MICROANALYSIS IN A FIB/SEM: EDX IN 3D WHAT CAN WE EXPECT, WHERE ARE THE LIMITS...?

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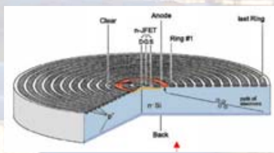
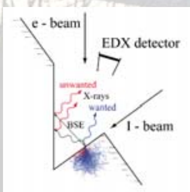
The 4 Challenges for 3D EDX

1) Acquisition of a stack
   speed, overhead, drift control
   Technique

2) Acquisition of EDX maps
   Detector solid angle, speed
   Technology

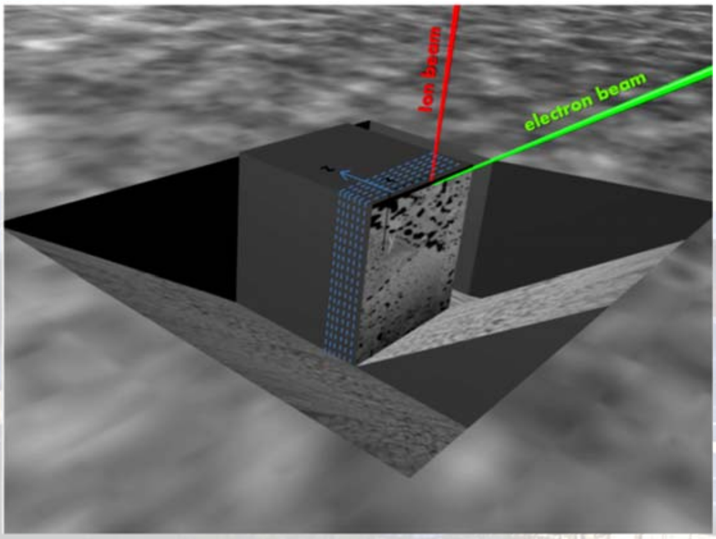


3) Interaction with specimen
   HT -> interaction volume
   Artifact x-rays
   Physics



4) Post processing
   Quantification
   “deconvolution”, poor statistics
   Computing

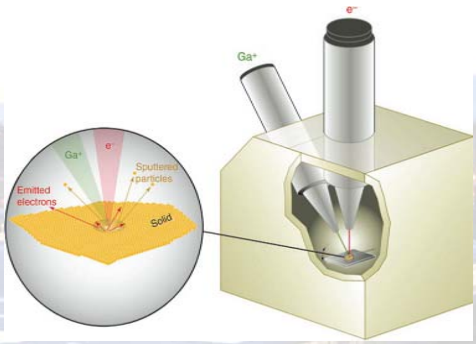
3D Microanalysis by FIB/SEM volume reconstruction

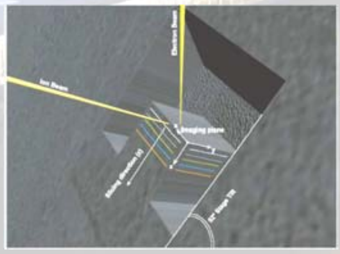


Three-dimensional analysis of porous $BaTiO_3$ ceramics using FIB nanotomography

L. HOLZER, F. INDUTNYI, PH. GASSER, B. MÜNCH & M. WEGMANN
EMPA, Swiss Federal Laboratories for Materials Testing and Research, Ueberlandstrasse 129, 8600 Dübendorf, Switzerland

Journal of Microscopy, Vol. 216, Pt 1 October 2004, pp. 84–95





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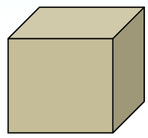
3D FIB/SEM: volume reconstruction

- **Isotropic resolution**
  - Slice thickness (z) = image pixel size (x,y)
  - *Z dimension ~ X or Y, typical: 10nm, possible 5nm (3nm)*
  - *Z- Resolution: low kV !!!*
- **High Throughput**
  - *Acquisition time "Image" ~1min / slice (~60 slices / hour)*
    -> high S/N ratio, beam current (1-1.5nA), detector efficiency
  - *Dwell times/pixel 5- 15µsec.*
  - *minimise overhead, no tilting, rotating, (drift correction)*



"Leitmotiv"
Isometric voxel size
x = y = z

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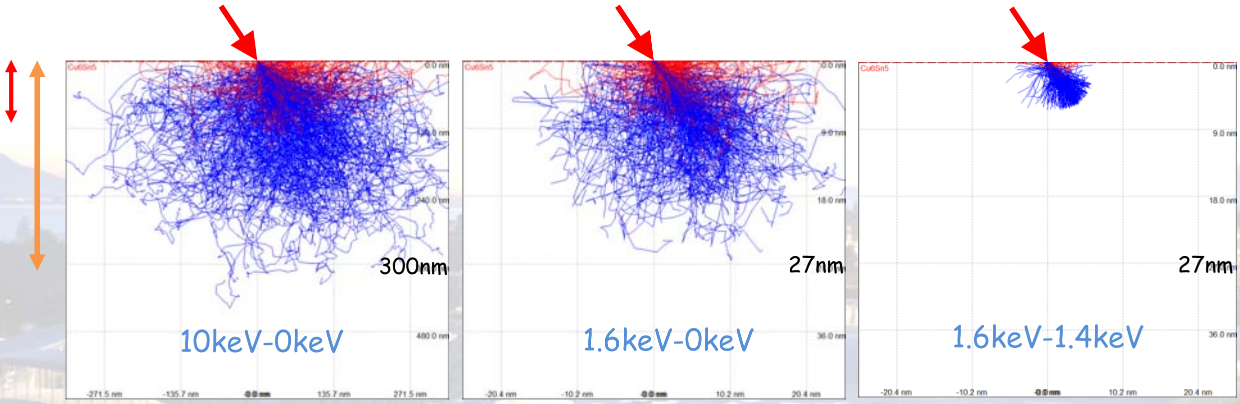
3D Microanalysis by FIB/SEM volume reconstruction

What is the spatial resolution of BSE electrons ?

Scatter range in Nb_3Sn:



HT	10keV	1.6keV	1.6keV (low loss, EsB grid at 1.4kV)
BSE esc. depth	100nm	10nm	2-3nm
penetration	300nm	20nm	(20nm)

Energy selective BS

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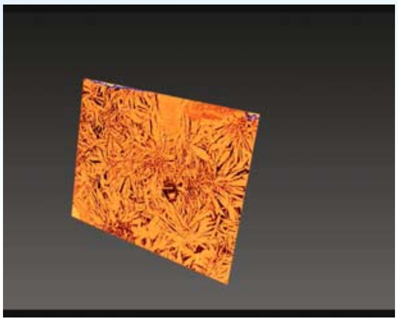
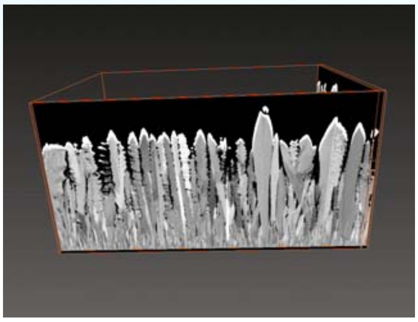
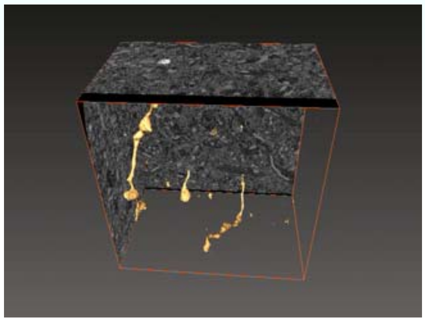


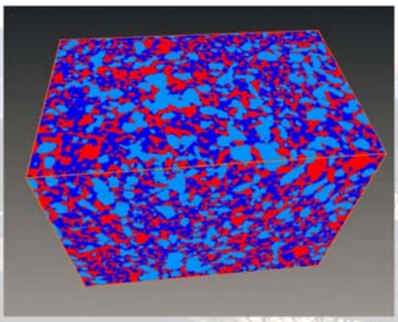
Cement, $(10nm)^3$ voxel



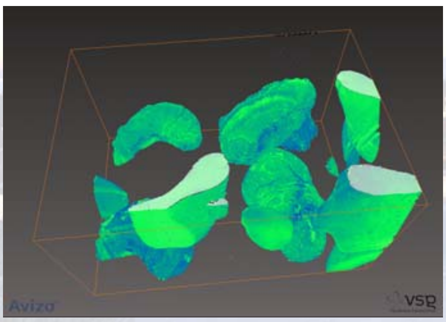
Solar cell: ZnO, $(10nm)^3$ voxel



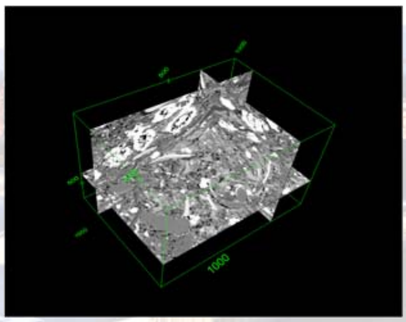
Rat brain, $(5nm)^3$ voxel



SOFC, $(10nm)^3$ voxel



Malaria parasite, $(8nm)^3$ voxel



clay, $(10nm)^3$ voxel

FIB/SEM Nanotomography, volume reconstruction
Typical voxel sizes

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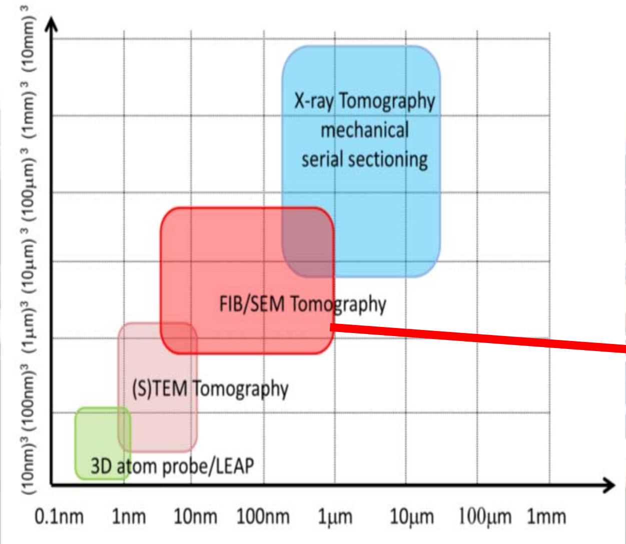
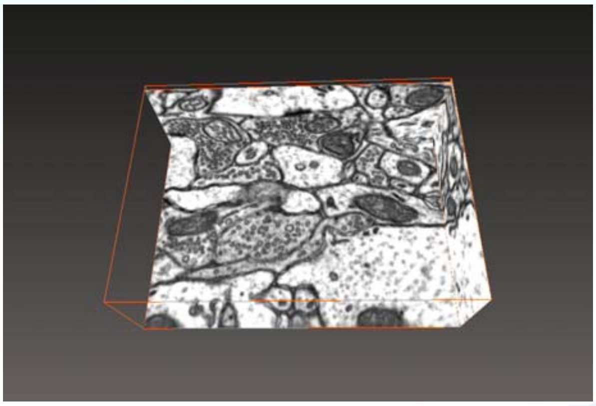
FIB-NT compared with other 3D-techniques

- Voxel size ~5-10nm
- Dwell time ~10µsec.
- 1 slice, image / min.
- HT: 1-2kV
- Escape depth of signal (BSE) ≤ 5nm





3x3x3 nm voxel brain tissue

New possibilities in 3D-microscopy: Combination with quantitative analytical SEM techniques: EBSD, EDX

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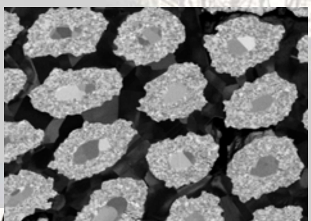
3D EDX with Si(Li) detectors, first steps

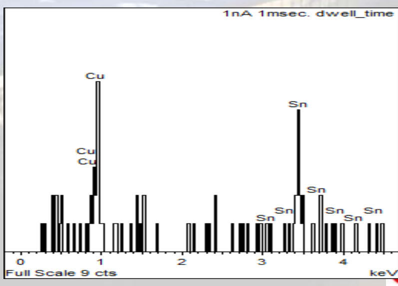
Signals

@ 20 keV: 100 electrons generate

~ 50-75 SE
~ 30-50 BSE
~ 0.7 X-rays

Method	signal required	detection solid angle	bottleneck
3D FIB/SEM	256 grey levels of BSE	small	current in small probe
EBSD	320x240 pixel image	big	camera speed
EDX	spectrum > 10000 counts	small (getting bigger)	detection speed





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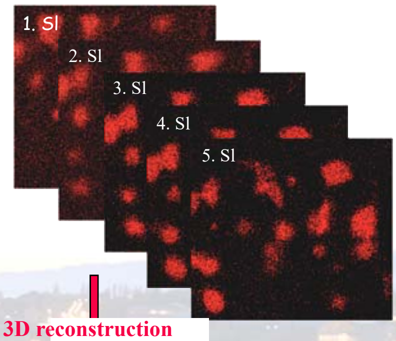
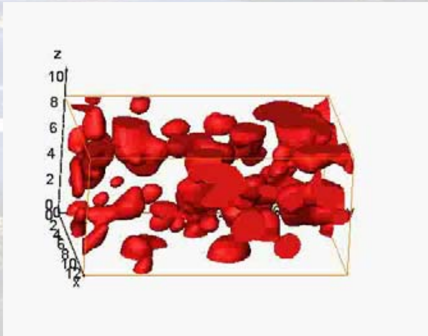
The "Si(Li) age"

Quantitative Chemical Analysis 3D EDX-microanalysis

2D Ca maps



3D reconstruction



- Separate volume of interest from the bulk
- Cut the sample slice by slice with the I-beam
- Map each cross-section with the e-beam and EDXS
- Reconstruct 3D-model from 2D maps

[1] Kotula et al, . Microsc. Microanal. 12 (2006), 36-48
[2] Schaffer et al, Ultramicroscopy 43 (2007), 587-597

Courtesy: Miroslava Schaffer

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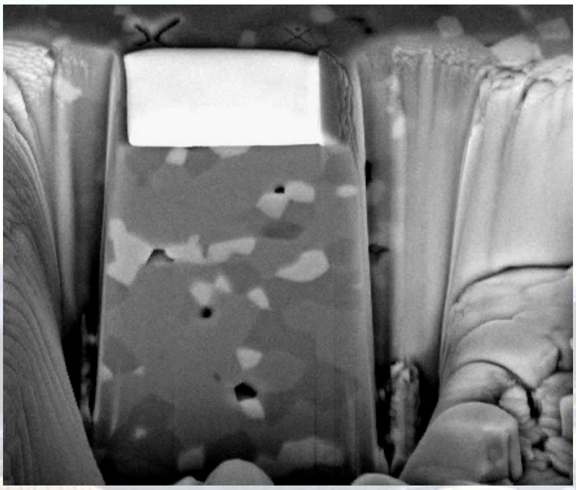
Fully automated 3D-FIB EDXS experiment

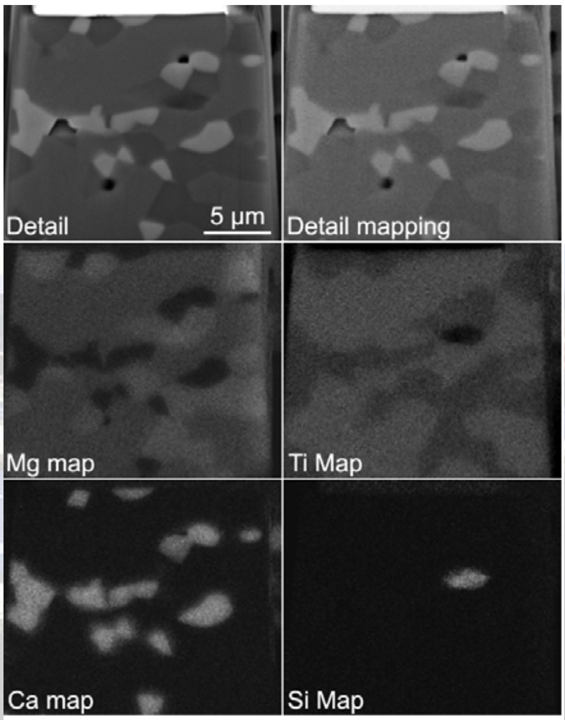
Overview SEM Images



preparation technique	U-pattern
ion beam current / voltage	3.0 nA / 30 kV
number of slices	30
nominal slice thickness	300 nm
electron beam current / voltage	6.2 nA / 15 kV
EDXS map size	256 x 200 pixels
EDXS map pixel size	70 x 89 nm²
mapping technique	EDXS spectrum images
pixel dwell time (EDXS)	25 ms
total time per slice	~ 60 min
reconstructed volume	12.32 x 17.26 x 9.0 µm³

[2] Schaffer et al, Ultramicroscopy 43 (2007), 587-597

Detail SEM Images and EDXS Maps



(Ca)MgTiO$_x$ ceramic

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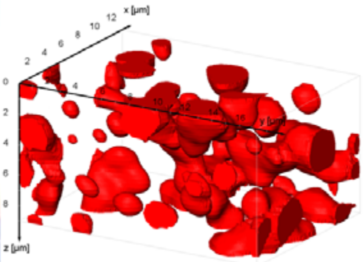
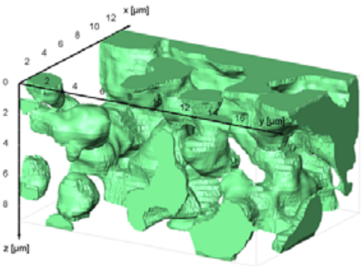
Fully automated 3D-FIB EDXS experiment

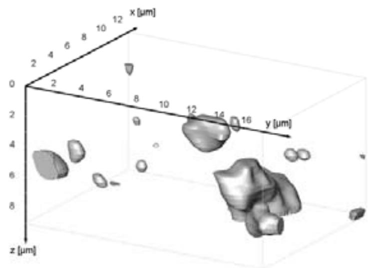
3D Ca distribution



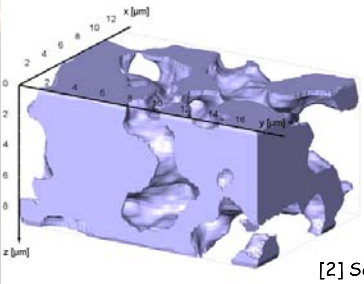
3D Mg distribution



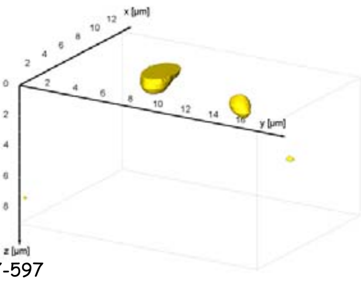
3D void distribution
(reconstr. from BSE images)



3D Ti distribution



3D Si distribution



[2] Schaffer et al, Ultramicroscopy 43 (2007), 587-597

F. A. Lasagni: EMAS 2009, Gdansk, Poland

3D NANO-CHARACTERISATION OF MATERIALS BY FIB-SEI/EDS TOMOGRAPHY

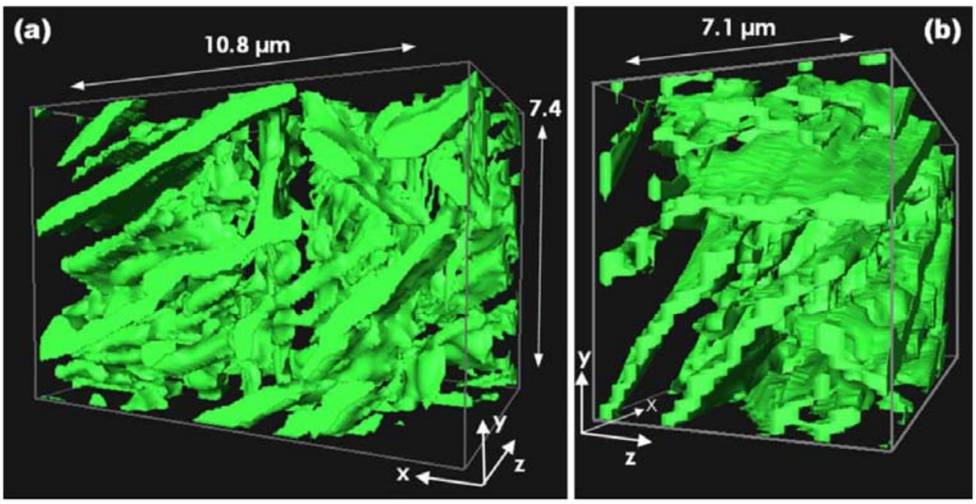
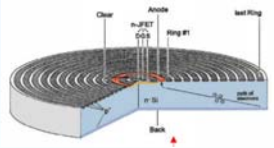


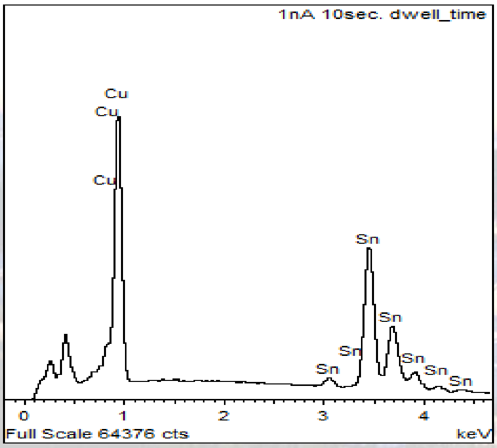
Figure 3. (a, b) 3D-reconstruction from EDS maps of the investigated AlSi12 alloy (Si: green, Al: transparent). Note the aliasing effect due to the large distance between serial slices (310 nm) in the turned volume (b).

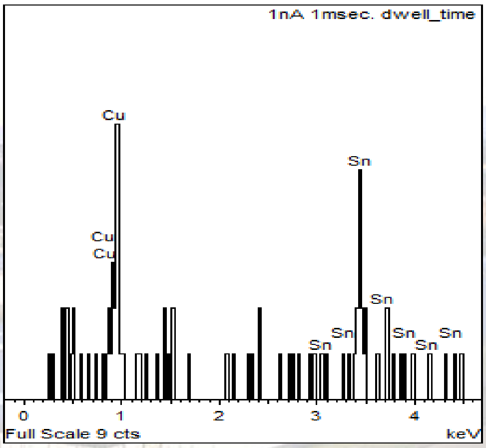
30min.- 40 min. per slice/map
310 nm voxel dimension (z)



The "SDD age"

New detectors speed up the acquisition !
faster processing and larger surface areas
dreaming of 1M counts/sec.
50-100k counts/sec. are more realistic at the moment





2008 ("SDD age")

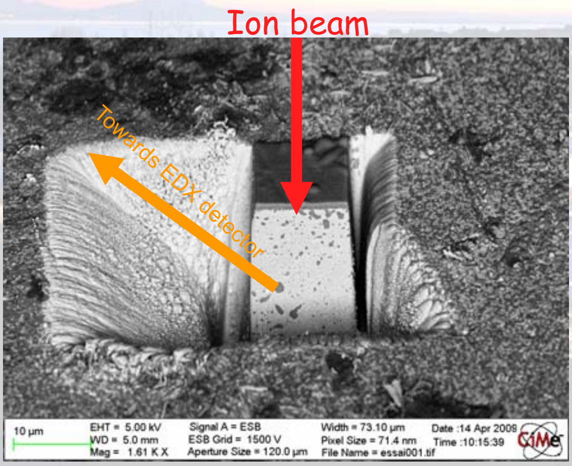
installation of Nvision 40 @ CIME
use the full potential of the machine

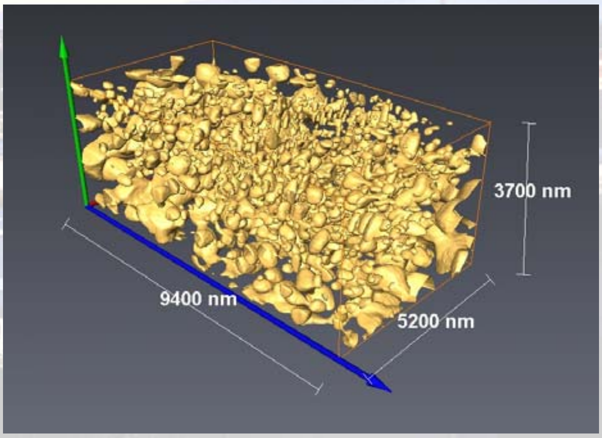
3D-EDX

Pierre Burdet: Ph.D. Thesis in collaboration with ZEISS

Goal: FIB Nano-Tomography based on EDX-elemental maps
new generation of EDX detectors (80mm², SDD)
Develop algorithms do "deconvolute" the interaction volume of characteristic X-ray

- Stack of 269 EDX maps
  - High tension : 5kV
  - Voxel size : 20 x 20 x 40 nm
  - Pixel per map : 256 x 192 (x 269)
  - Time per slice : 4+1 minutes
  - Time of acquisition : 24 hours





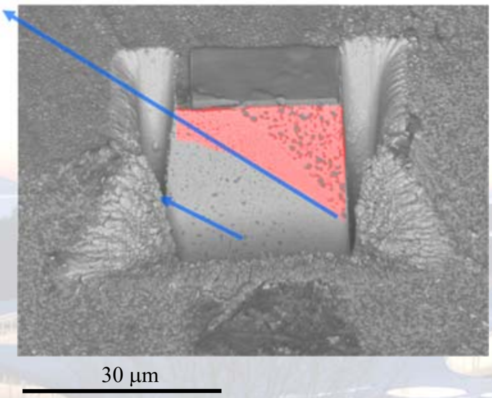
Sample: Al/Zn, Jonathan Friedli, STI-LSMX

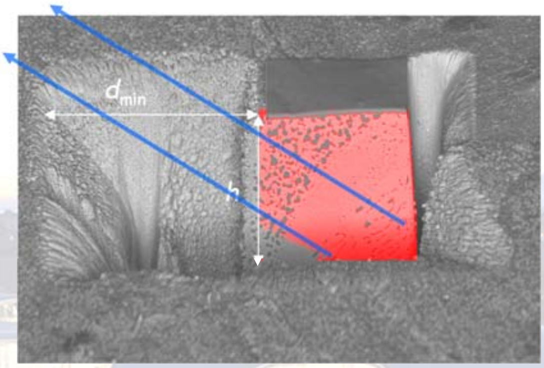
EDX geometrical limitations

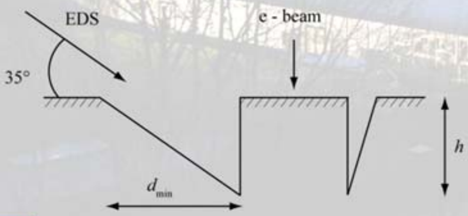
3D EDX is not like FIB/SEM Tomography

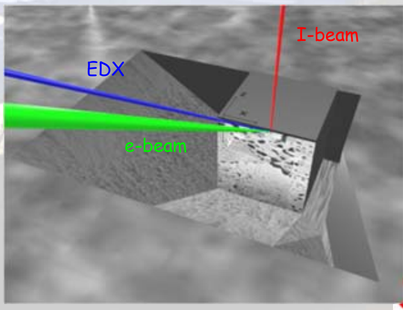
"The detector doesn't see everything"

- Not all X-rays reach the detector









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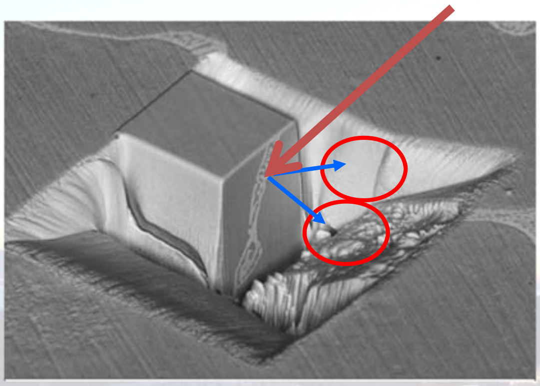
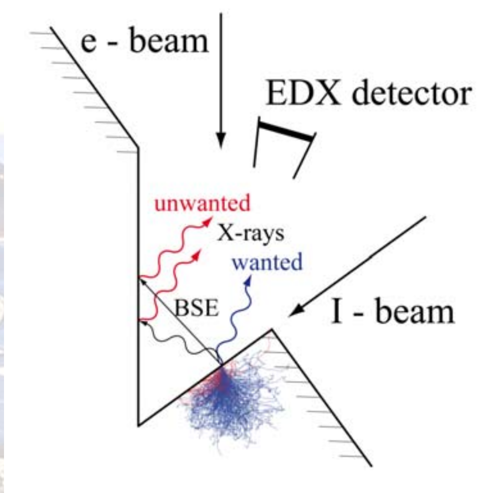
EDX limitations

"The detector sees everything…."





- Parasitic X-rays generated by :
  - BSE hitting the trench walls
  - X-rays hitting the trench walls (Fluorescence)

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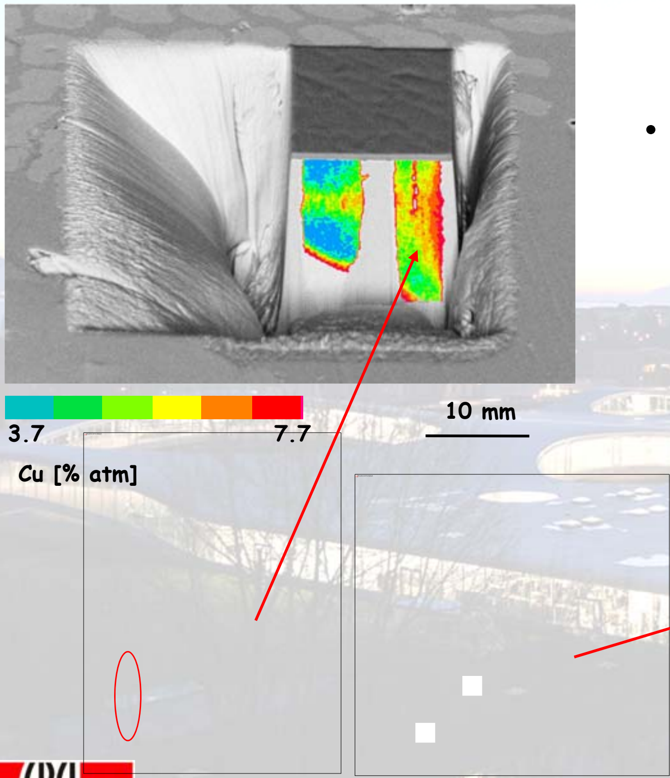
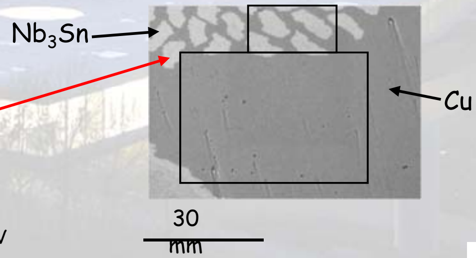
EDX limitations

Parasitic X-ray s



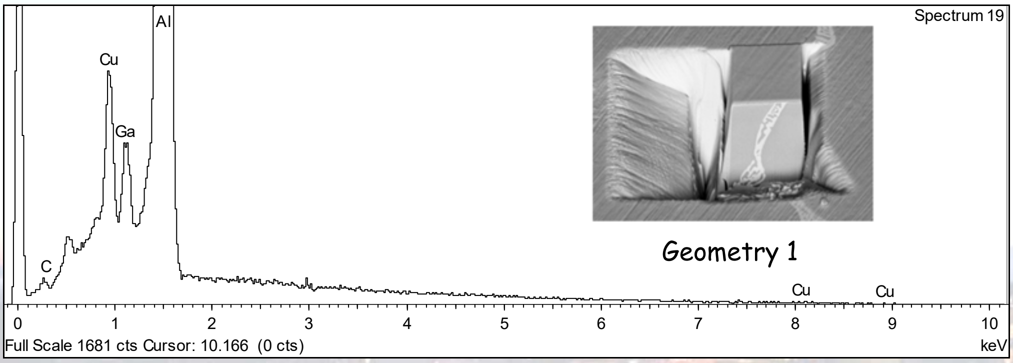
Nb_3Sn (no Cu) in Cu matrix

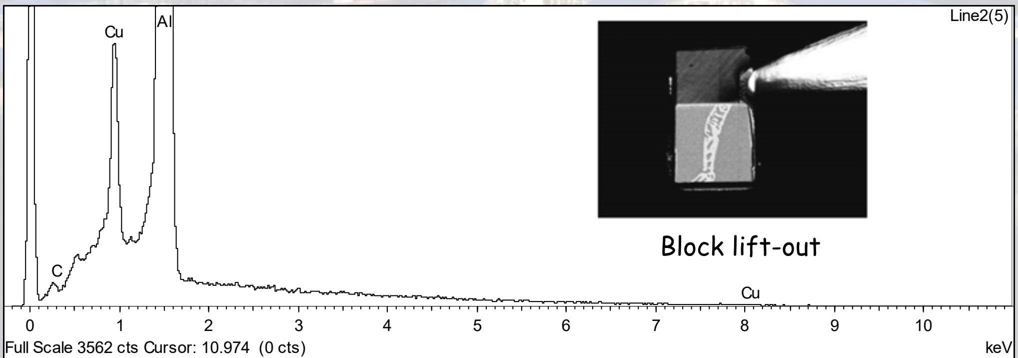
- Parasitic signal of Cu
  Up to 7% at (@ HT = 7 kV)
  Up to 20% at (@ HT = 20kV)
  Depends on position on the face



EDX limitations

Ga concentration as indicator of redeposited material

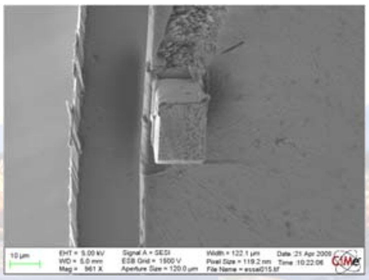


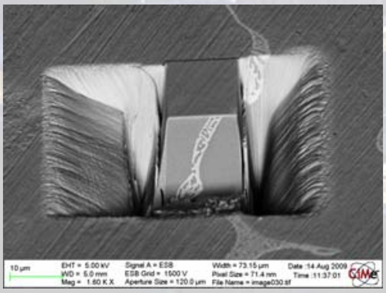


EDX limitations

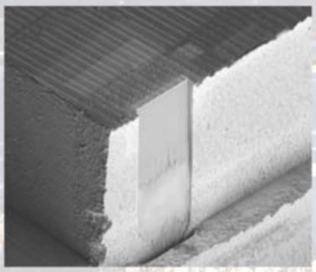
- Parasitic X-ray signal depends on:
  - Geometry and composition of surrounding
  - Detector position

- Solutions
  - Remove VOI out of surrounding : Block lift-out
  - Move the wall facing detector further away

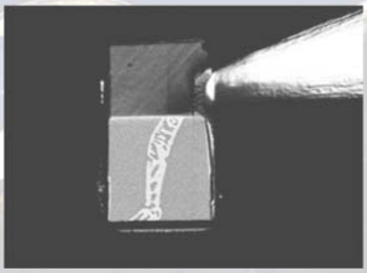




Bigger trenches



Edge geometry (similar to 3D-EBSD)

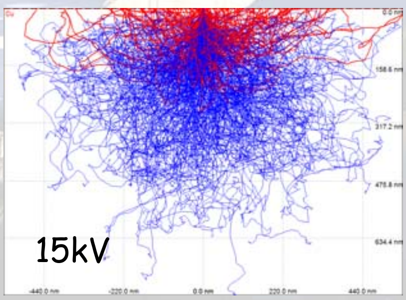


Complete lift-out

EDX resolution

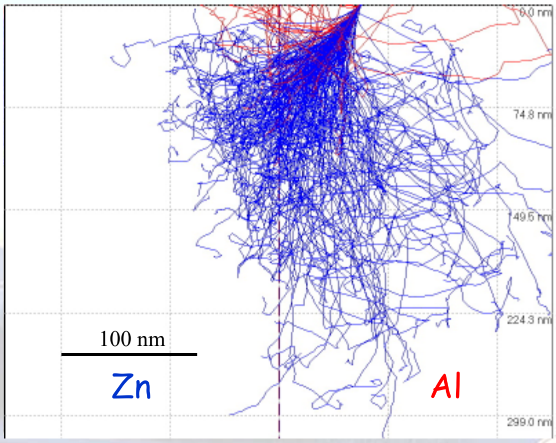
Resolution limit: Interaction volume

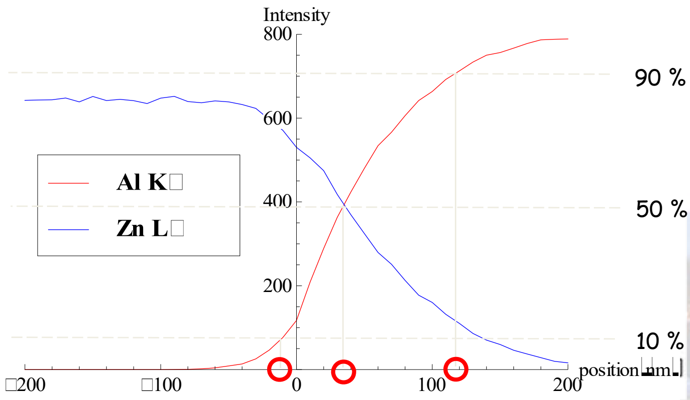
- Lower the high tension as much as possible
- Big voxels (voxel > interaction volume)
- Small voxels: “convolution” problem
  - Delocalisation (metrology !)
  - Quantification (inhomogeneity, interfaces, multiple phases)



EDX resolution

evaluation of delocalisation: model system





- Simulated linescan across the interface normal to y
  - Signal is shifted towards Al because of the incident angle
  - Positions of threshold (10 %, 50 % and 90 %) are used to compare with other geometries

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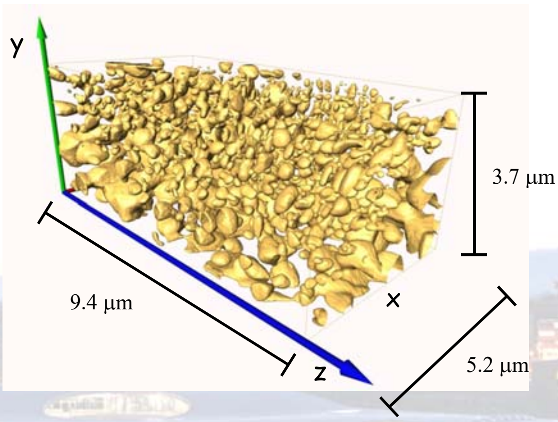
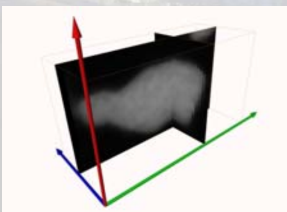
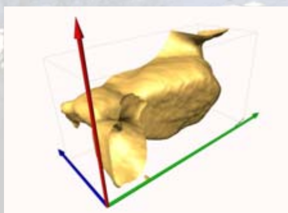
EDX resolution

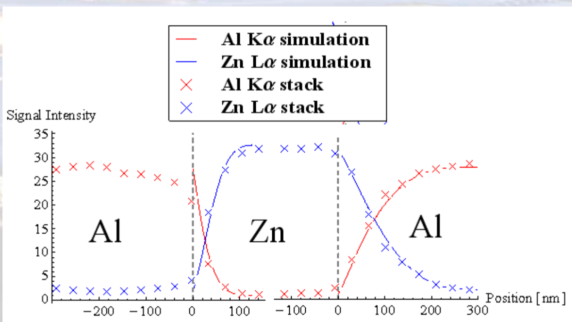
model system: AlZn

- Stack of 269 EDX maps
  - Acquisition parameters
    - High tension : 5kV
    - Voxel size : 20 x 20 x 40 nm
    - Pixel per map : 256 x 192 (x 269)
    - Times per map : 4+1 minutes
    - Time of acquisition : 24 hours
  - Al Kα elemental map, x/y aligned, smoothing filter (median 3D), surface reconstruction with a single threshold
- Study of the delocalisation of interface (normal to main axes)









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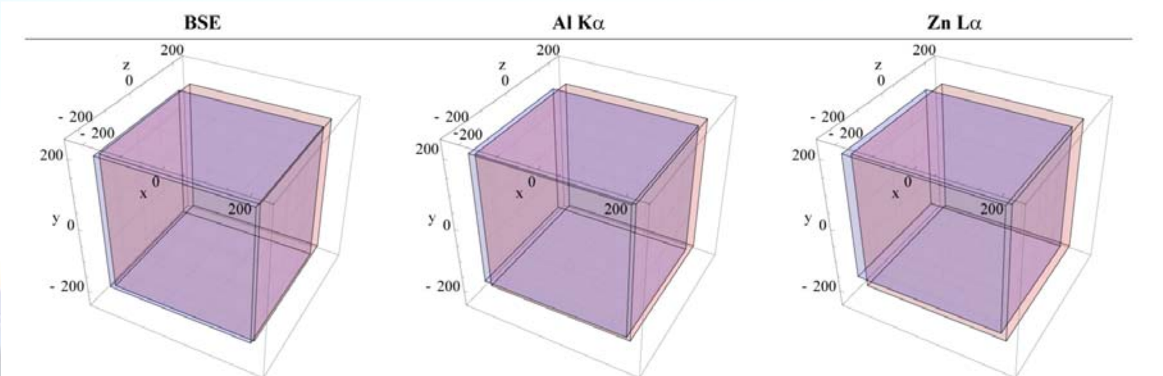
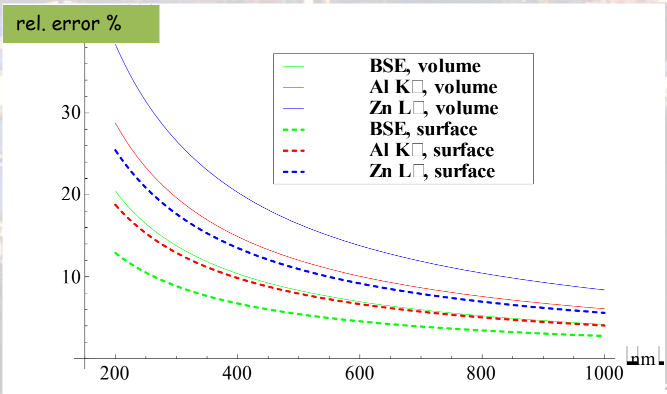
EDX resolution

Delocalisation of interfaces



- Implication of delocalization
  - Cubic Al precipitates in Zn matrix (edge 400nm)
  - Errors in volume and surface v.s. edge length of the precipitates



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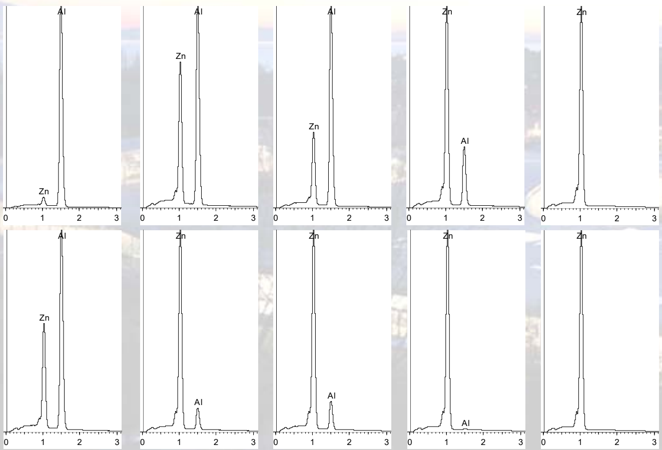
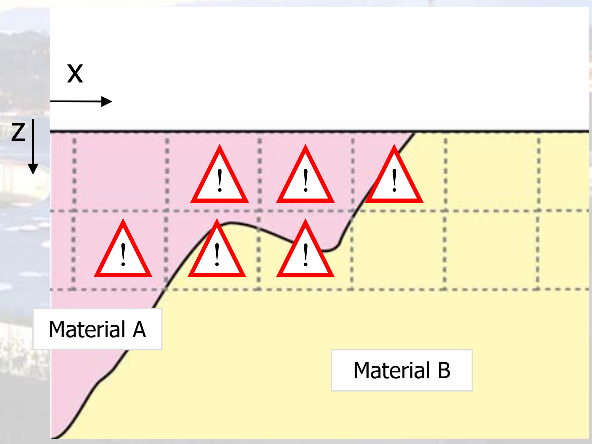
Improving 3D quantification : Idea

- When interaction volume is bigger than voxel size
  - Each spectrum contains a contribution of neighboring voxels
  - Standard quantification inappropriate for voxels close to GB
  - Possibility of quantification enhancement

Recorded spectrum



Scan through x and z of a grain boundary



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Improving 3D quantification : Idea

Algorithm to enhance 3D EDX quantification

- Recursive relation
- Composition of a voxel depends also on the subsequent voxels (along z)
- Sample considered as stratified
  - f function: Thin film $\phi(\rho z)$ quantification*

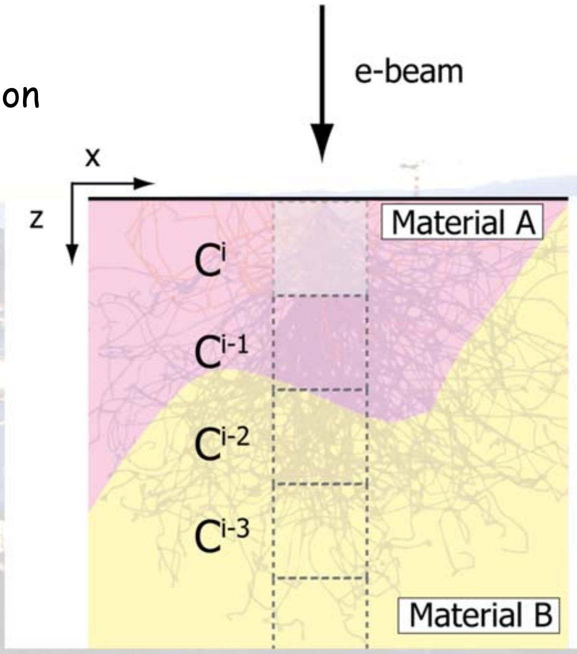
Recursive relation

z index (layer)

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

Element index

Grain boundary and voxels in depth



PhD thesis of Pierre Burdet

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

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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

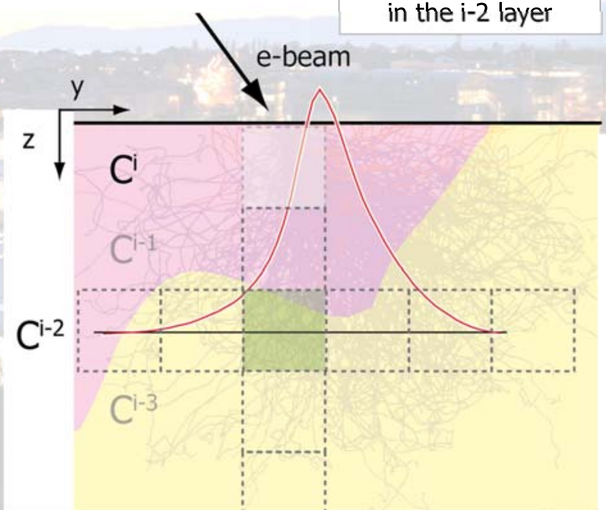
Recursive relation

z index (layer)

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

Element index

Electron distribution in the i-2 layer



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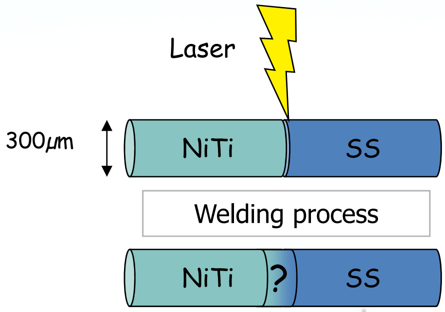
Application Example: NiTi-Steel

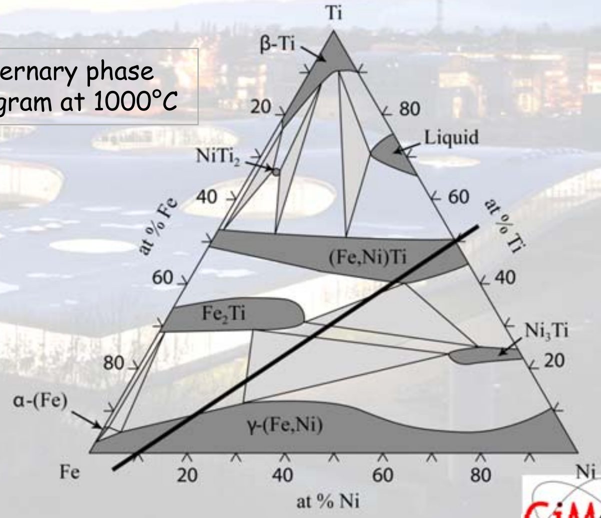
NiTi - steel welding

Jonas Vannod, EPFL-CIME /LSMX

- Wire welding by laser
  - NiTi wire
  - Stainless steel wire
  - 300 mm of diameter
- Molten region
  - Liquid diffusion (fast)
  - Phase formation during solidification
- Characterization
  - Microstructure and composition of the different phases



Ternary phase diagram at 1000°C



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

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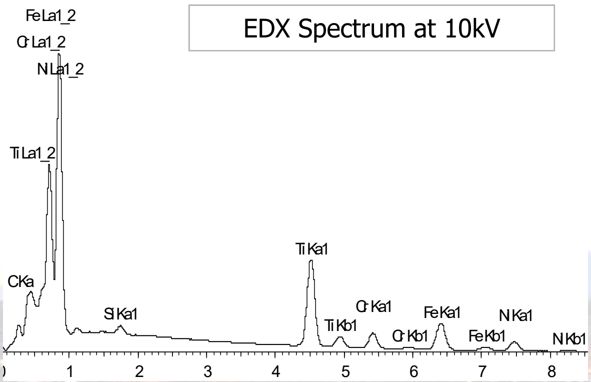
CiMe

Application Example

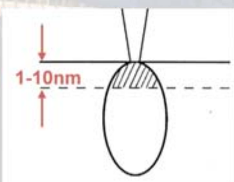
Experimental: E_0 and voxel size

- EDX spectrum image
  - C Kα, Ti Kα, Cr Kα, Fe Kα, Ni Lα
  - Fe Kα (6.4 kV) → 10kV
  - Max X-ray range: 500 nm
  - Voxel size for z: 100 nm
  - For x, y: 100 nm (isotropic)
- SEM image
  - SE image → 12.5 nm for z
  - For x, y: 12.5 nm (isotropic)

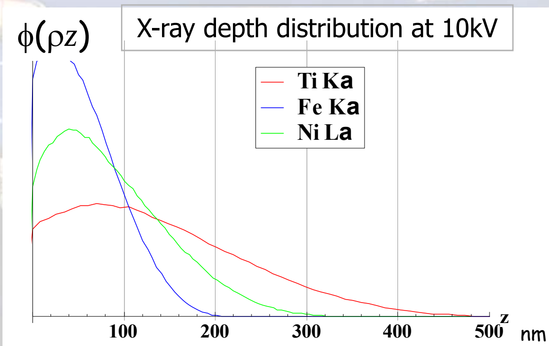
EDX Spectrum at 10kV



SE escape depth



X-ray depth distribution at 10kV



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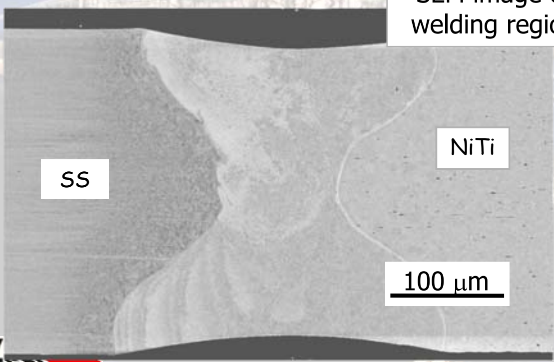
CiMe

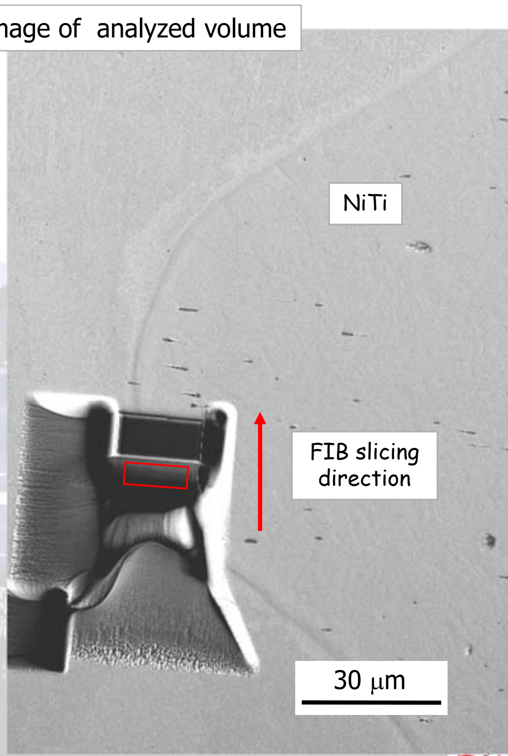
Experimental : Analyzed volume

- On NiTi side
  - Phases of main interest
- Analyzed volume
  - Surface: 12.8 x 4.4 μm
  - Depth: 9.6 μm
- 44 EDX maps
  - 6 min per map

SEM image of welding region



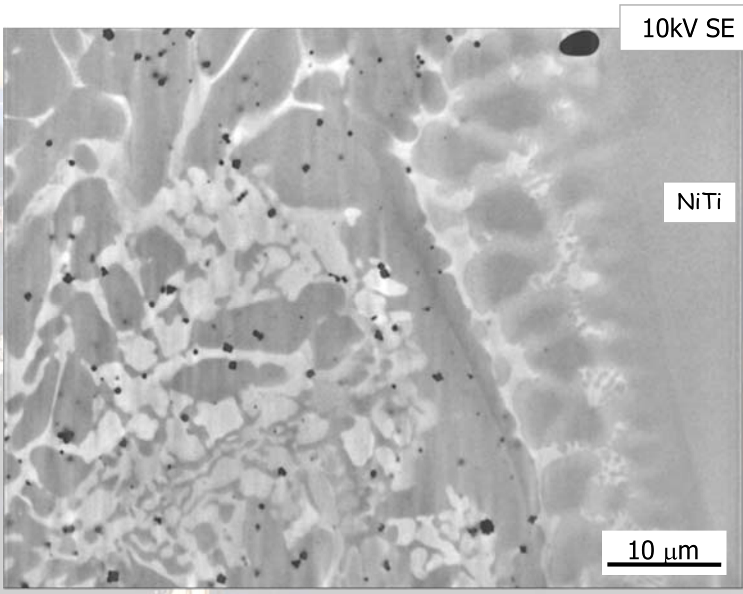
SEM image of analyzed volume



Results: SEM image contrast

- SEM image
  - SE (Secondary e^-) contrast: no direct interpretation
  - Mean z roughly similar (excluding TiC) → low contrast for BSE (Backscatter e^-)

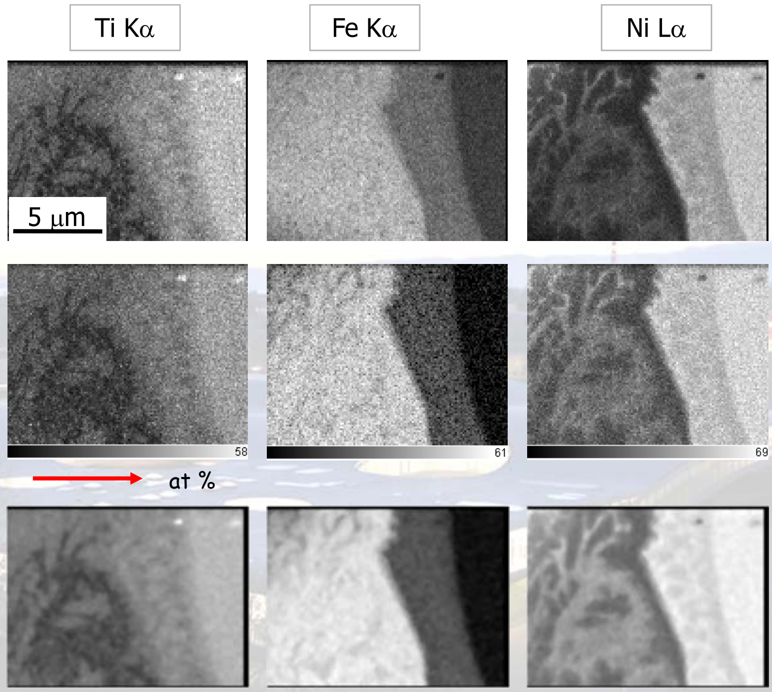
10kV SE image



Application Example: NiTi-Steel

Results: EDX map

- Intensity Maps
  (X-ray line intensity)
- Quant Maps
  Standard EDX
  procedure
- Noise treatment
  - 3D Median filter
    (3x3x3)



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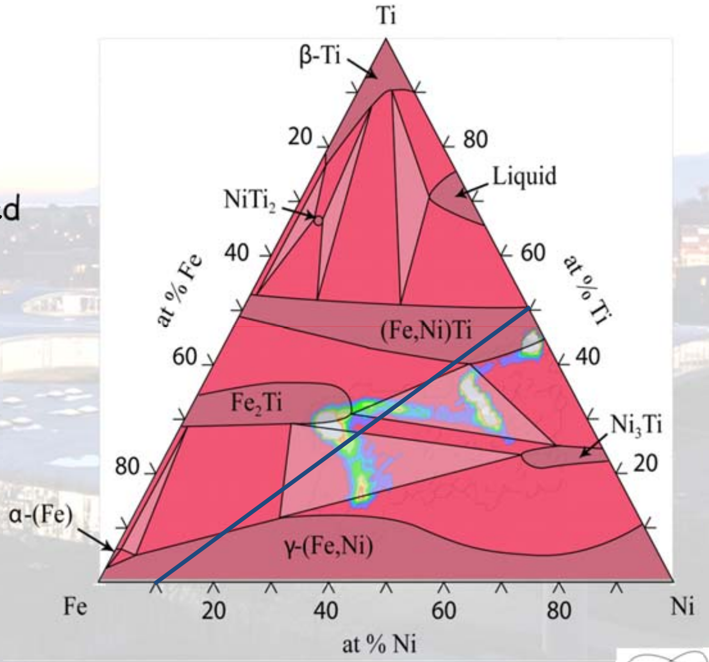
Application Example

Phases identification: Ternary histogram

- Ternary EDX map histogram
  - From three main EDX quantified maps (noise treated)
  - Compared to ternary phase diagram
- Phase identification
  - $min_A \le C_A < max_A$ (A=Ti,Fe,Ni)
  - min_A and max_A refined with SE image contrast

Ternary phase diagram at 1000°C with ternary histogram



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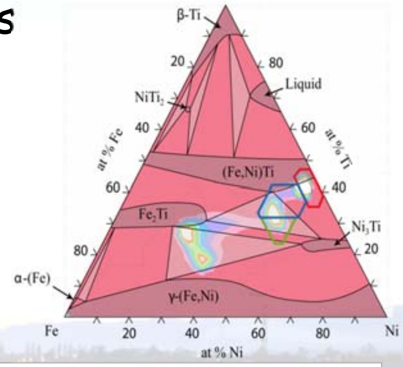
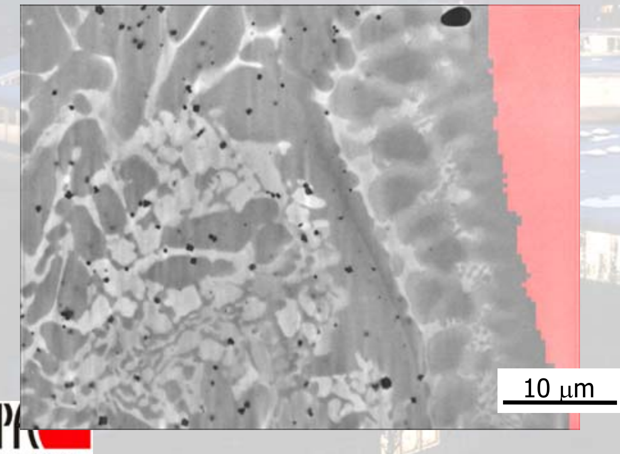
Phase identification: Fe-poor phases

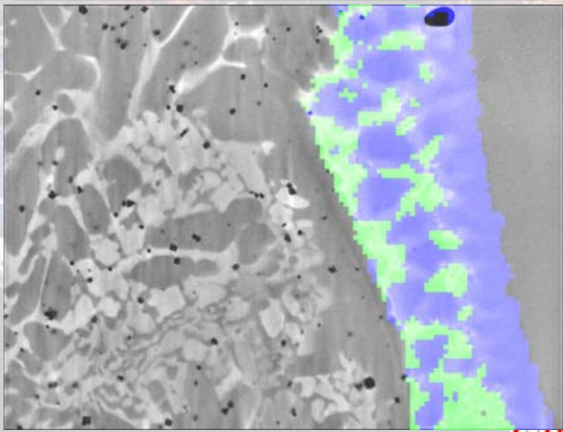
- Red: NiTi
- Blue: Between (Fe,Ni)Ti and Ni_3Ti
- Green: Ni_3Ti



SE image with NiTi phase



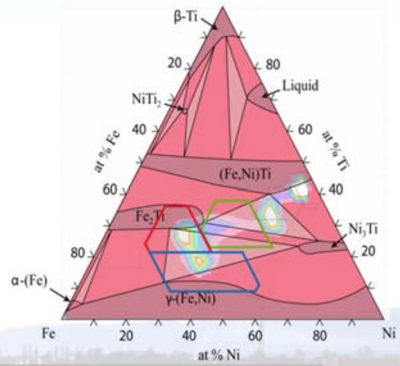
SE image with (Ni,Fe)Ti and Ni_3Ti phases



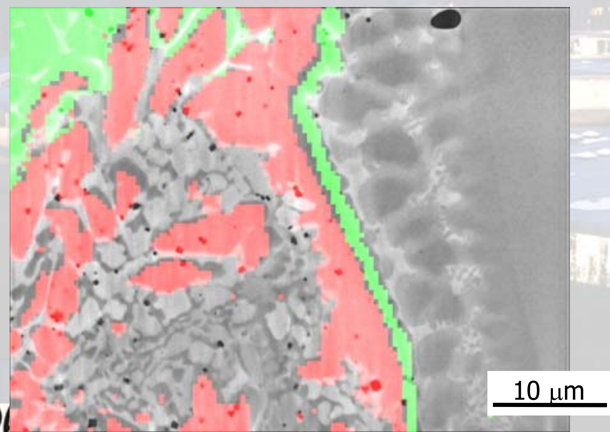
Application Example

Phase identification: Fe-rich phases

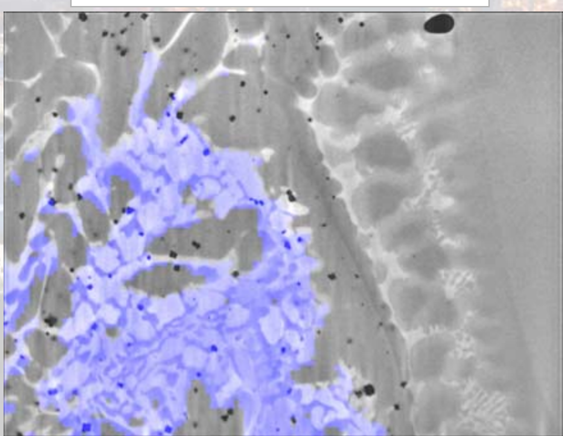
- Green: Between Ni_3Ti and Fe_2Ti
- Red: Fe_2Ti
- Blue: γ-(FeNi)



SE image with Ni_3Ti and Fe_2Ti phases



SE image with γ-(FeNi) phase



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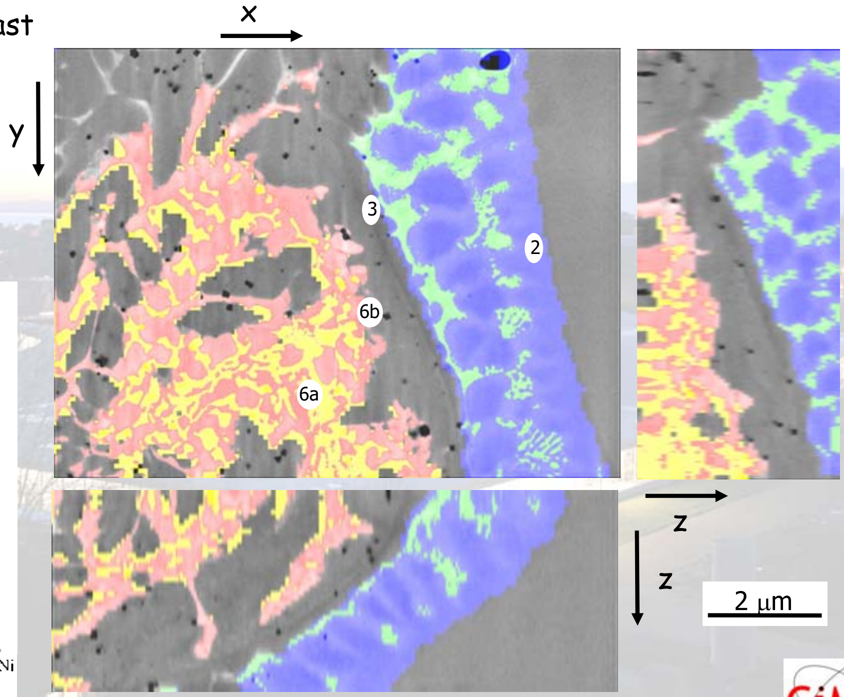
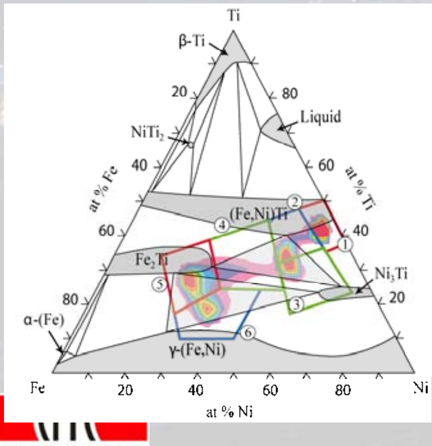
FÉDÉRALE DE LAUSANNE

Applications: NiTi - steel welding

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



Ternary diagram



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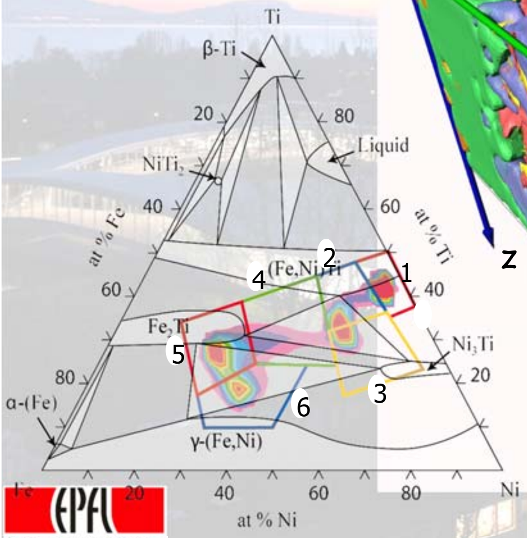
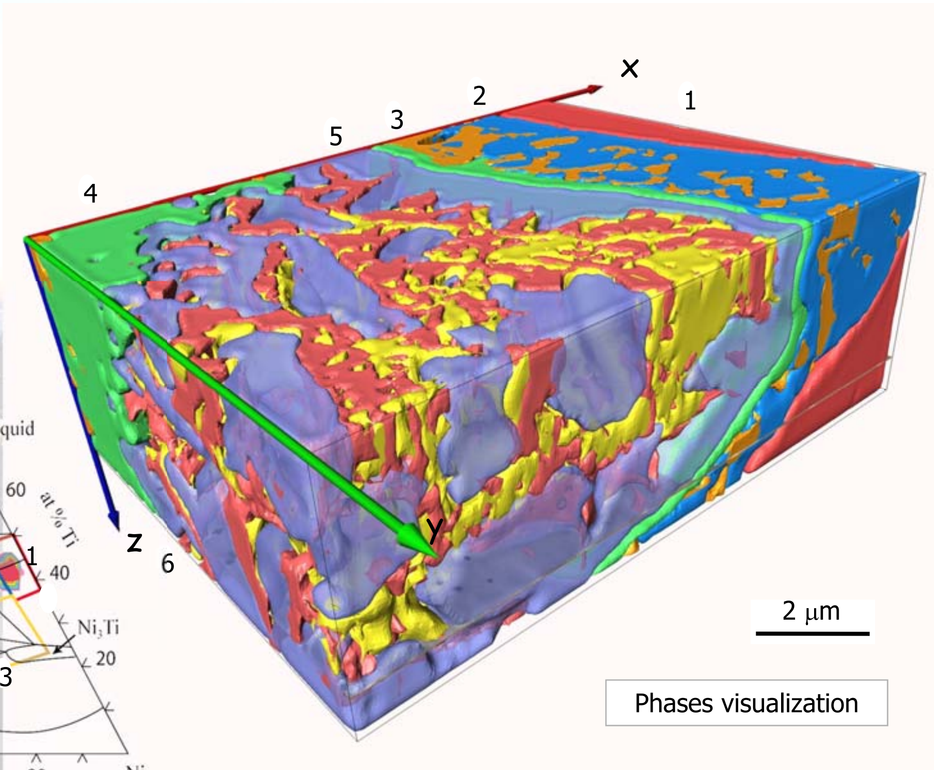
Applications: NiTi - steel welding

– Visualization

Ternary diagram





Phases visualization

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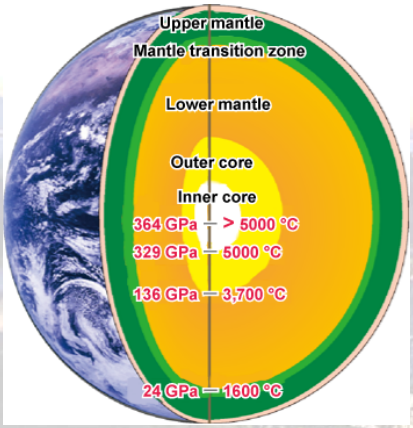
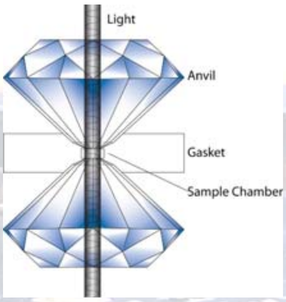
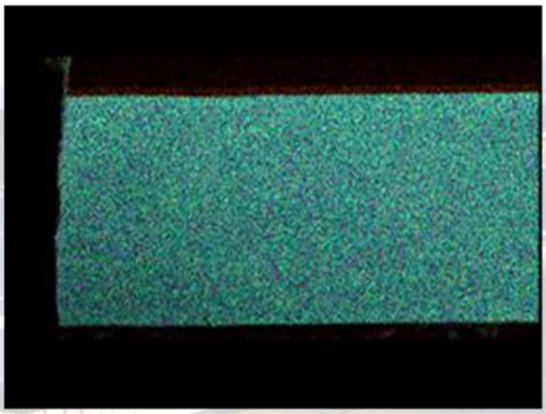
"Micro-Planet Earth"

F. Nabiei: 3D Chemical imaging of chemical distribution from melting in laser-heated diamond anvil cell





3000K
~100 GPa



MICROANALYSIS IN A FIB/SEM:
EDX IN 3D
WHAT CAN WE EXPECT, WHERE ARE THE LIMITS...?

- FIB/SEM Nano-Tomography: powerful tool for micro(structure)analysis at the nano-scale
- 3D-EDX: Experimental challenges: choice of parameters, geometrical constraints
- 3D EDX: careful interpretation of results

Deconvolution procedures (at least locally)
Statistical treatment of data (PCA,ICA etc.)

Acknowledgements:
Zeiss (PhD Thesis P. Burdet)

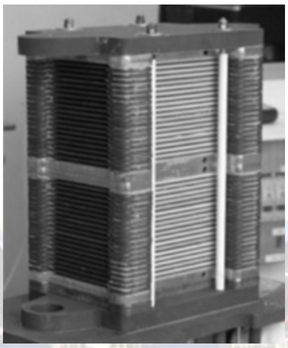
EPFL Group of Energy Materials

Jan van Herle:

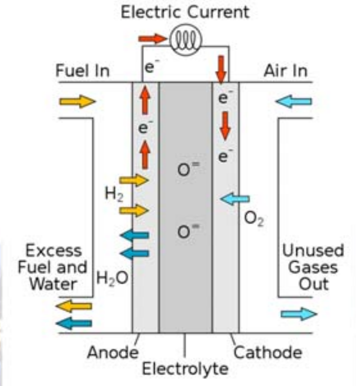
Solid-Oxide-Fuel Cells

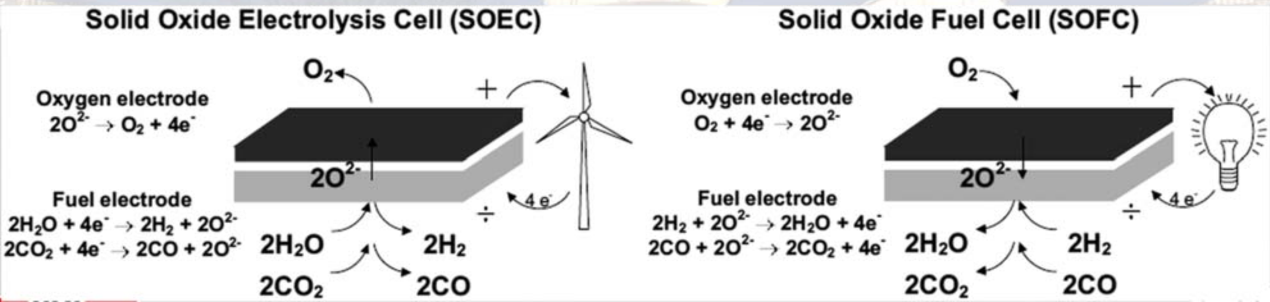
Solid-Oxide-Electrolysis Cells (reverse mode)

In reverse mode, solid oxide electrolysis cells (SOEC) are being developed intensely for storing growing excess renewable electricity into gas (H2, CH4), reaching close to 100% electrical-to-H2 efficiency. The challenge remains to mitigate the performance degradation with time.



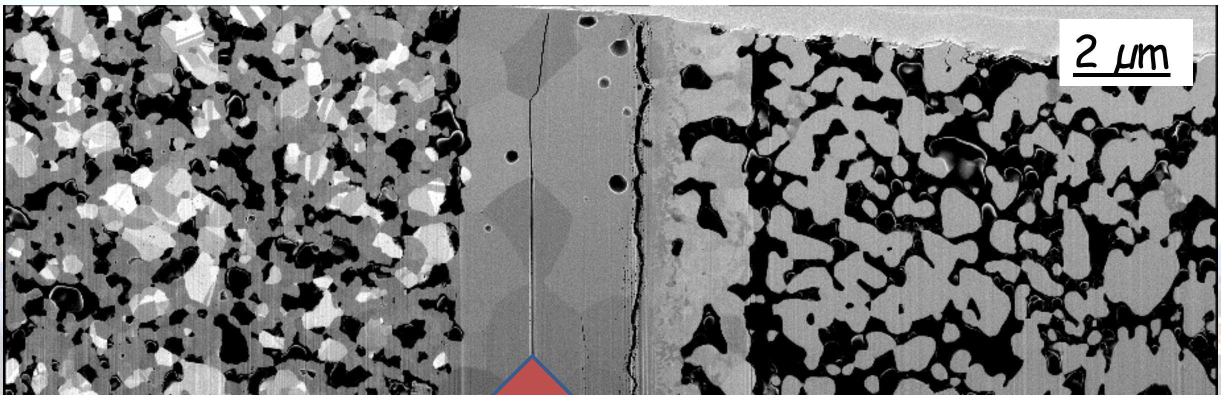
60-cell stack, 80 cm^2 (1 kWe)





Solid-Oxide-Electrolysis Cell

full structure



Ni-YSZ hydrogen **electrode**

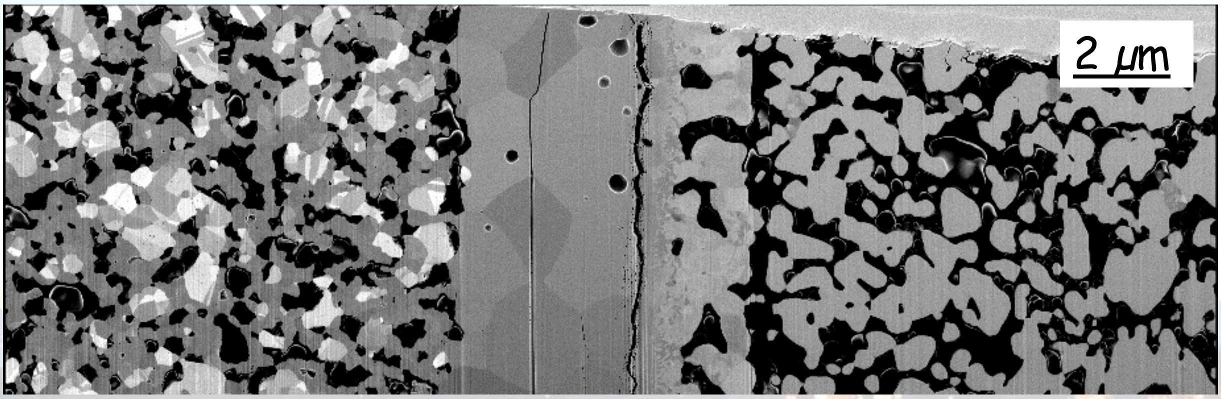
yttria-stabilized zirconia (YSZ) **electrolyte**

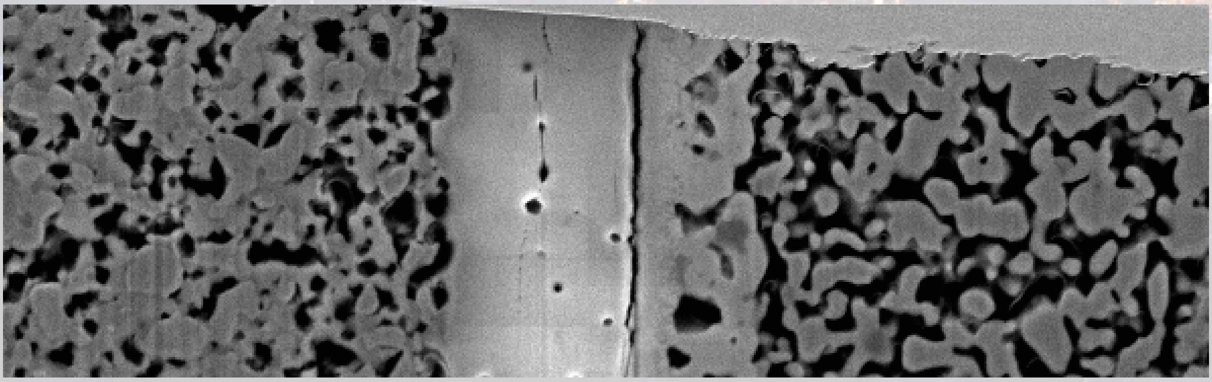
gadolinia-doped ceria (GDC) compatibility layer

lanthanum strontium cobalt ferrite-based oxygen **electrode**

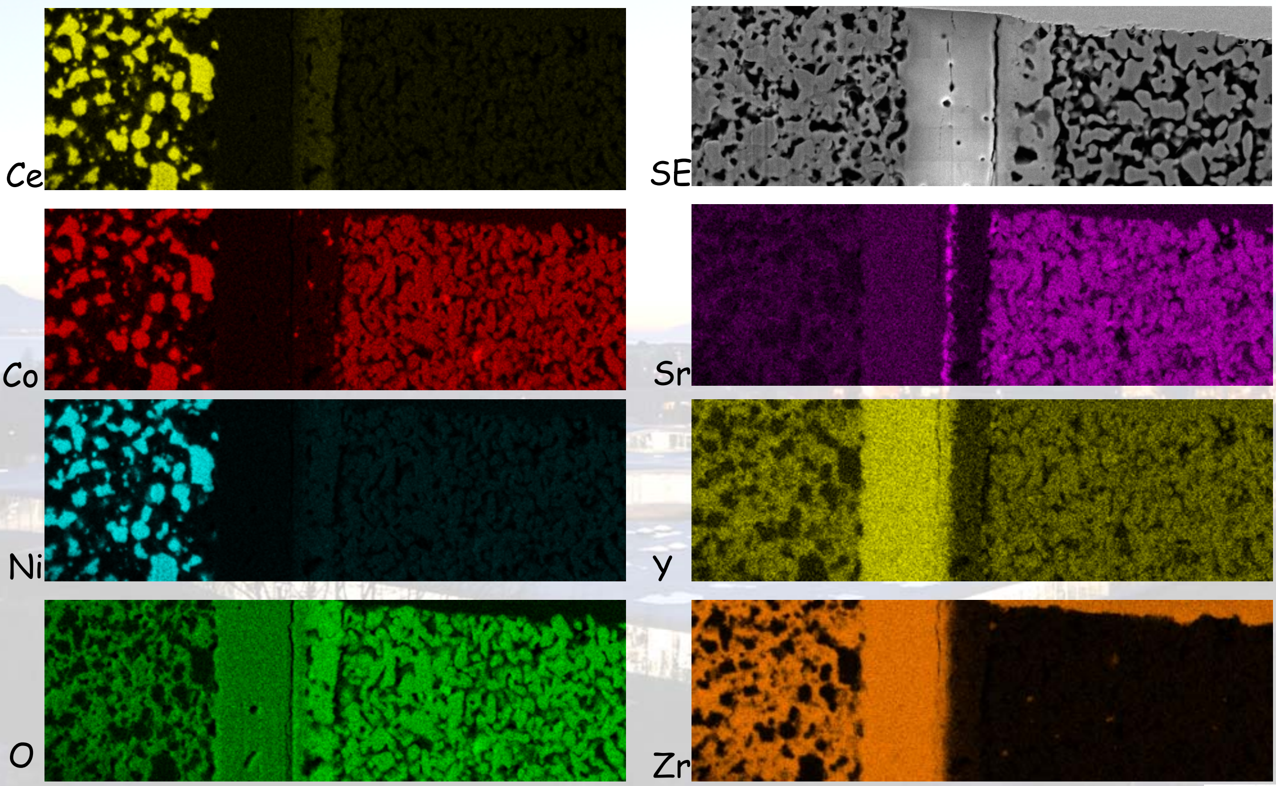
Degradation causes morphological, chemical and crystallographic changes due to intrinsic material instabilities and impurities

Imaging with 1.8 kV electrons, 2.5nA current, inLens detector, 10nm pixel size





Imaging with 10 kV electrons, 4.5nA current, SE detector, 40nm pixel size.



Putting things together

- **SmartSem**
  Microscope control
  TEM-lamella preparation
  Micro-machining
  Etc.

Slave

Master

- **INCA-3D**
  EDX-mapping
  no drift correction
  only one signal (SE or BSE)
  need for higher kV (ionisation)

- **Atlas-3D**
  Nano-Tomography
  drift-correction
  auto-focus
  Simultaneous milling and imaging
  Multiple detectors
  high resolution at low kV
  excellent contrast at low kV

Obsolete… ☹

Take the best of everything

- **SmartSem**
  Microscope control
  TEM-lamella preparation
  Micro-machining
  Etc.

Slave

- **Atlas-3D**
  Nano-Tomography
  drift-correction
  auto-focus
  Simultaneous milling and imaging
  Multiple detectors
  high resolution at low kV
  excellent contrast at low kV

Master

- **AzTec**
  EDX-mapping
  need for higher kV
  (ionisation)

Slave

ABSOLUTELY necessary:High-Tension switching !

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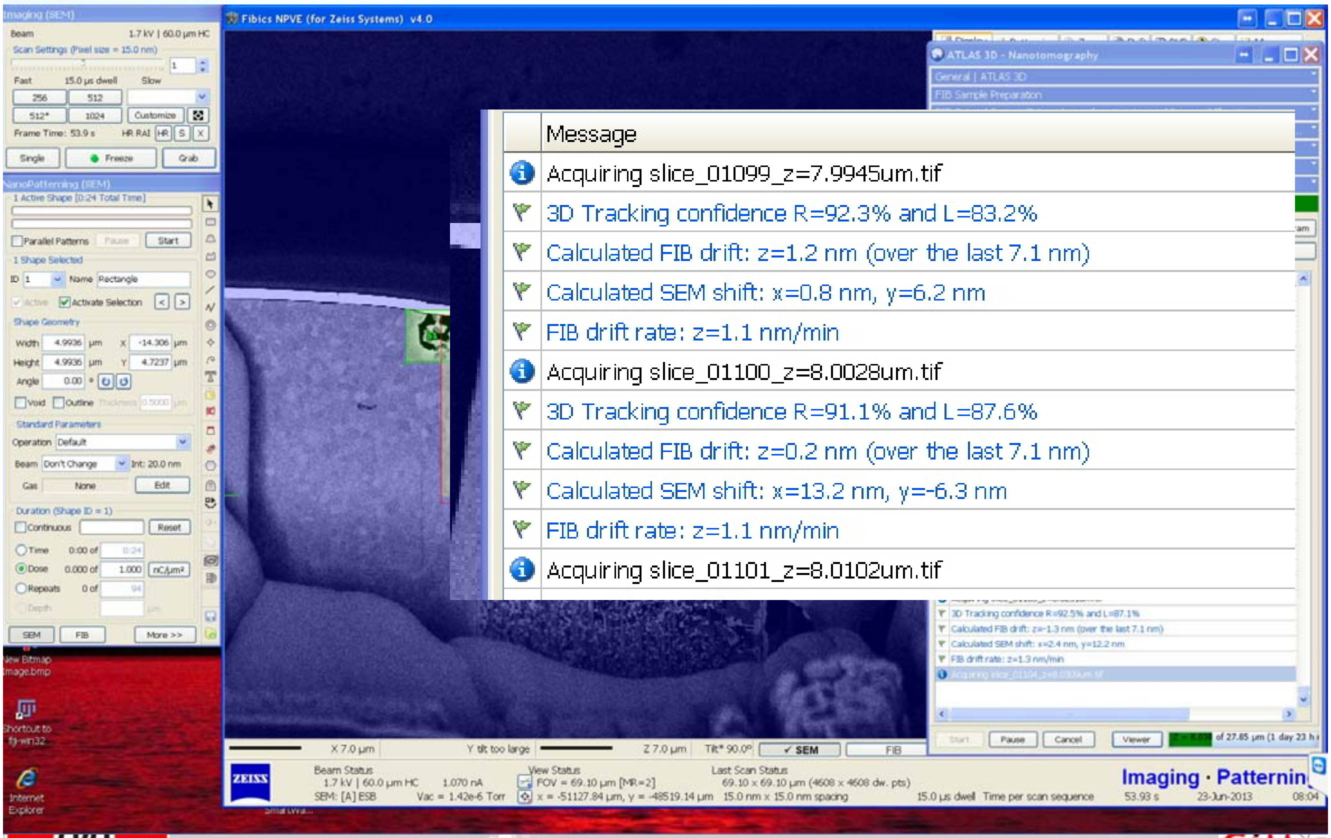
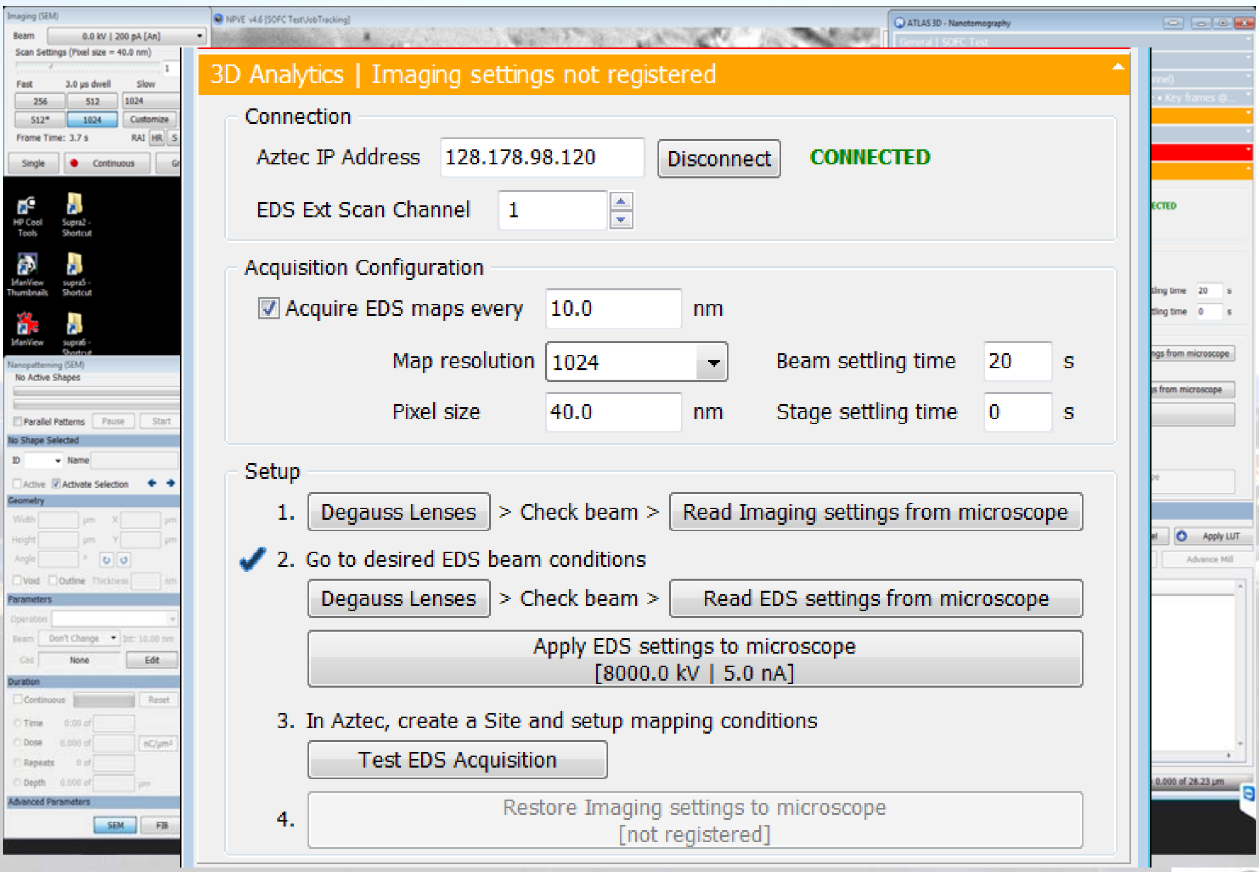
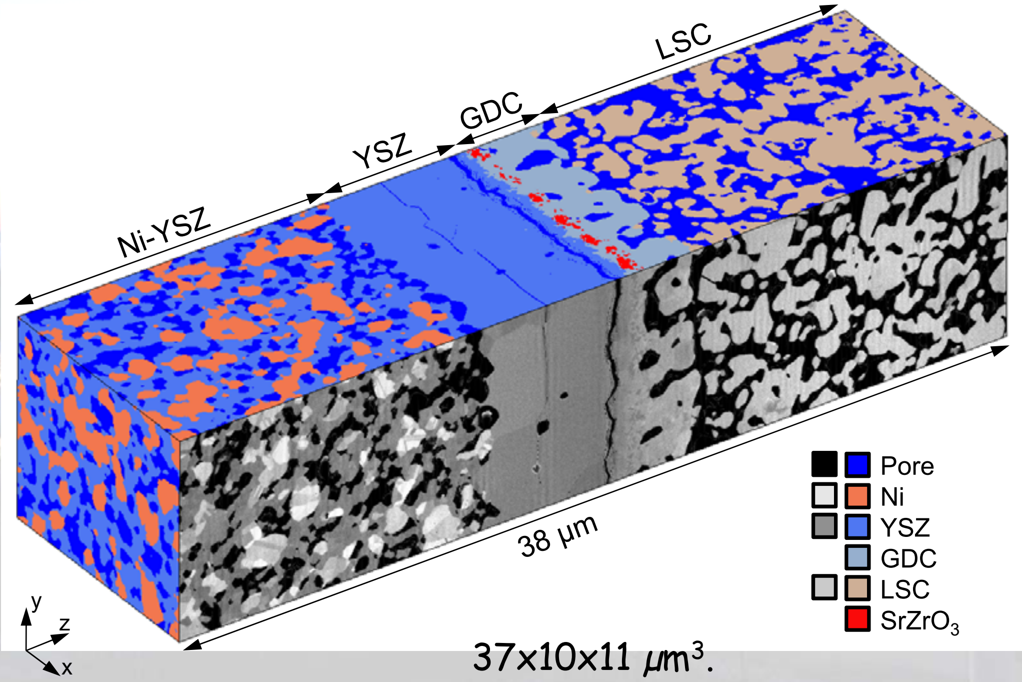
Zeiss/Fibics Atlas-3D package





SE(InLens) & BSE imaging
@1.8 kV 2.5nA
10x10x10nm

EDX mapping
@10kV, 4.5nA
40x40nm every 10slices (100nm)



$37 \times 10 \times 11\ \mu m^3$.

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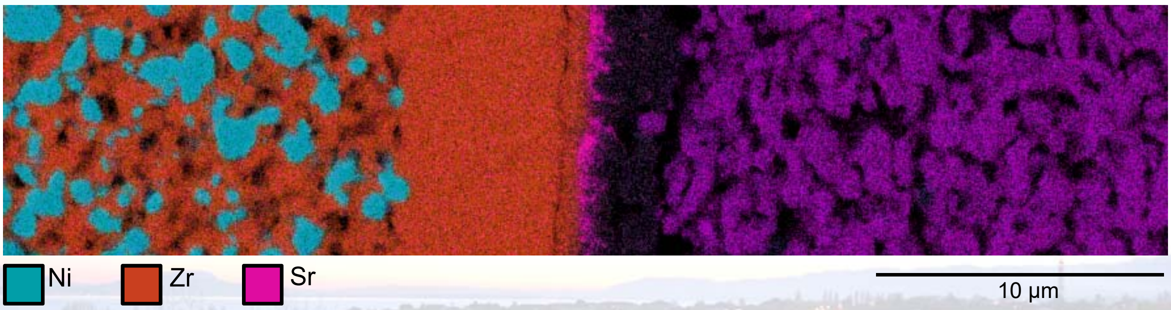
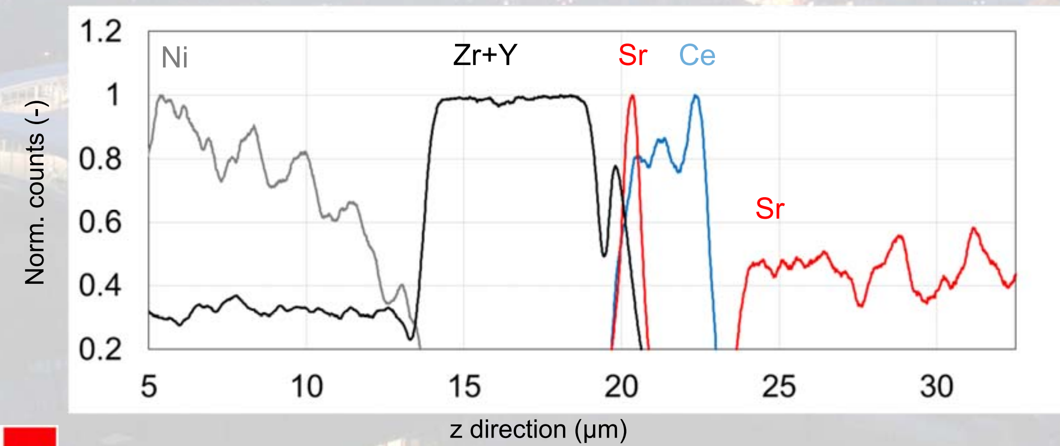
Chemical information





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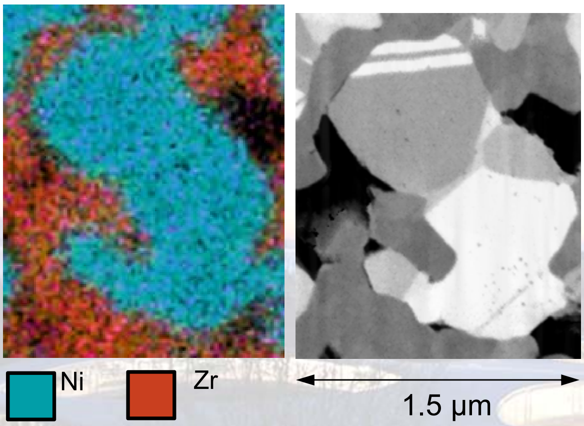
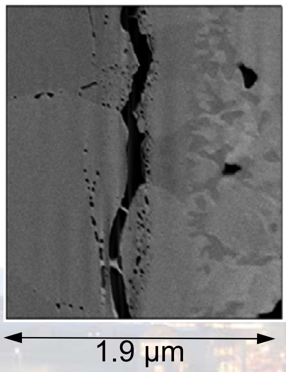
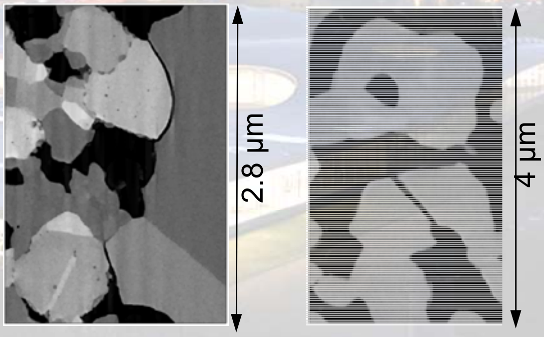
Additional information



Micro-
cracks





Ambigous segmentation
InLens: channeling effects, percolation effects

conclusions

- FIB Nano-Tomography (FIB-NT)
  low kV imaging in a SEM/FIB, the right selection of your detector, high resolution in z direction
- Atlas 3D Engine: High throughput with simultaneous milling and imaging, parallel recording of detector signals, drift correction.
- 3D EDX: SDD detector technology makes it possible
  - delocalisation and inhomogeneous interaction volumes
  combine low kV SEM imaging with EDX mapping at higher kV (HT switching)

Not yet automated: merging of the data sets (different scan generators…)


Thank you for your attention !