvolume
    - microvolume > slice thickness
  - Post-processing algorithm
    - Enhanced quantification

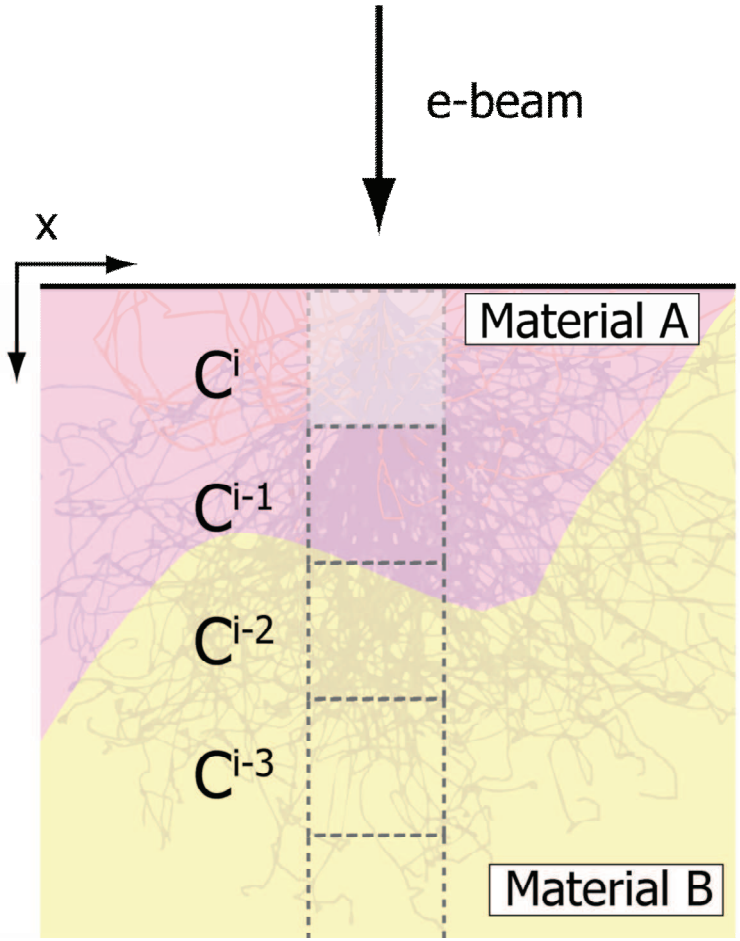




Enhanced quantification: Implementation

- Recursive relation
  - C^i depends on
    - Measured k-ratios
    - C^{i-z}
- f recurrence relation
  - Sample considered as stratified
  - f : thin film $\nearrow(\Pi z)$ quantification*

Grain boundary and voxels in depth



Recursive relation

z index (layer)

$$C^i_A = f(\text{k-ratios}^i, C^{i-1}, C^{i-2}, \ldots)$$

Element index

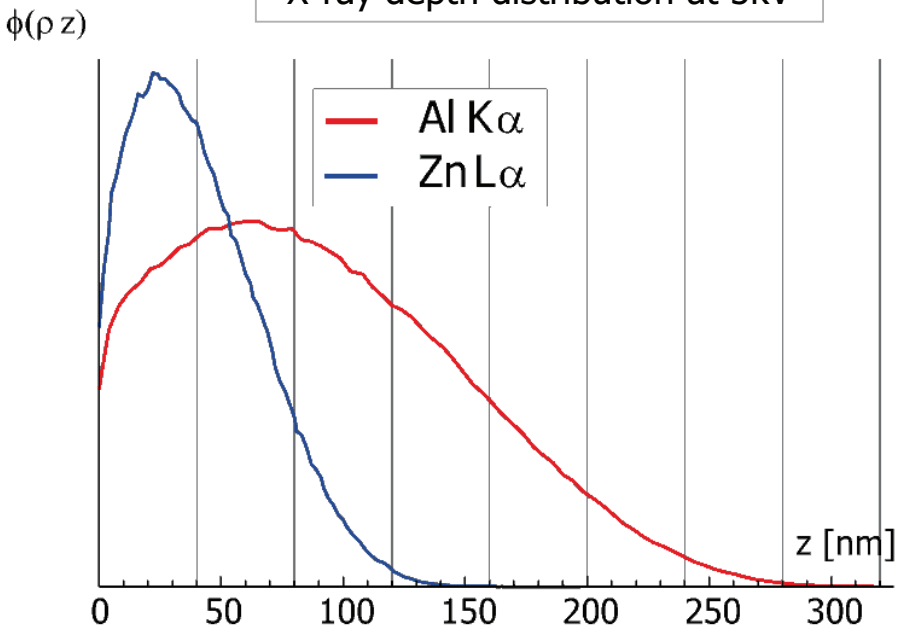
k-ratio = $I_{sample}/I_{standard}$

* Pouchou, J. Analytica Chimica Acta 283(1), pp. 81–97 November (1993).

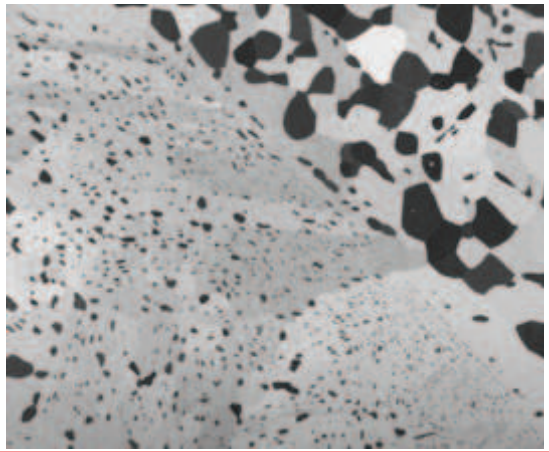
Enhanced quantification: Al-Zn acquisition

- Al precipitates in Zn matrix
  - E_0 = 5 kV
- EDX map
  - Voxel: 40 x 40 x 40 nm
  - 60 ms per spectrum
- Se image
  - Voxel: 5 x 5 x 5 nm

X-ray depth distribution at 5kV



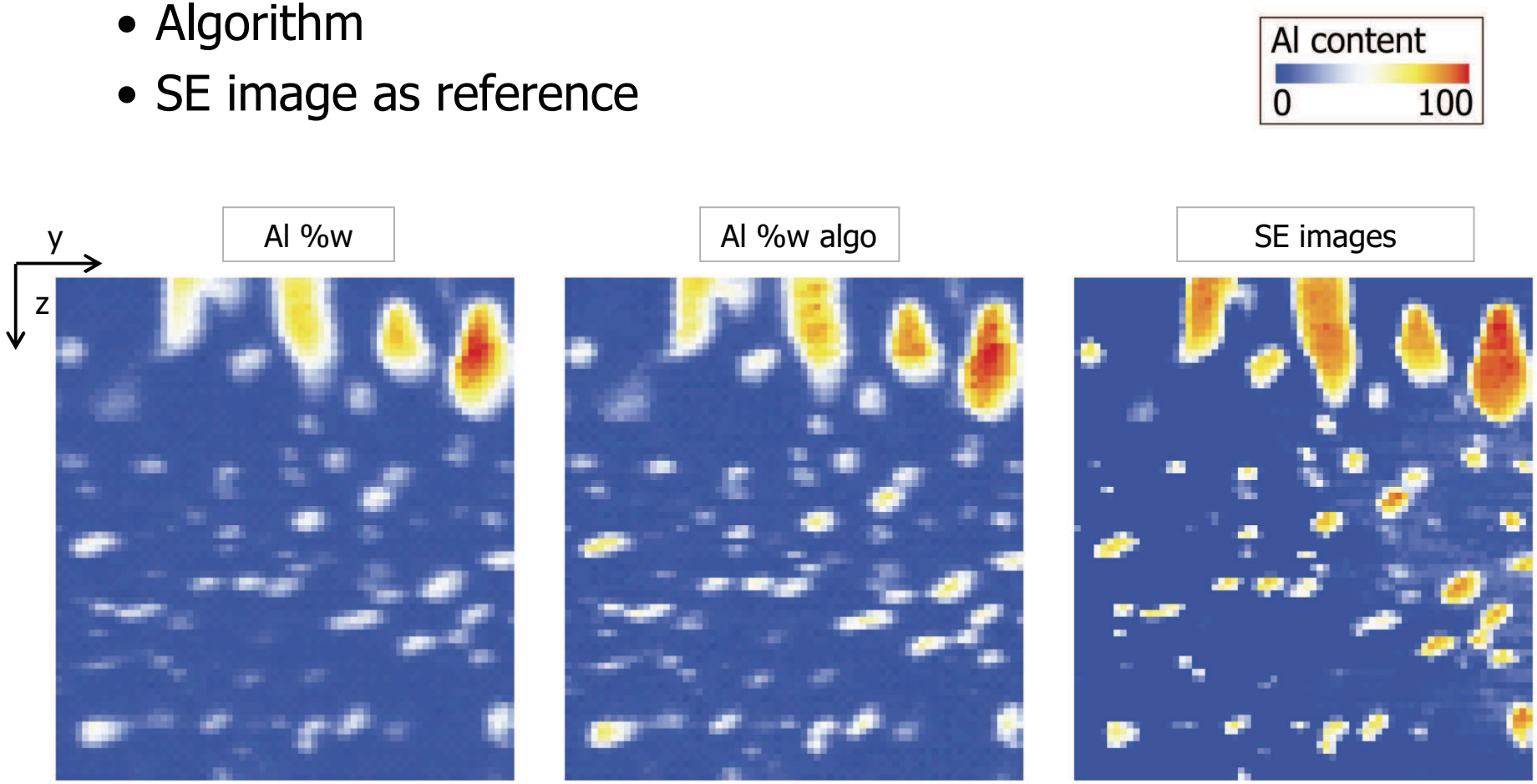
Al precipitate



2 µm

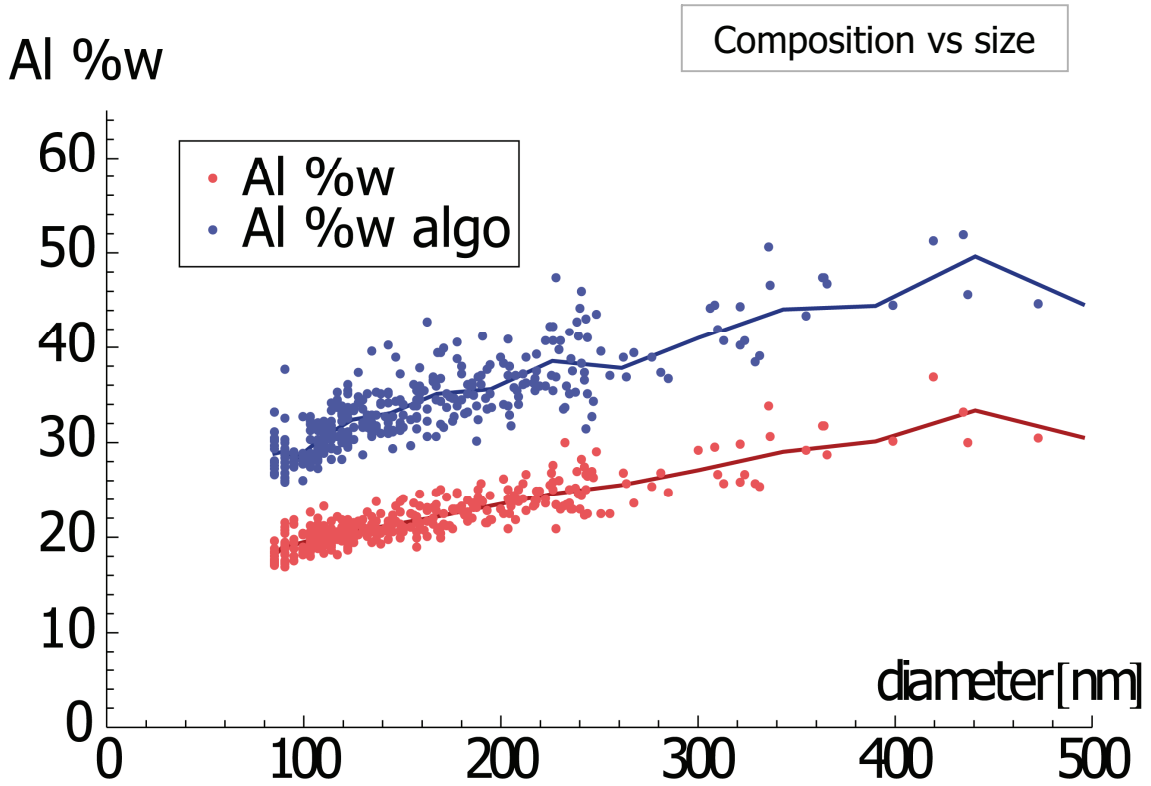
Enhanced quantification: Al-Zn stack

– EDX maps processing
  - Noise filtering
  - Algorithm
  - SE image as reference



Enhanced quantification: Al-Zn results

– Al particles
  - Al %w vs. diameter



Conclusion

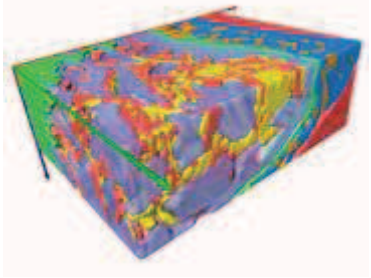
Resolution Delocalization → - E_0 > 2* Ec
- Materials Z and ρ

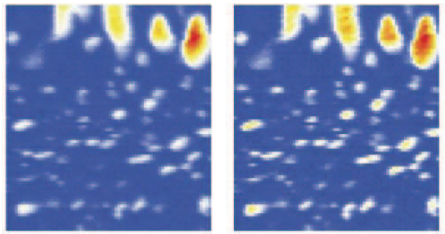
Volume → - Time total ~ 24 hours
- Time per sequence < 1 hour

Analyze → Precision → - Time per pixel >10 ms
- Detector acquisition rate (SiLi, SDD, mm^2)

Analyze → Accuracy → - Quantification
-Parasite X-rays → Adapted geometry
-Microvolume → Post-processing Algorithm for enhanced quantification (Al-Zn)

- Complex phases sample in 3D
-Resolution below EDX limit (SE image)





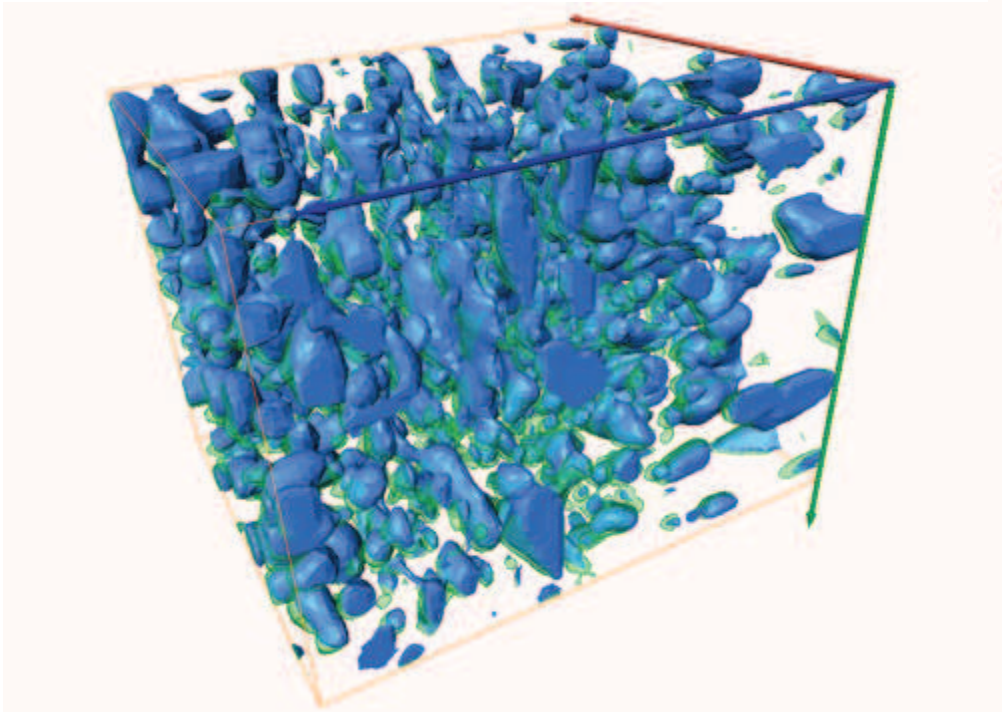
Acknowledgment

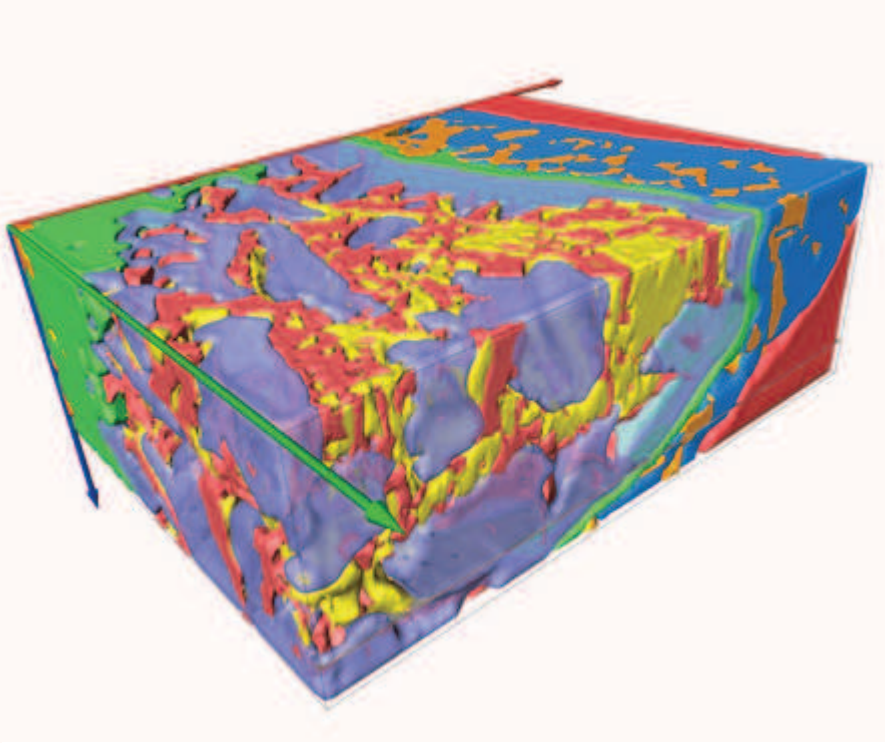
– Acknowledgment

- Carl Zeiss SMT
- Oxford Instrument
- J. Friedli and J. Vannod (LSMX, EPFL) for providing the samples

Thank you for your attention

Questions?

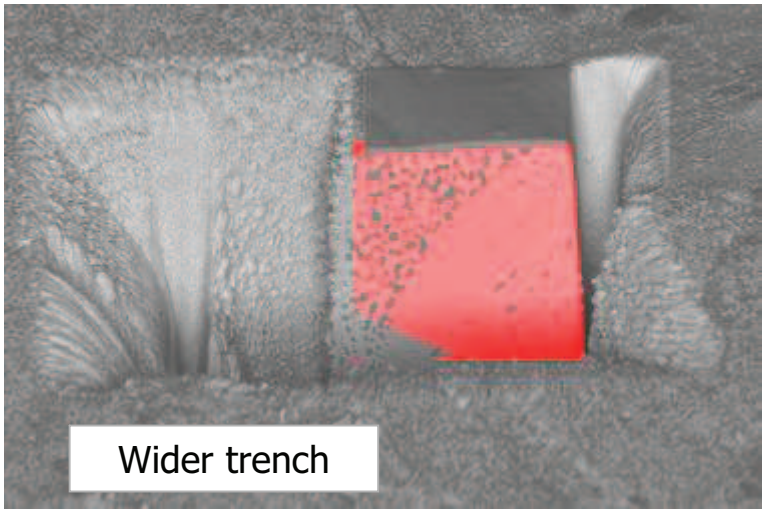


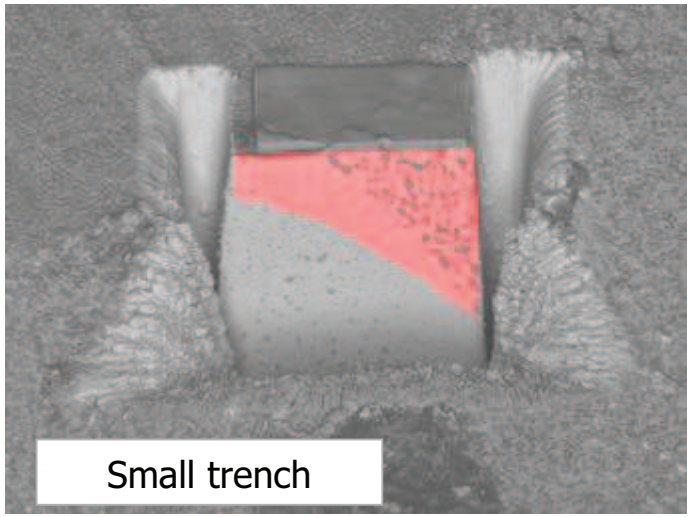


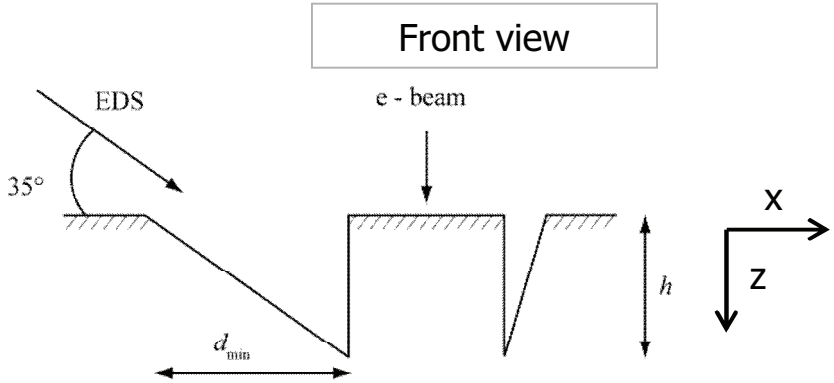
This research is supported by Carl Zeiss SMT

Limits: Acquisition geometry

- Shadowing
  - Not all the X-rays reach the detector
- Solutions
  - Adapted trench geometry

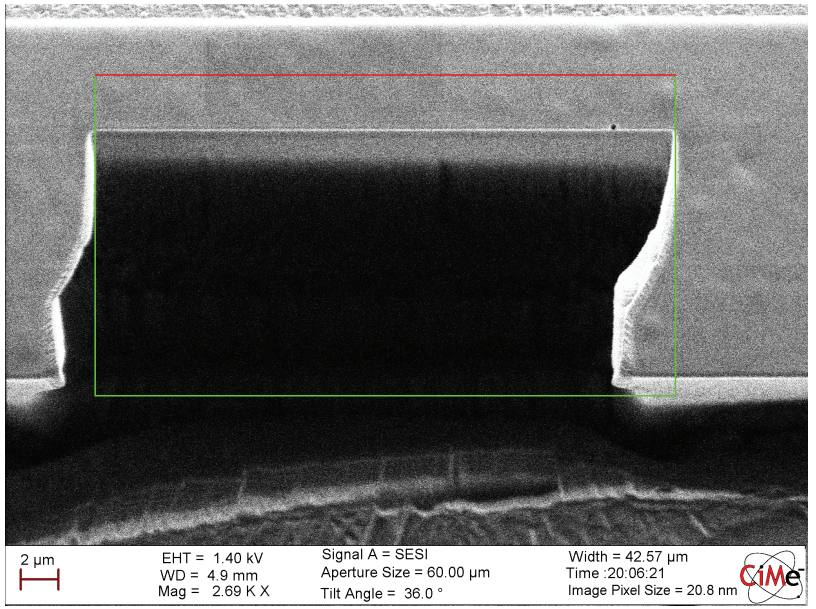






Milling strategy : Drift

- Drift
  - Thermal
  - Mechanical
  - Magnetic
- Solutions
  - Stable system
  - Drift compensation
    - On-line drift correction
    - Off-line drift correction



Application: Enhanced quantification

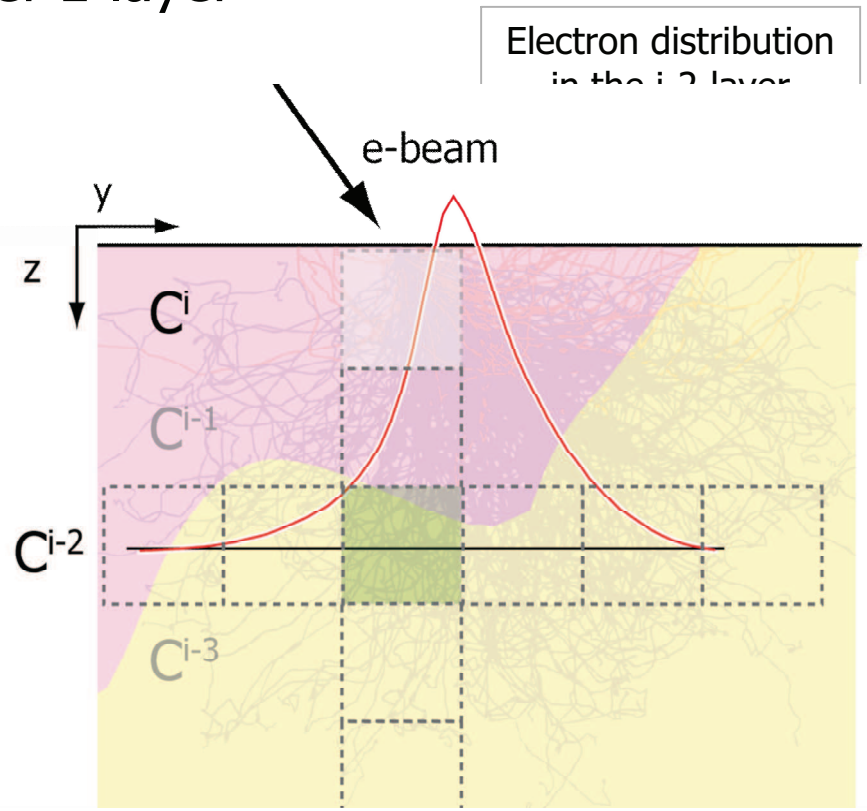
- Geometry of acquisition : tilt of 36°
  - Interaction volume delocalized in y
- C^{i-z} = weighted mean of neighbors in y
  - Mean electron y-distribution per z-layer
  - Simulated from pure material

Recursive relation

z index (layer)

$$C^{i}_{A} = f(\text{k-ratios}^{i}, \mathbf{C}^{i-1}, \mathbf{C}^{i-2}, \ldots)$$

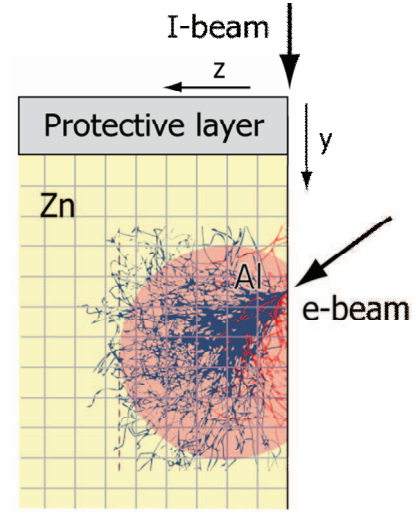
Element index



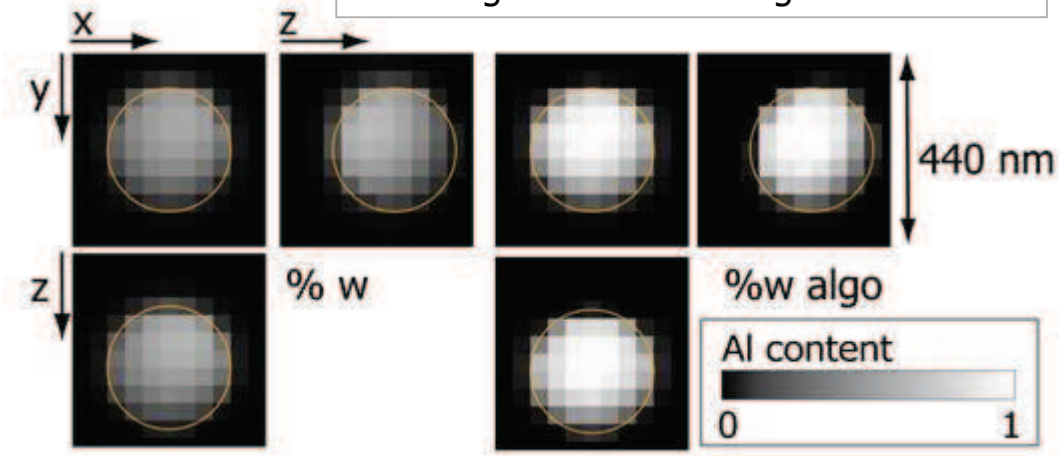
Case study Al-Zn: Spherical particle

– Simulation of Al sphere in Zn matrix
  - Diameter : 280 nm (7 voxels x 40 nm)

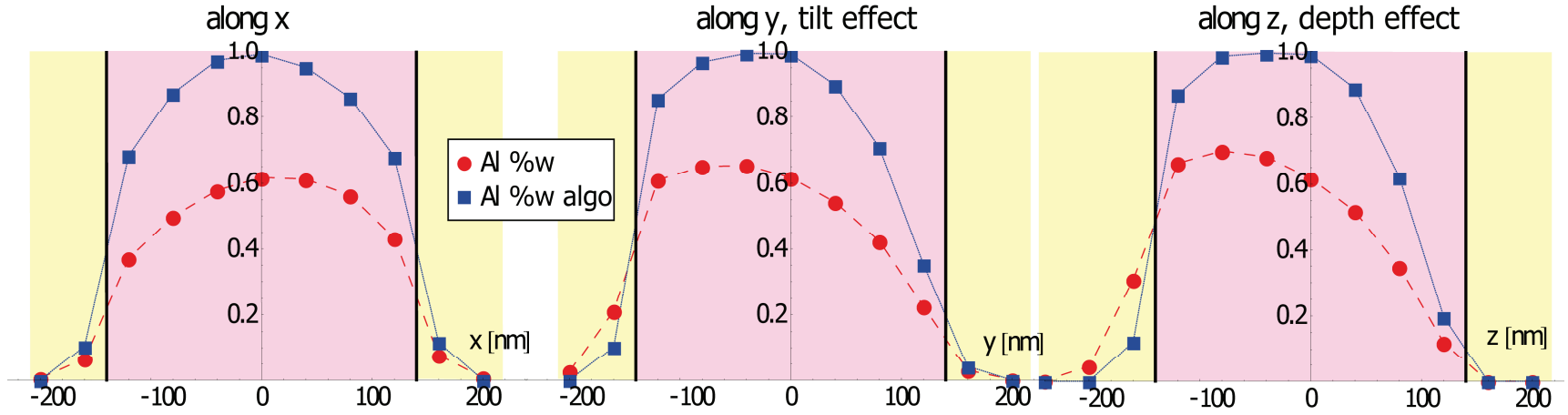
Schematic view



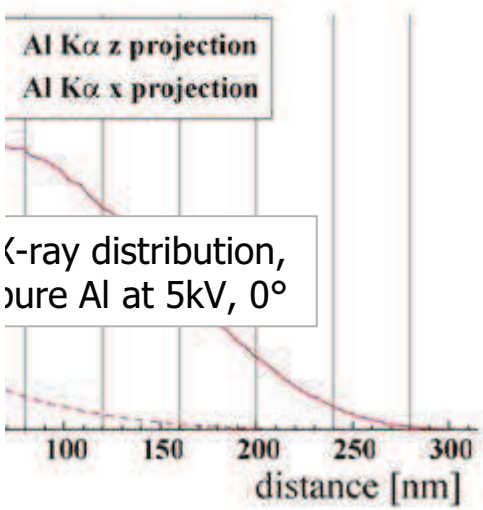
Orthogonal views through the center



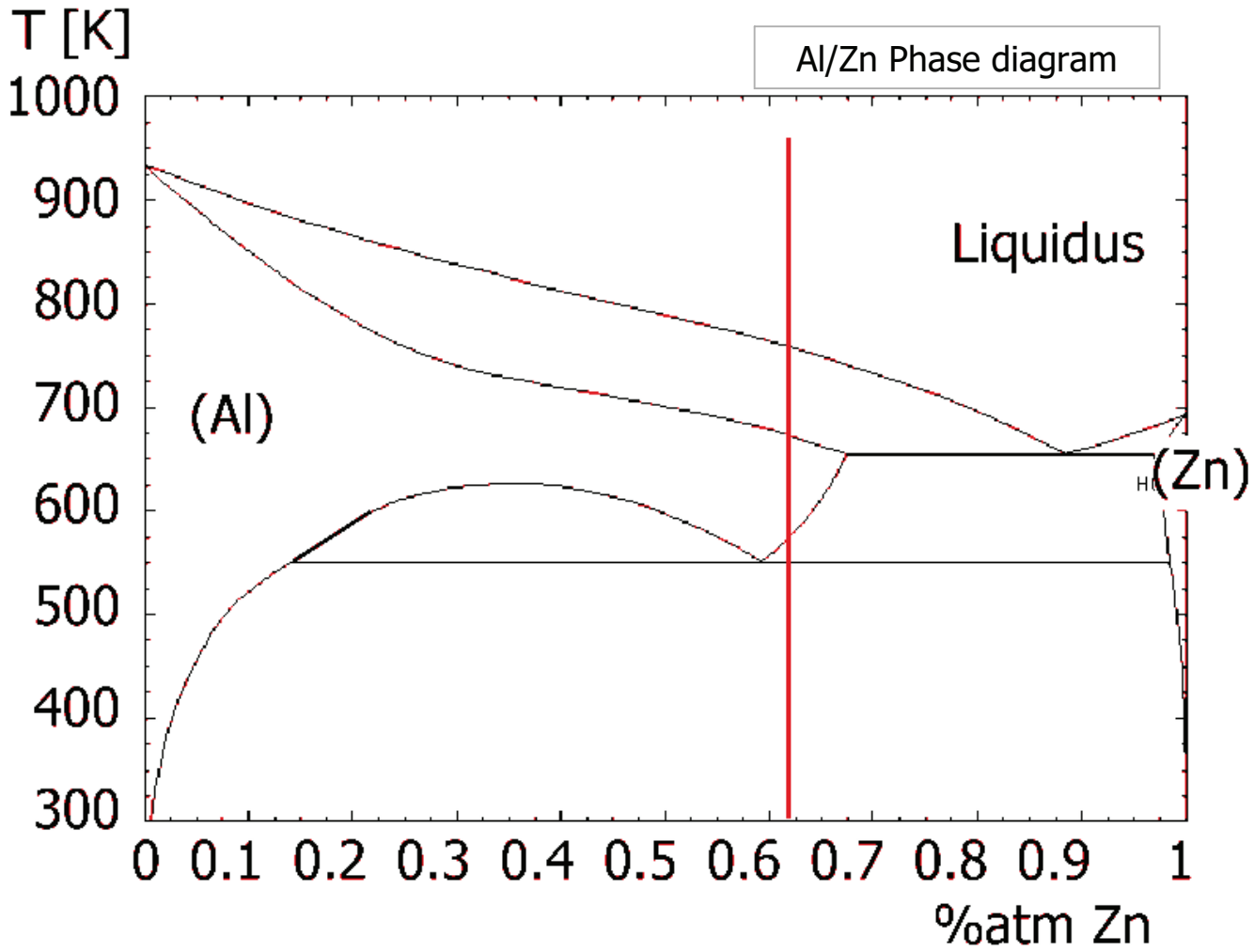
Linescan through the center



Applications: Enhanced quantification



X-ray distribution,
bure Al at 5kV, 0°



Enhanced quantification: Al-Zn results

– Al particles
  - Al %w vs. diameter
  - Relative position to SE images