

Analysis of paper materials using modern FIB-SEM electron microscope

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Optical microscope

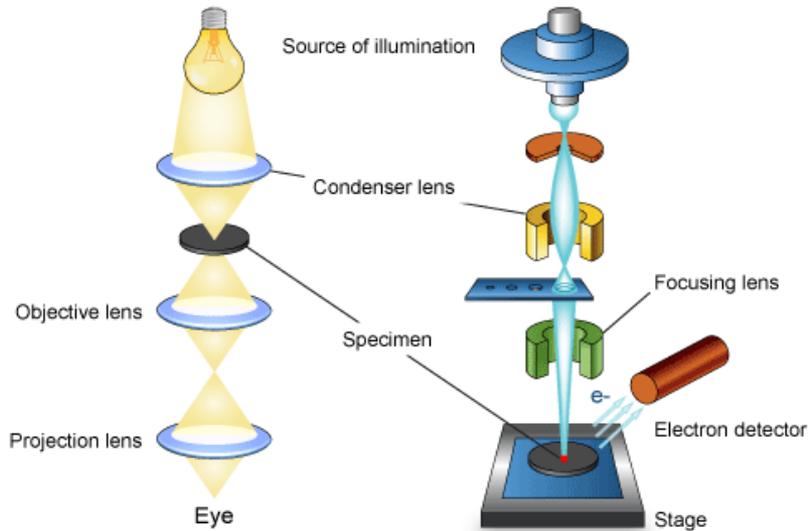
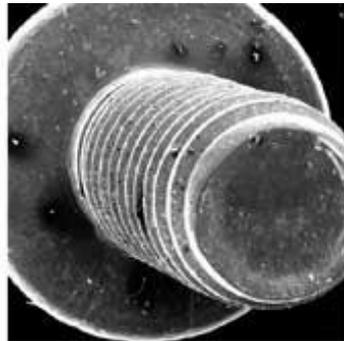


Image source: <http://www.ammr.org.au/myscope/sem/background/>



plane image



depth image !

Scanning electron microscope

The main advantages of SEM microscope

- High resolution (below 1 nm)
- High magnifications
- Large depth of field
- Analytical imaging
- Chemical analysis (EDXS)
- Crystallography analysis (EBSD)
- Several other upgradable extensions...

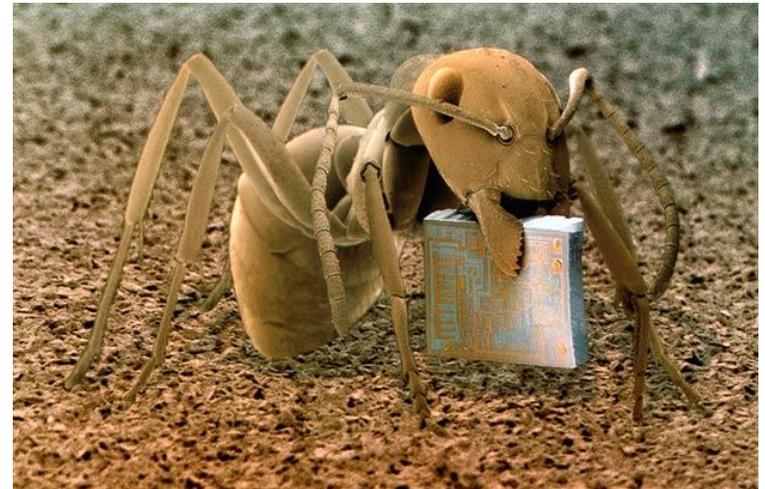
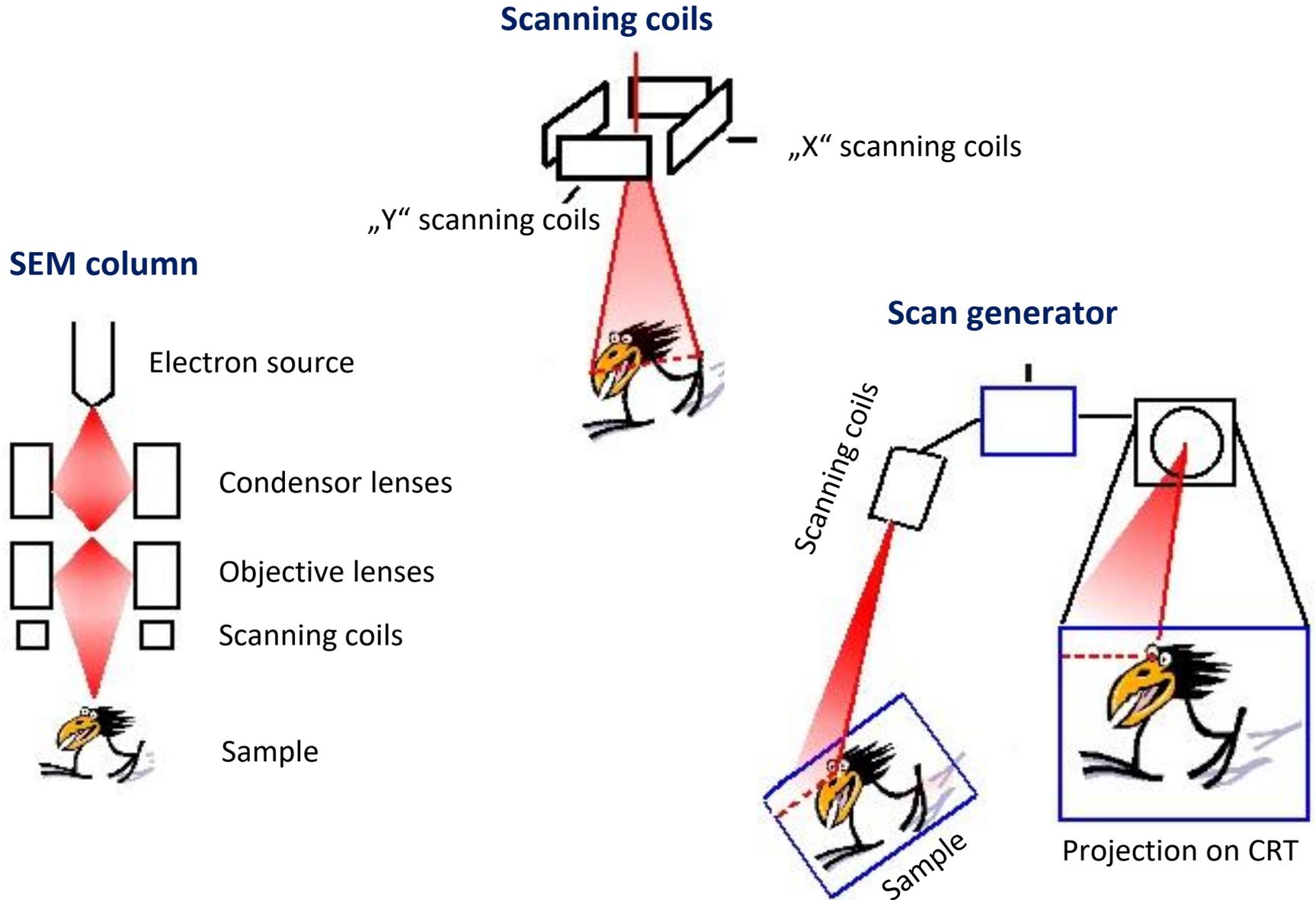
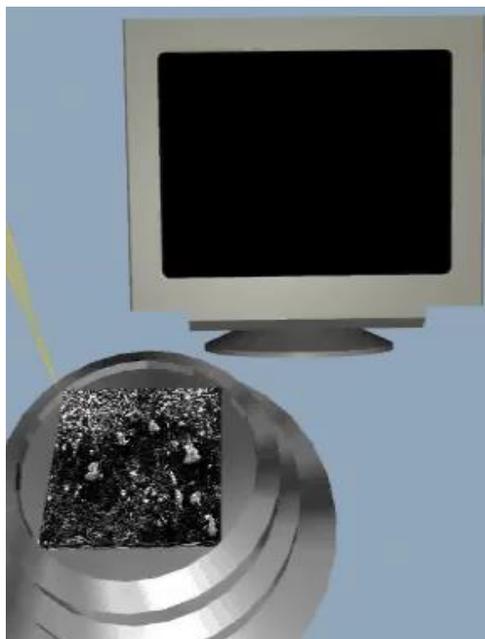


Image source: <http://www.telegraph.co.uk/>

Scanning Electron Microscope – basic concept of operation



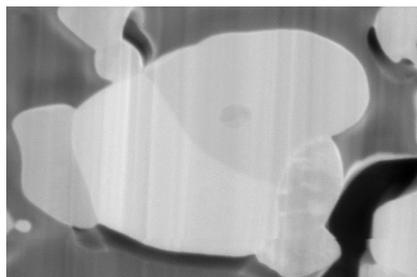
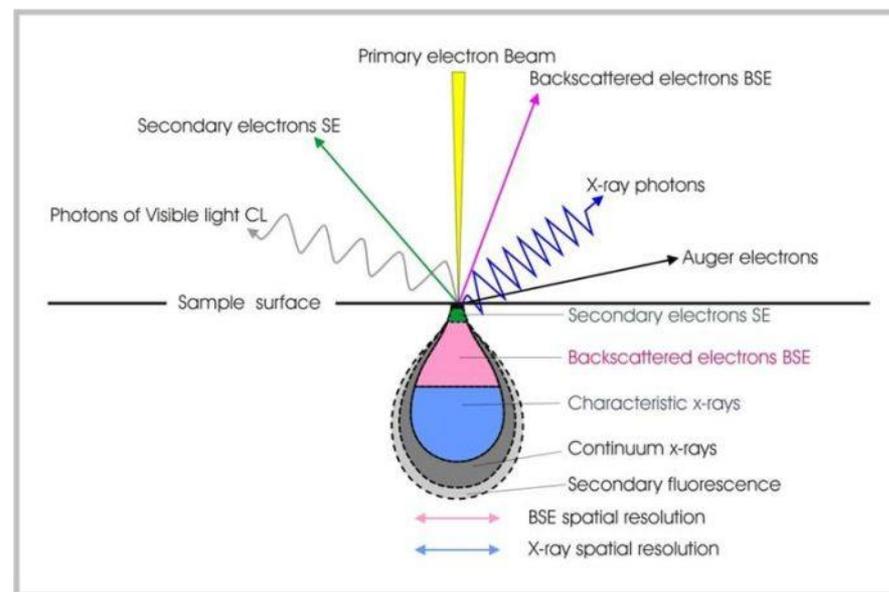
Scanning Electron Microscope – basic concept of operation



Area Scanned On Sample

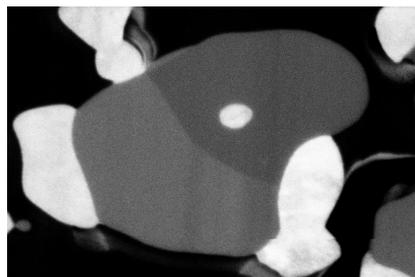


Image on CRT



100 nm EHT = 1.00 kV Signal A = SE2 Min Signal = 0.0000 ESB Gain = 200 V WD = 4.2 mm Aperture Size = 30.00 µm File Name = SDC_164661_020.tif Operator Name = C Date: 8 Oct 2011

SE image



100 nm EHT = 1.00 kV Signal A = ESB Min Signal = 0.0000 ESB Gain = 200 V WD = 4.2 mm Aperture Size = 30.00 µm File Name = SDC_164661_021.tif Operator Name = C Date: 8 Oct 2011

BSE image

Conventional SEM vs. modern high resolution SEM

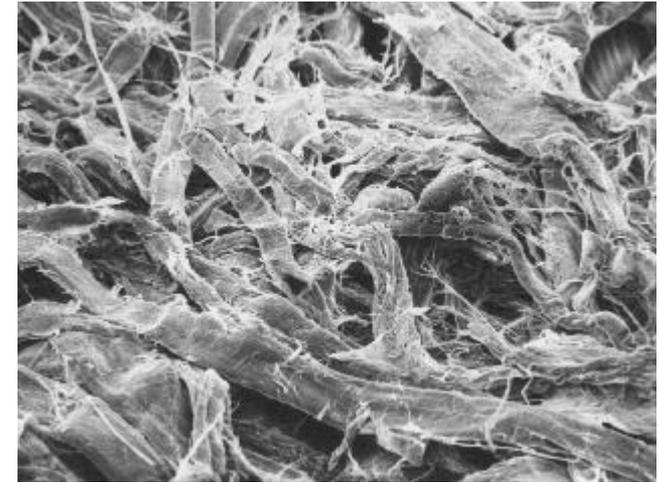


Conventional SEM



JEOL T300

Conductive layer is mandatory



high kV (gold coated sample)

Modern HR-SEM

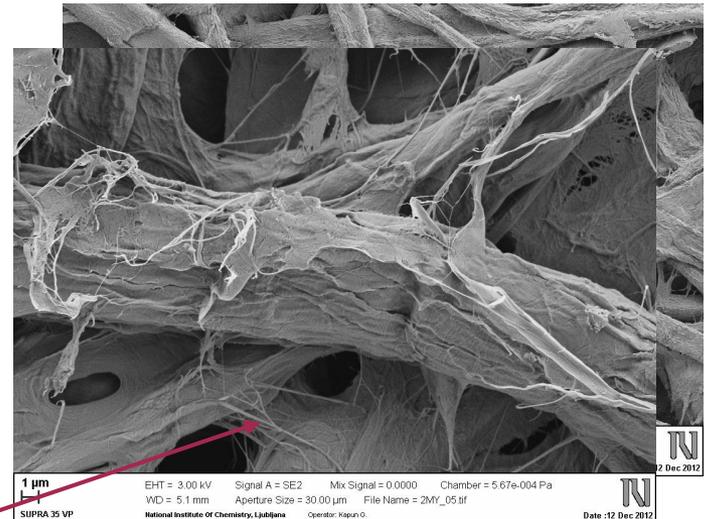


Zeiss Ultra+

Conductive layer not necessary

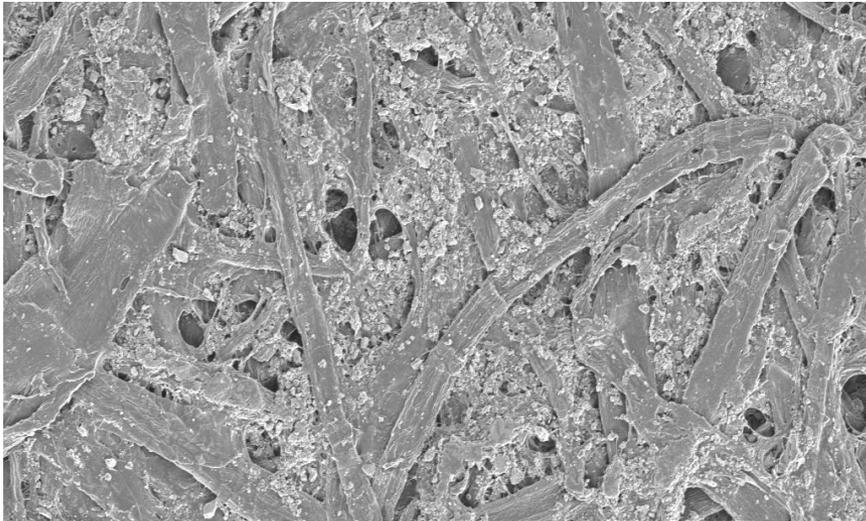


True surface information, revealing detailed structures!



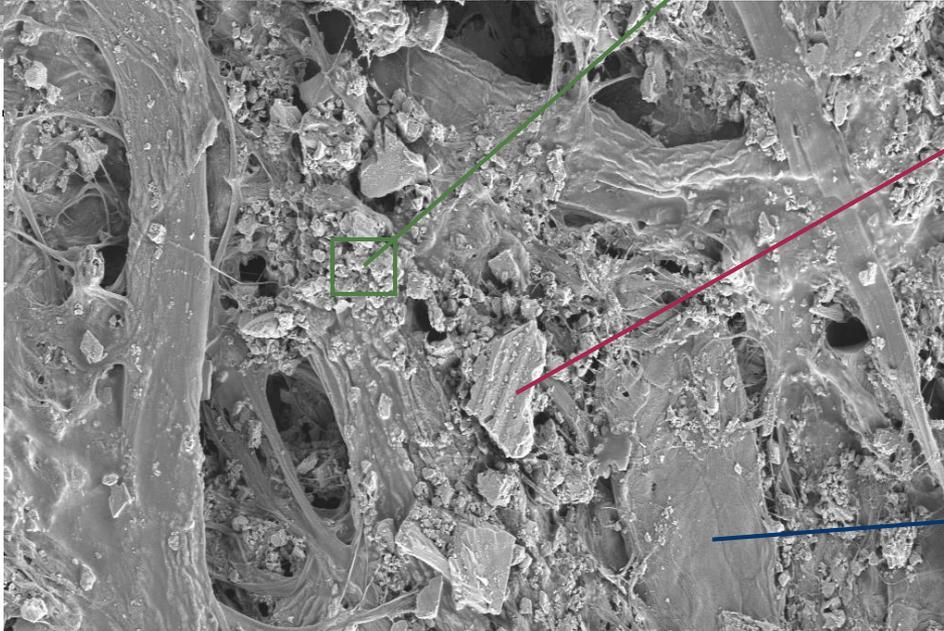
low kV (uncoated sample!)

HR-SEM: surface analysis of commercial paper material



10 μ m
Zeiss, Ultra Plus

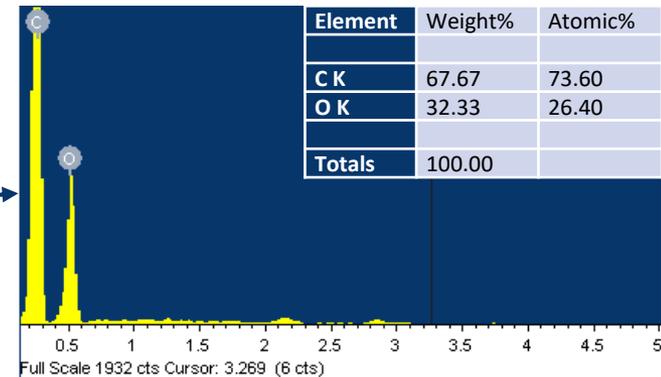
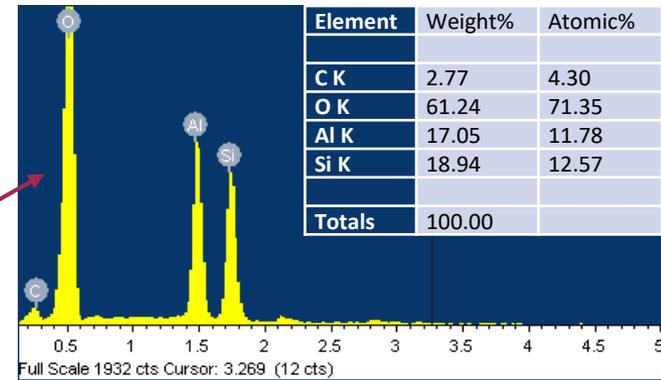
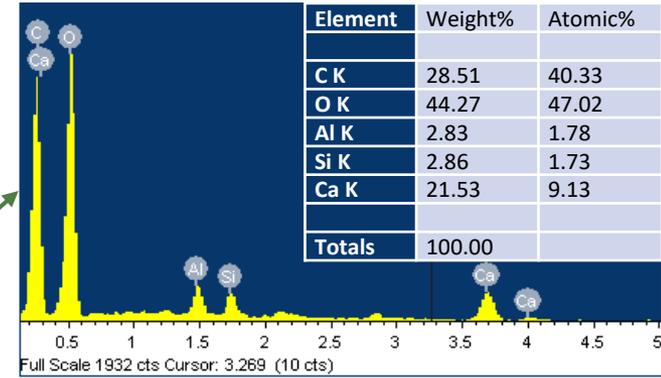
EHT =
WD =
National



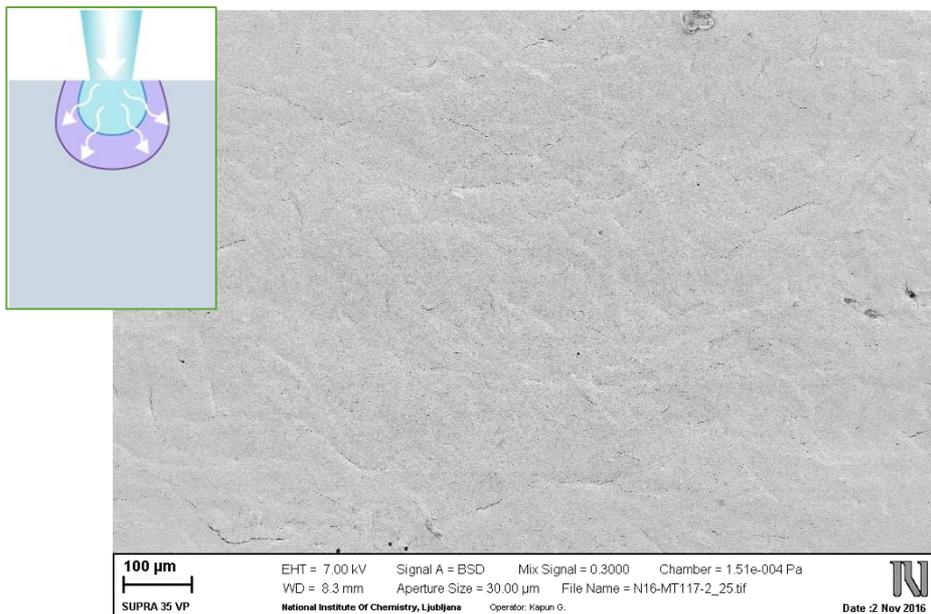
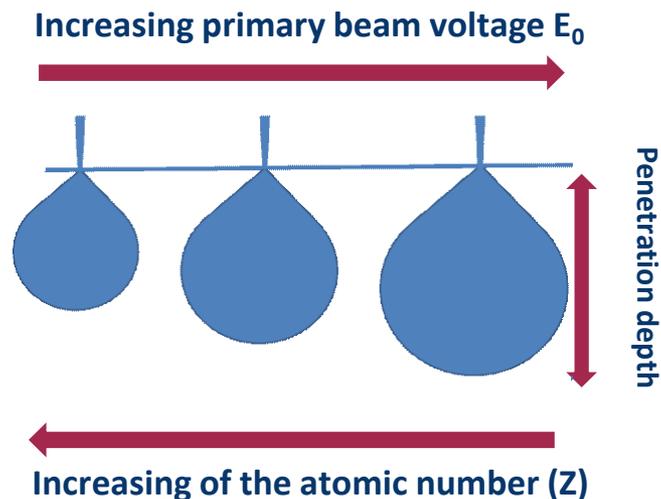
10 μ m
Zeiss, Ultra Plus

EHT = 3.00 kV Signal A = SE2 Mix Signal = 0.0000 ESB Grid = 859 V
WD = 5.0 mm Aperture Size = 30.00 μ m File Name =

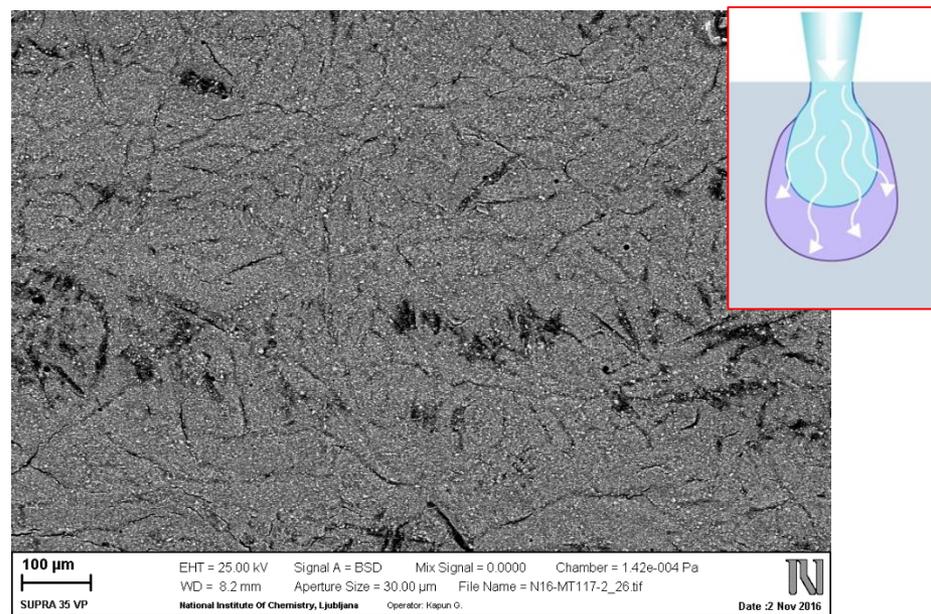
N
Date :11 Dec 2015



SEM-BSD: coating homogeneity on the paper surface

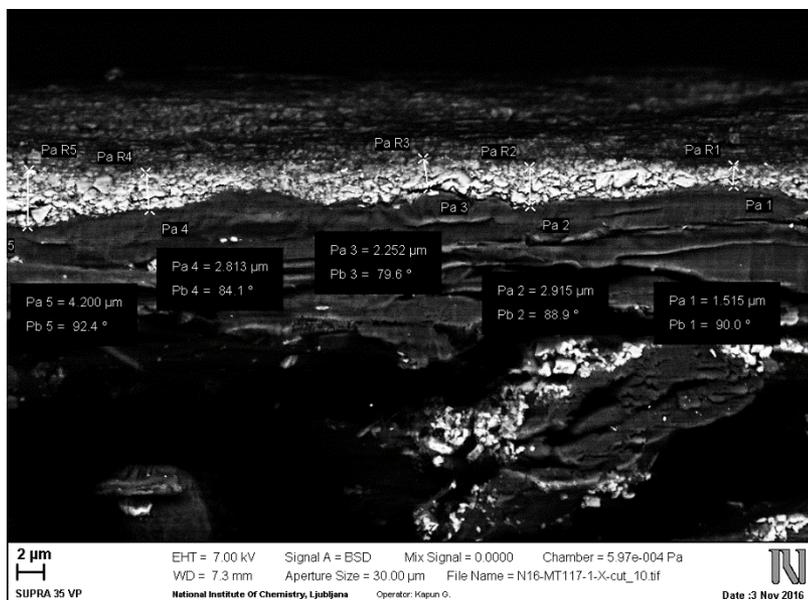
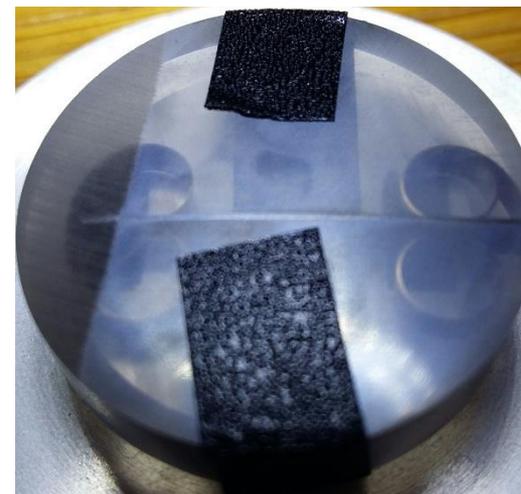
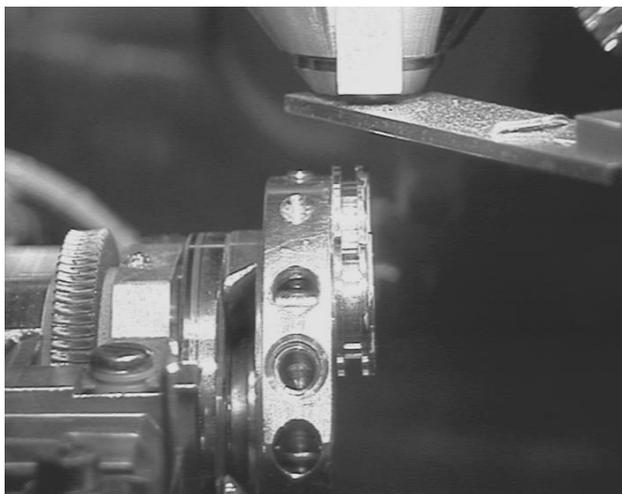


Surface of commercially coated paper: **BSD @7kV**

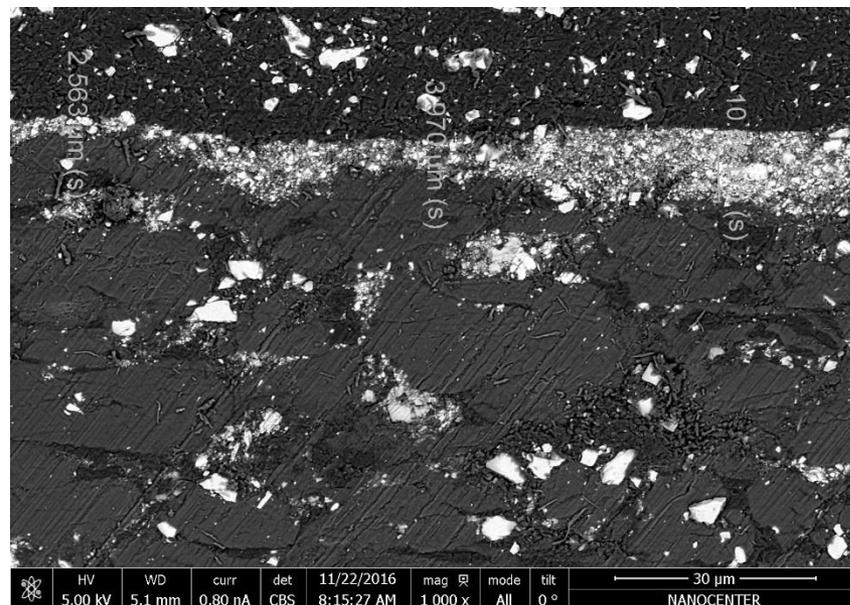


Surface of commercially coated paper: **BSD @25kV**

HR-SEM: conventionally cross-section analysis of paper material

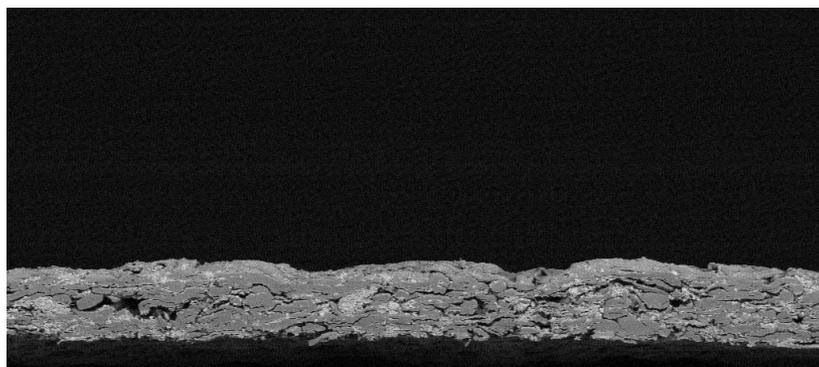


Mechanically prepared cross-section: **BSD @7kV**



Analysis of polished paper cross-section: **BSD @5kV**

HR-SEM: conventionally cross-section analysis of paper material

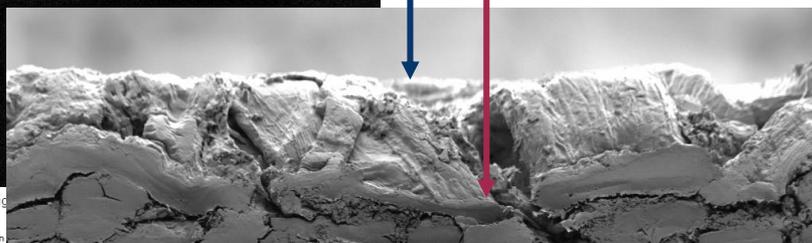


Real thickness

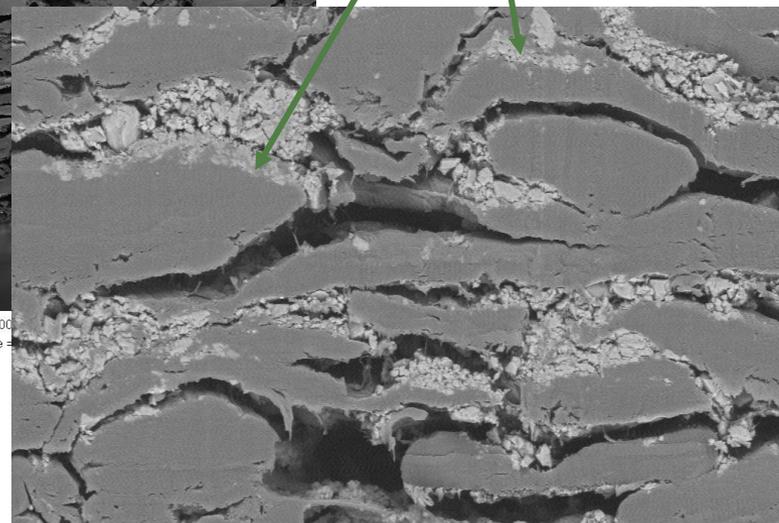
Mechanical deformation!

Displacement of harder material across soft matter during preparation of mechanical cross-section

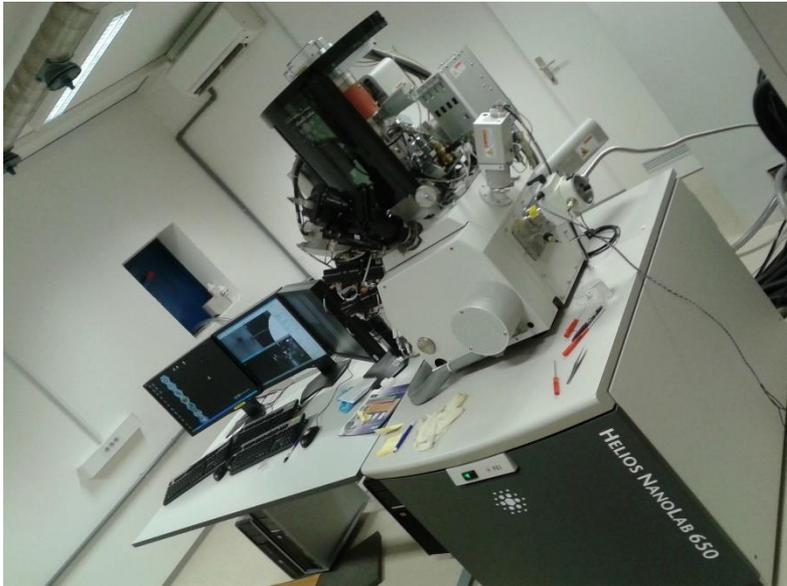
100 μm
Zeiss, Ultra Plus
EHT = 7.00 kV Signal A = AsB Mix Signal = 0.0000
WD = 5.0 mm Aperture Size = 30.00 μm
National Institute Of Chemistry, Ljubljana Operator: Kapun G.



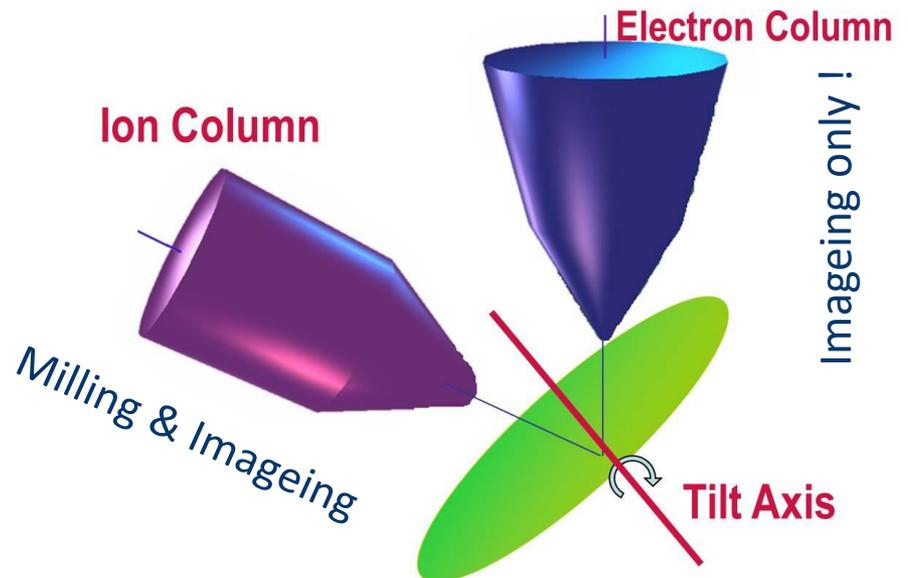
10 μm
Zeiss, Ultra Plus
EHT = 1.00 kV Signal A = SE2 Mix Signal = 0.0000
WD = 5.2 mm Aperture Size = 30.00 μm File Name =
National Institute Of Chemistry, Ljubljana Operator: Kapun G.



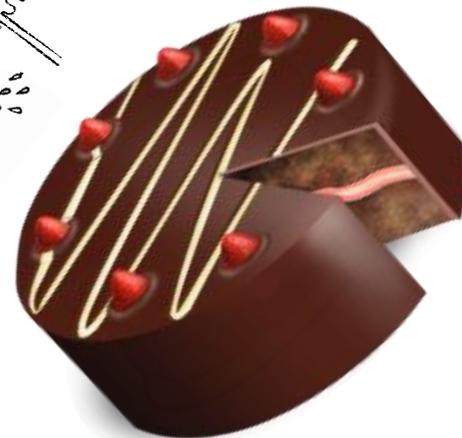
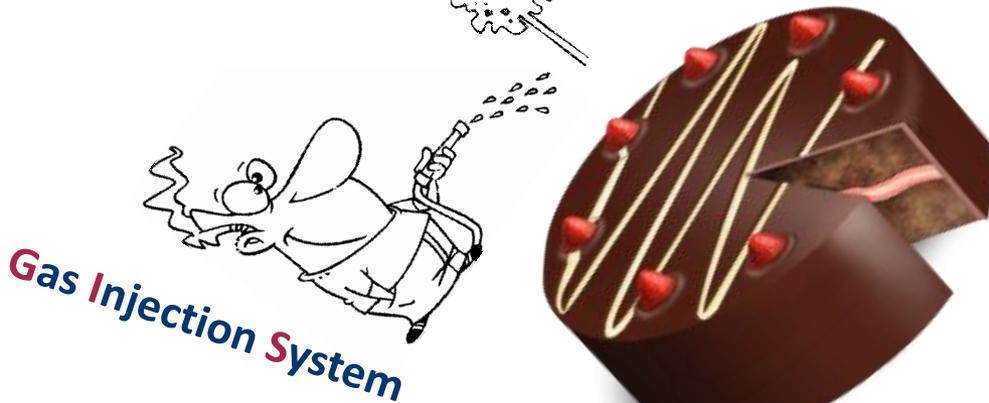
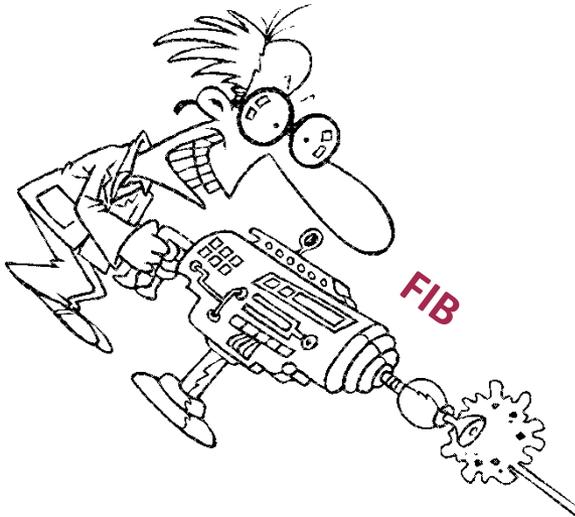
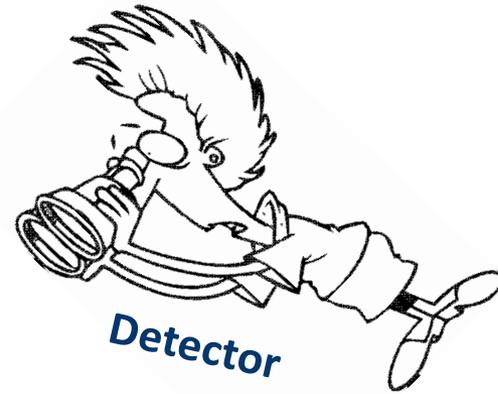
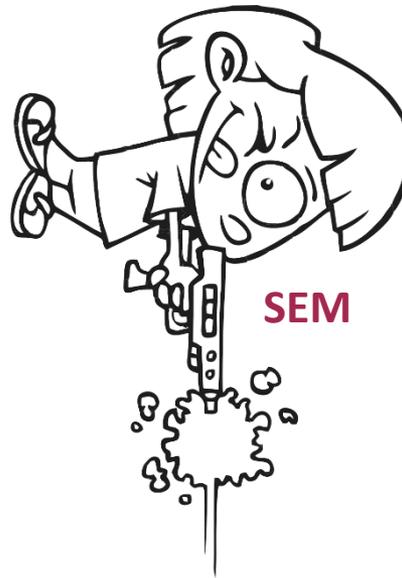
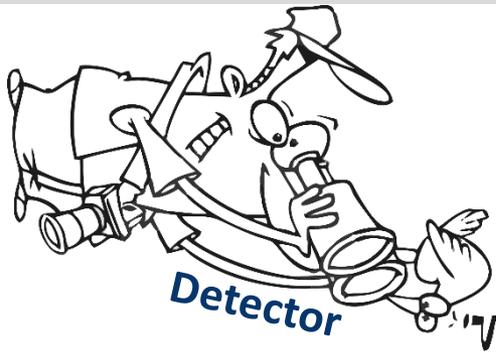
3 μm
Zeiss, Ultra Plus
EHT = 7.00 kV Signal A = AsB Mix Signal = 0.0000 ESB Grid = 859 V
WD = 5.1 mm Aperture Size = 30.00 μm File Name = N15-MT145-X-CUT_010.tif
National Institute Of Chemistry, Ljubljana Operator: Kapun G.



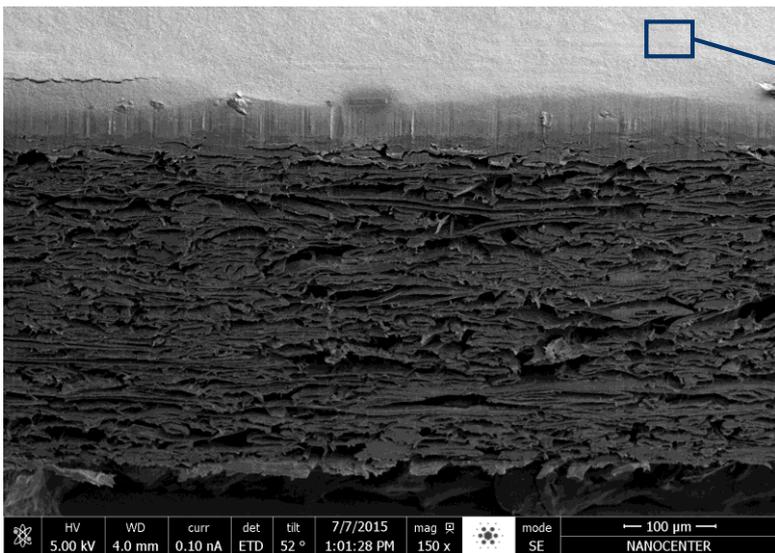
- FIB-SEM dual beam system incorporates:
electron column → **focused electron source**
+
ion column → **focused ion source**
- Instrument is used for nano-patterning, TEM sample preparation, 3D tomography and deposition of thin conductive or dielectric films via ion-beam induced deposition.



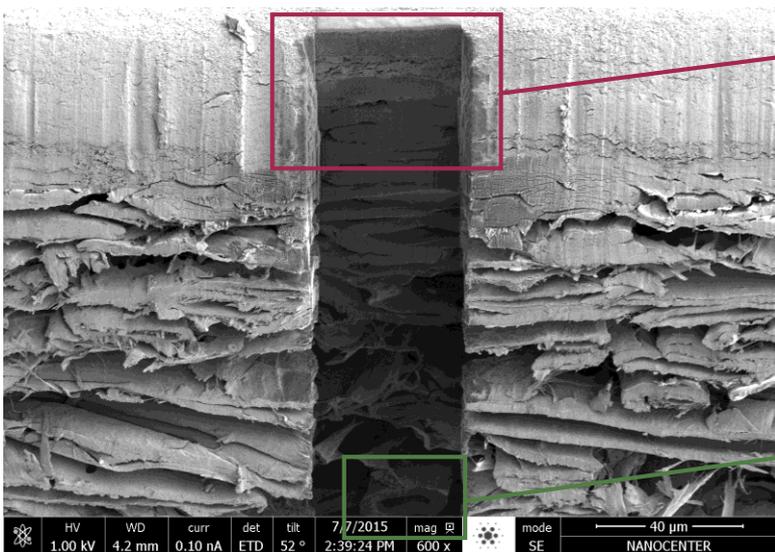
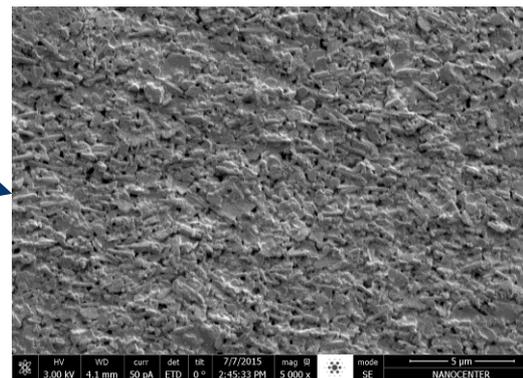
FIB-SEM – basic concept of operation



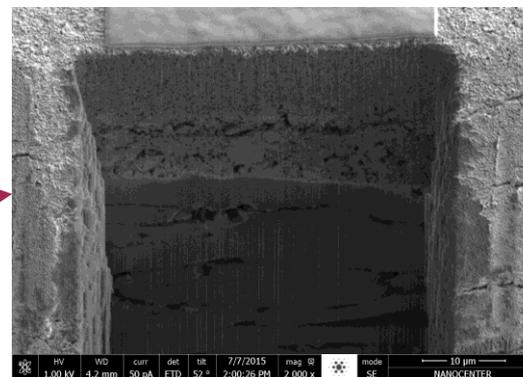
FIB-SEM: ion polished cross-section of cardboard packaging



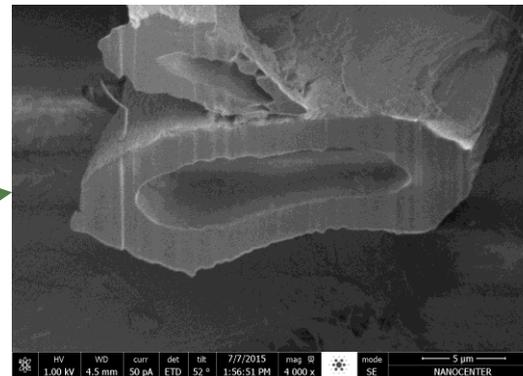
Surface



Coating-paper interface



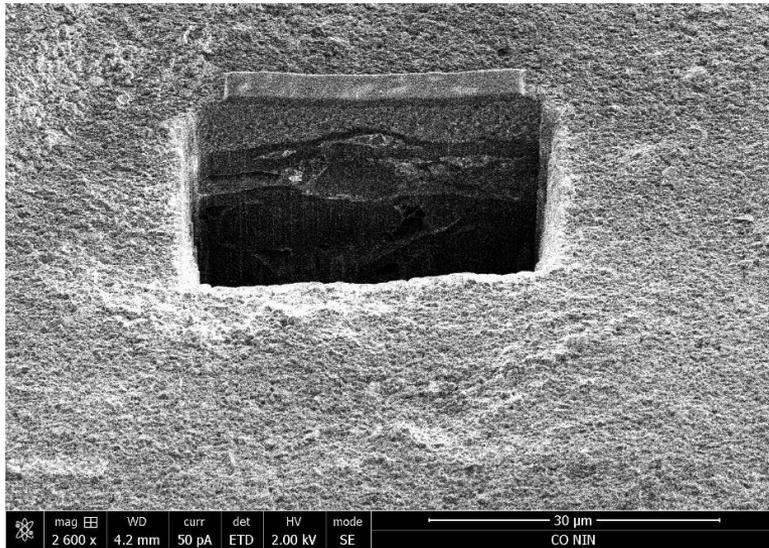
paper fibre cross-section



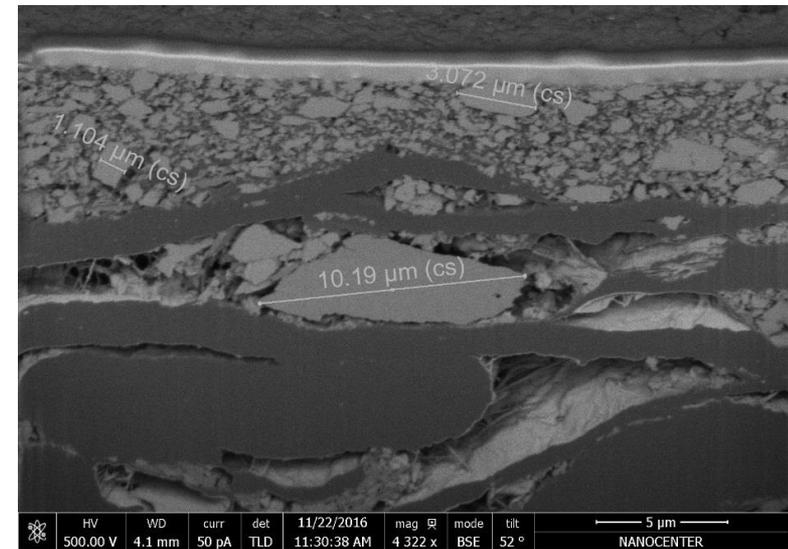
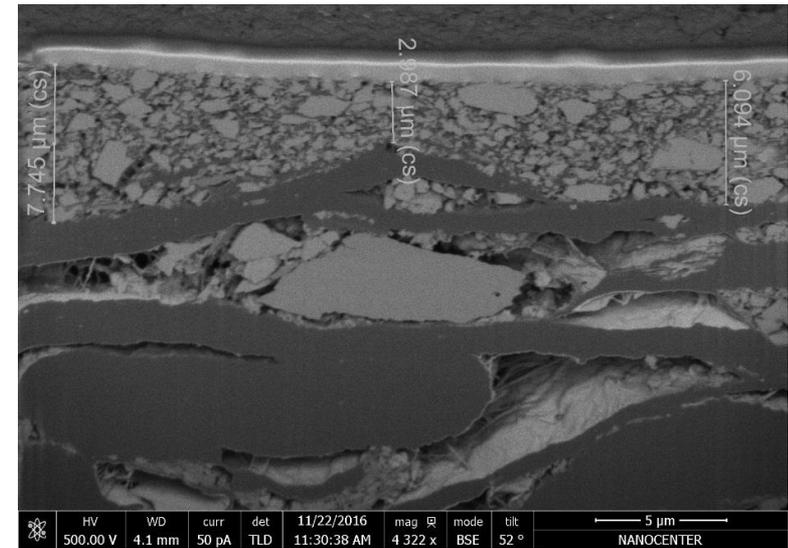
FIB-SEM: paper material – very challenging for electron imaging



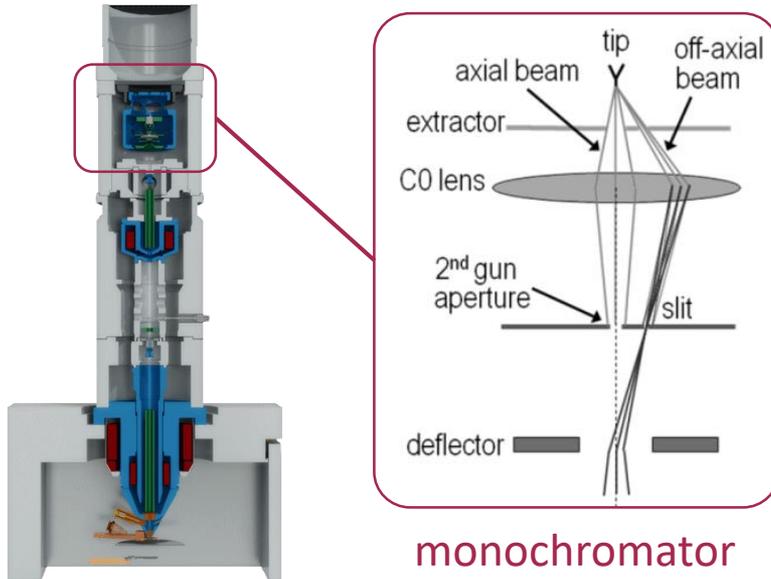
Conventional low kV e-beam imaging



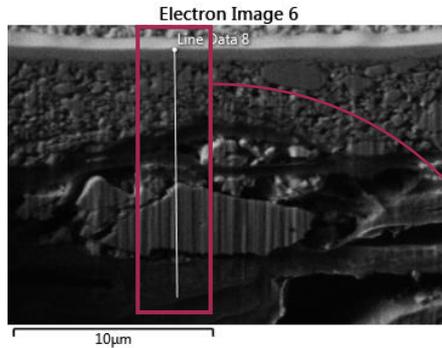
Very low kV e-beam imaging + U-mode



Analytical image with Z-contrast information!

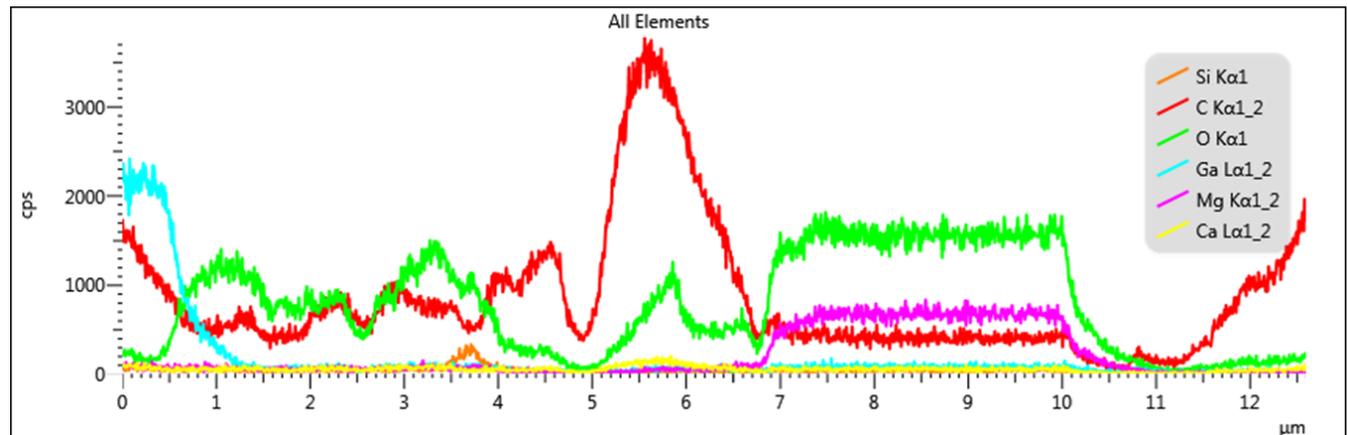
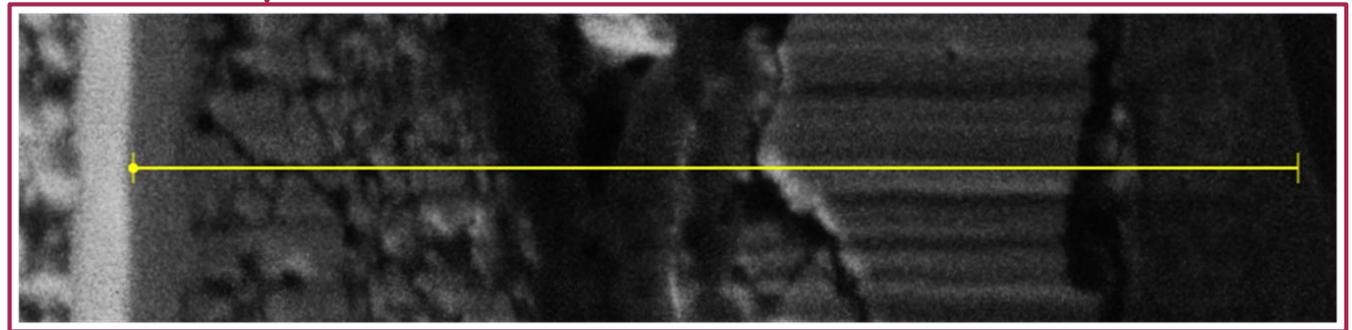


FIB-SEM: paper material – low kV EDXS line profiling

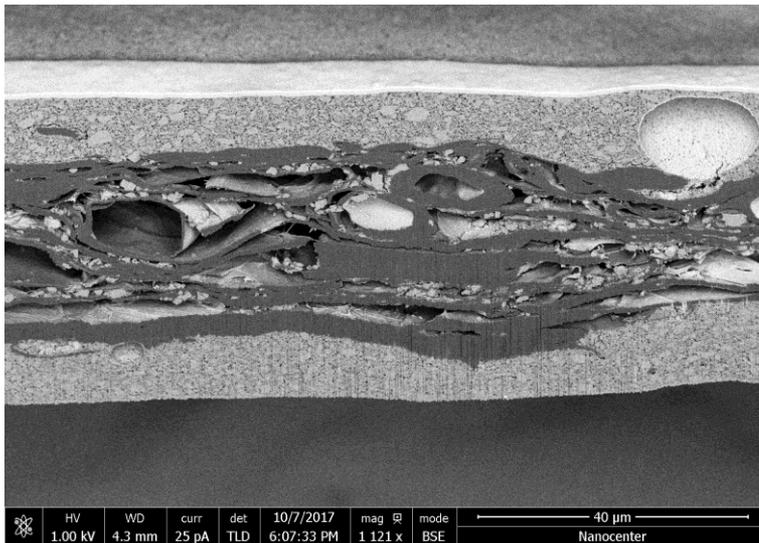
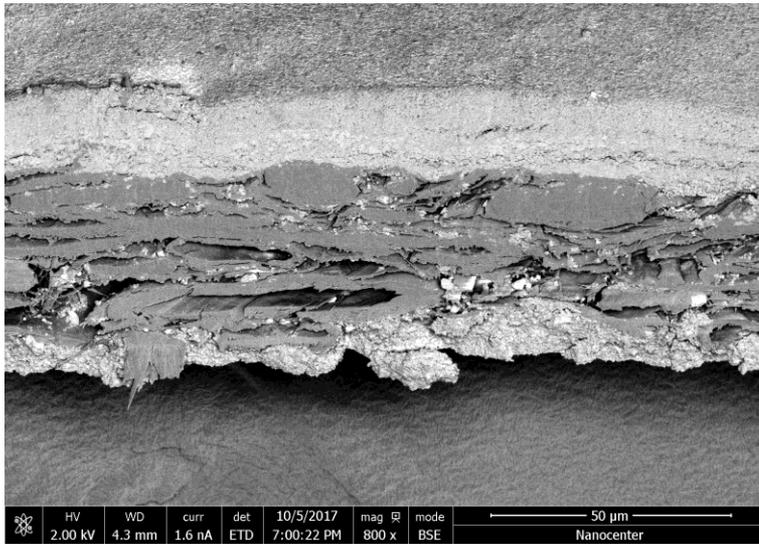


Low kV EDXS line profile:

- Thickness of layers according to their elemental composition
- In particular case coating layer and filler material has different composition

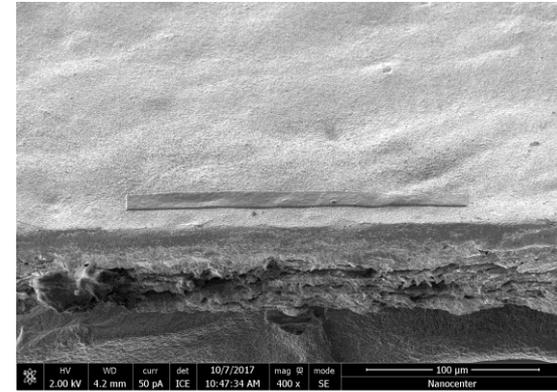


Mechanical prepared cross-section

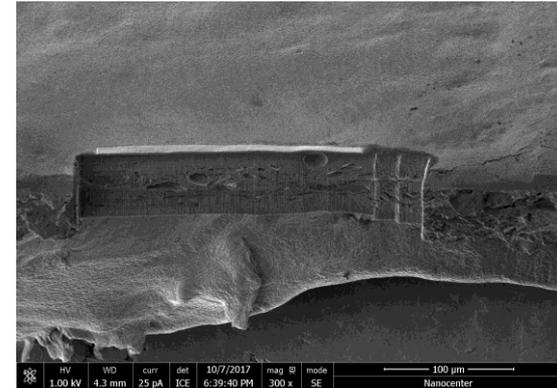


FIB-SEM prepared cross-section

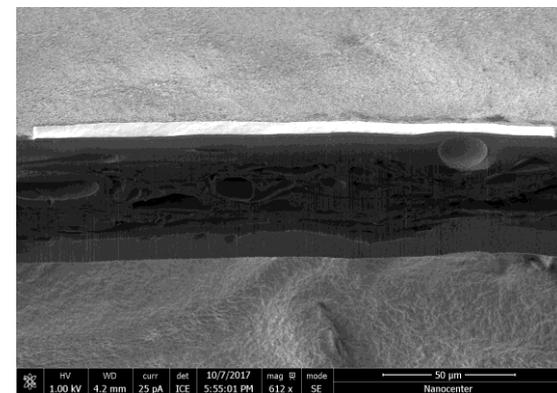
FIB-SEM cross-section preparation steps



„in situ“ Pt protection
layer deposition



Rough cut using high
current focused ions

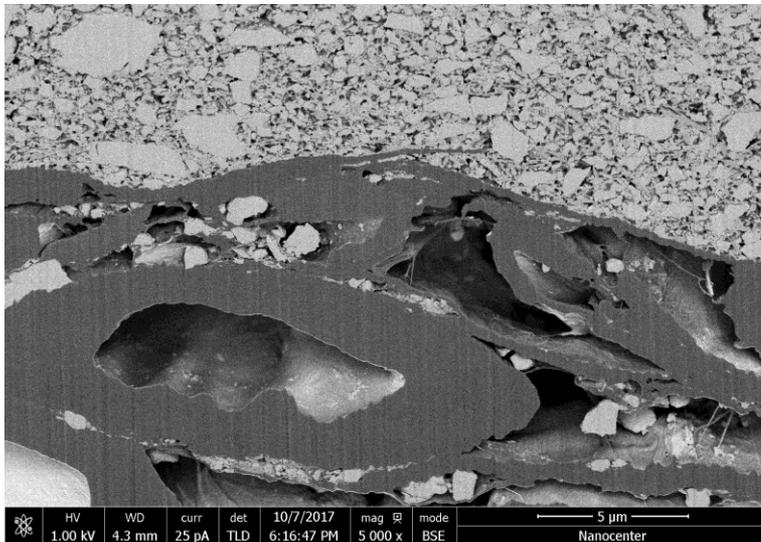
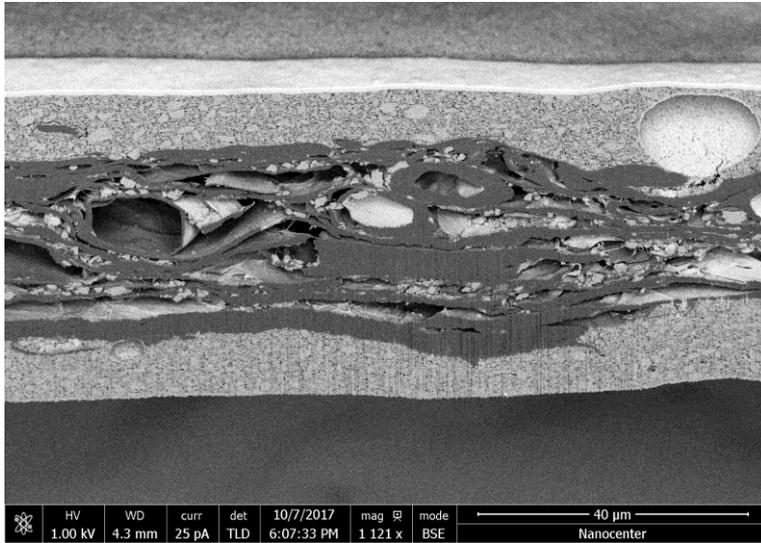


Polishing using low
current focused ions

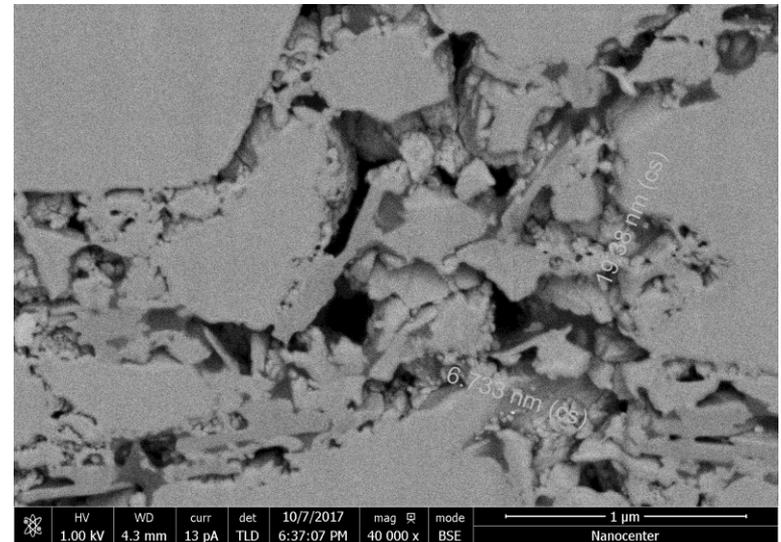
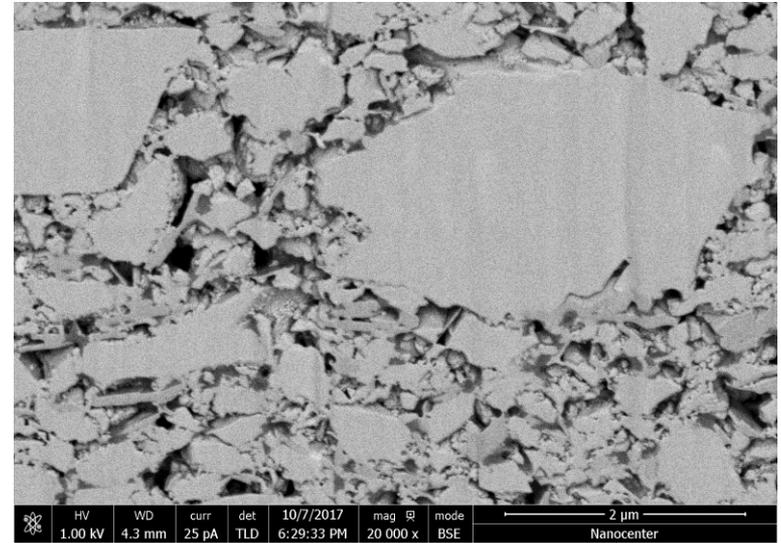
FIB-SEM: paper material – very challenging for electron imaging



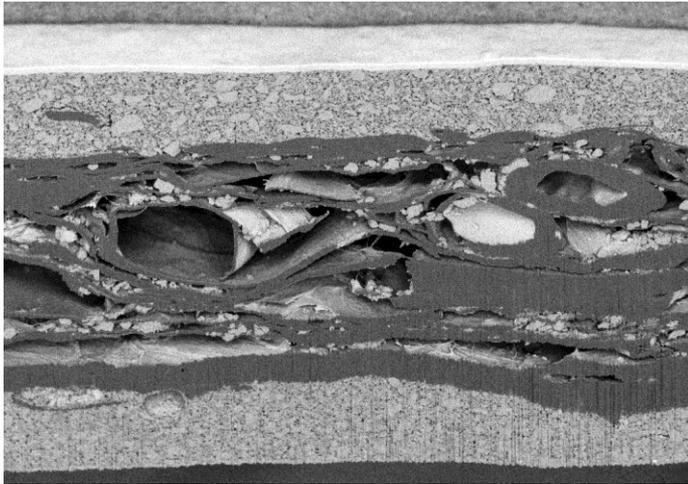
FIB-SEM prepared cross-section of double side coated commercial paper using focused ions and imaged with low energy pre-monochromated electron beam (UHR U-mode, 1kV@25pA – Z contrast)



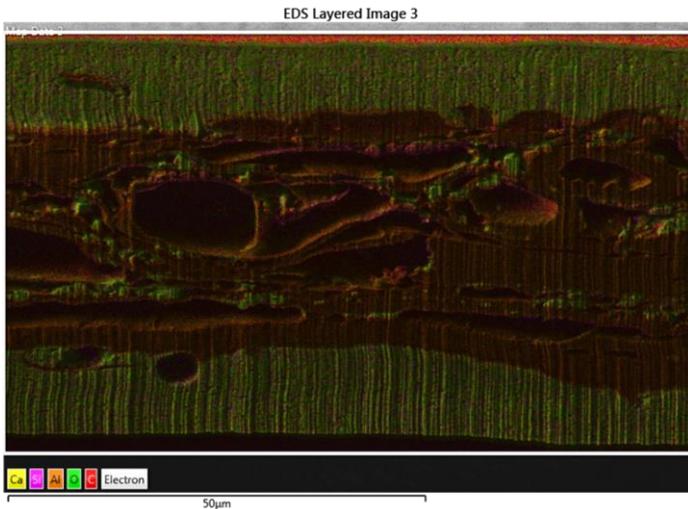
Cross-sectional images of coating acquired at UHR conditions



FIB-SEM: paper material – very challenging for electron imaging



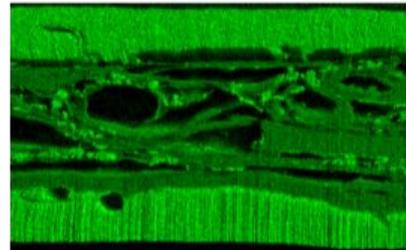
FIB-SEM prepared cross-section of double side coated commercial paper using focused ions and imaged with low energy pre-monochromated electron beam (UHR U-mode, 1kV@25pA, Z contrast)



Low kV EDXS TrueMap analysis

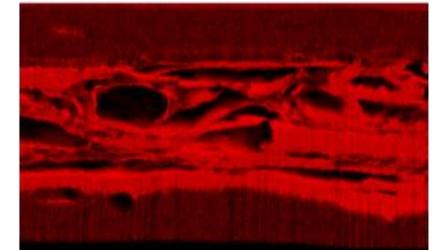


O K series



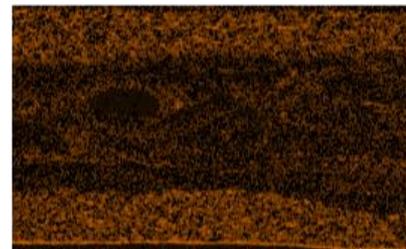
25µm

C K series



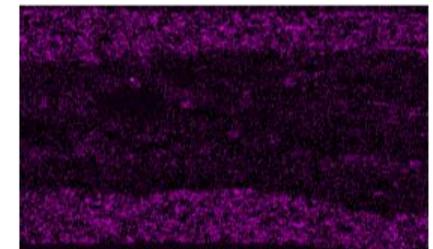
25µm

Al K series



25µm

Si K series



25µm

FIB-SEM as analytical tool: paper combined with cost effective fillers



Expensive fillers



Side products as cost effective fillers



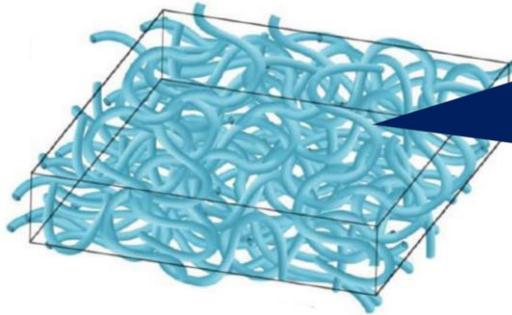
OR

BUT !

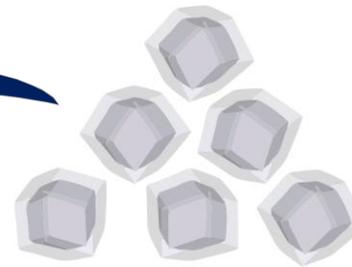
CHALLENGE

Cost effective
Industrial process

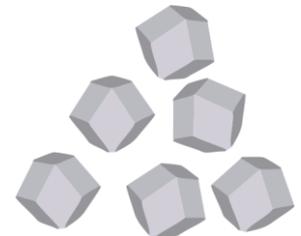
SOLUTION



Cellulose fibers



Coated $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
(stable)



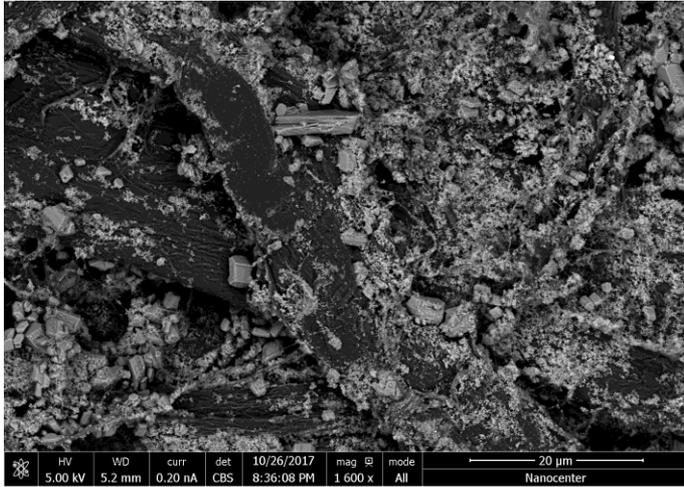
Raw $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
(soluble)



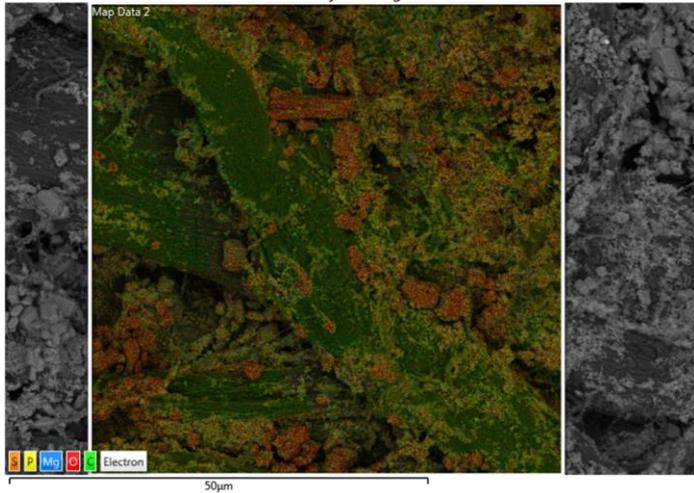
Research + Good analytical support!



„in situ“ preparation of Na_2HPO_4 coating on $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ filler

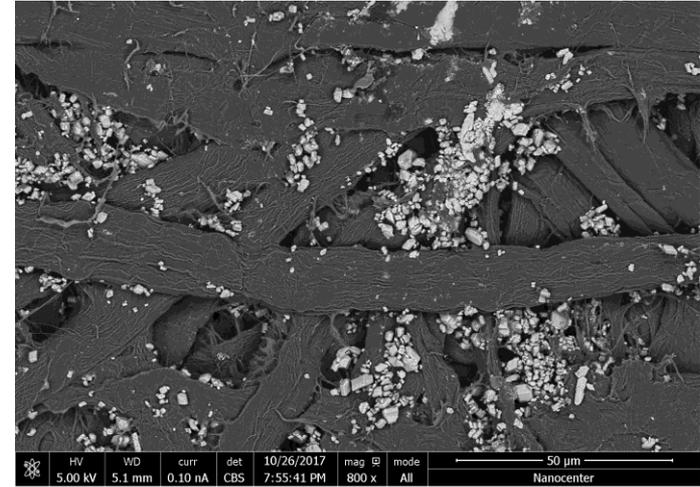


EDS Layered Image 2



SEPARATED

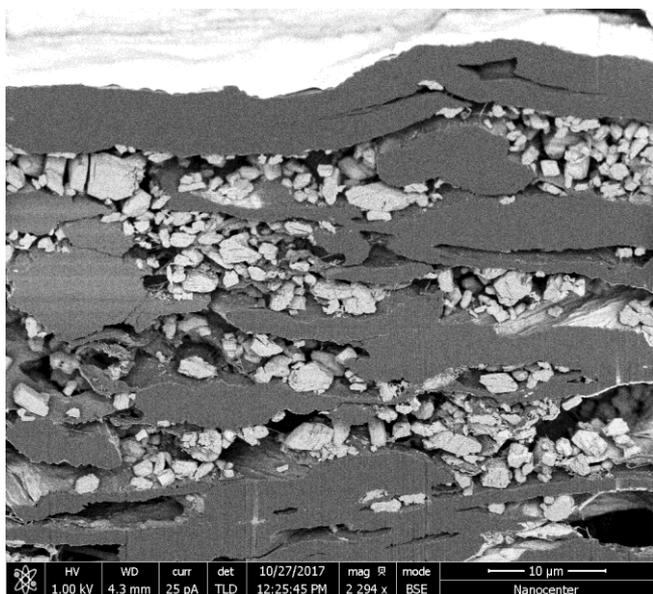
„in situ“ preparation of Na_2CO_3 coating on $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ filler



EDS Layered Image 1

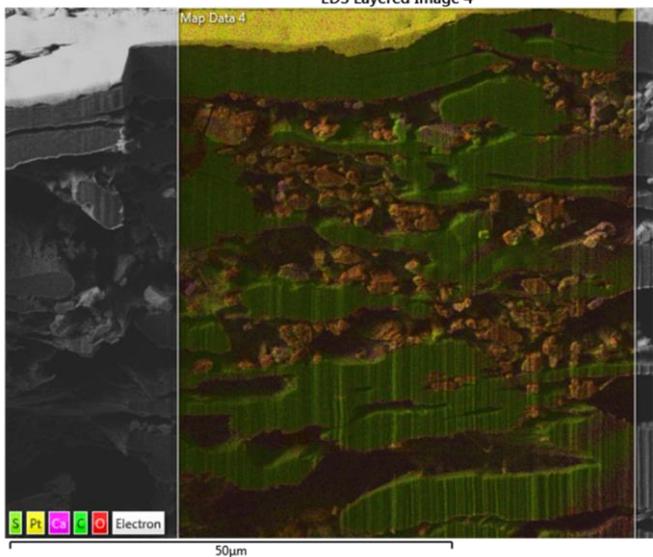


SUCCESSFUL COATING PROCEDURE



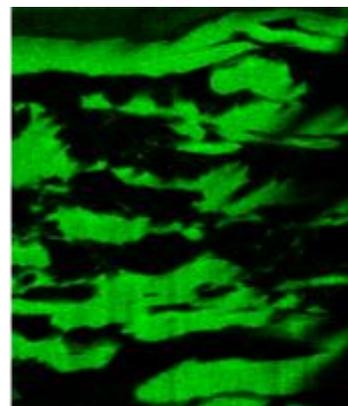
HV 1.00 kV WD 4.3 mm cur 25 pA det TLD 10/27/2017 12:25:45 PM mag 2.294 x mode BSE

EDS Layered Image 4

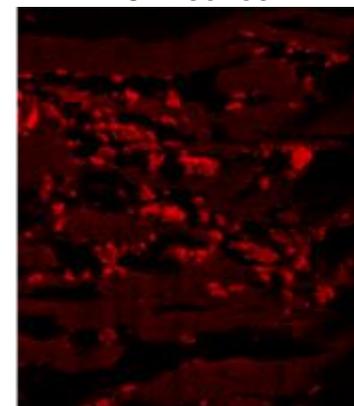


Low kV EDXS TrueMap analysis

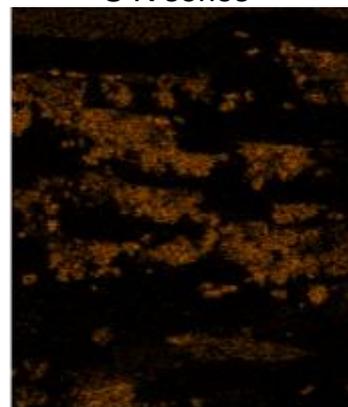
C K series



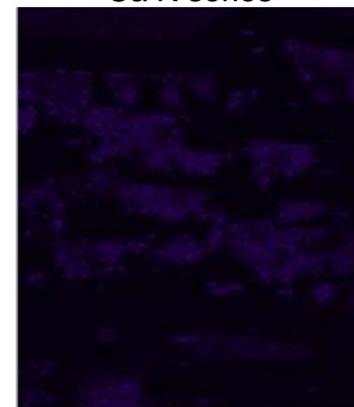
O K series



S K series



Ca K series

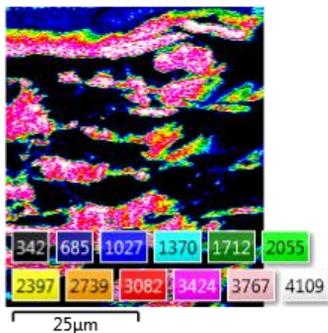




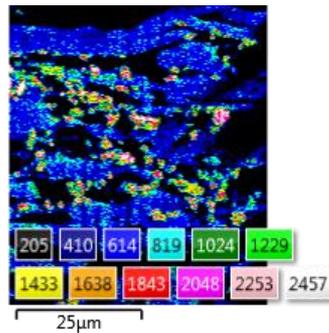
EDS Layered Image 4

Low kV EDXS spectrum imaging – quantitative results

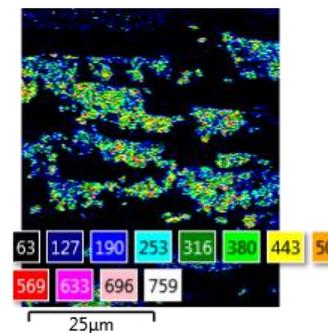
C K series



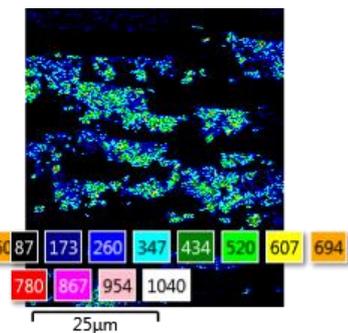
O K series



S K series

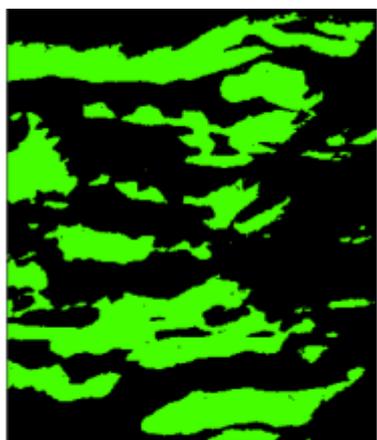


Ca K series



Phase analysis of quantitative spectrum imaging data

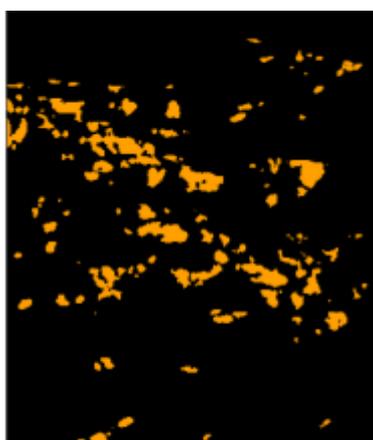
Phase 1 CO



Cellulose fibers

25µm

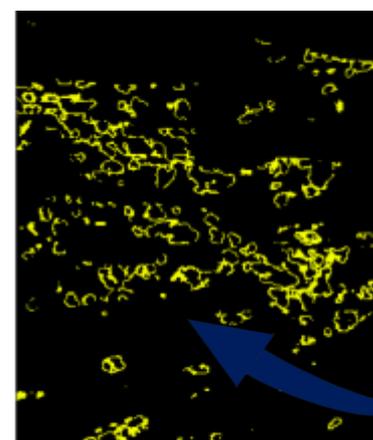
Phase 2 CaSO



Calcium sulphate

25µm

Phase 3 CCaSO



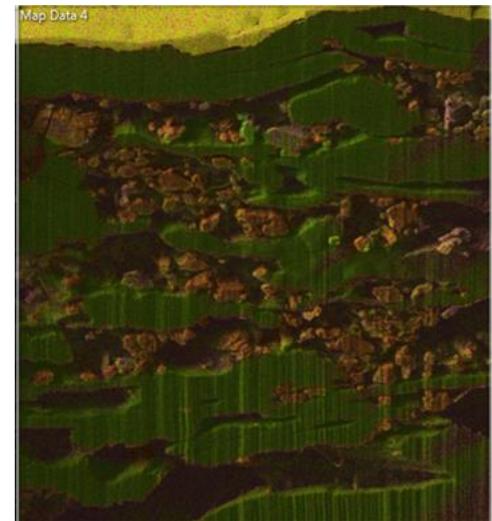
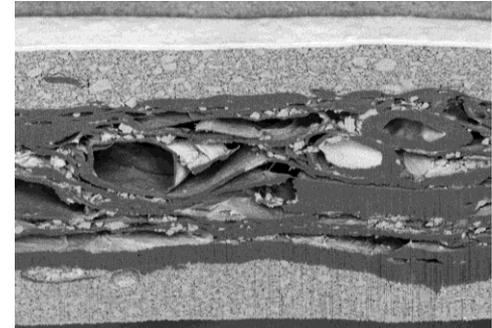
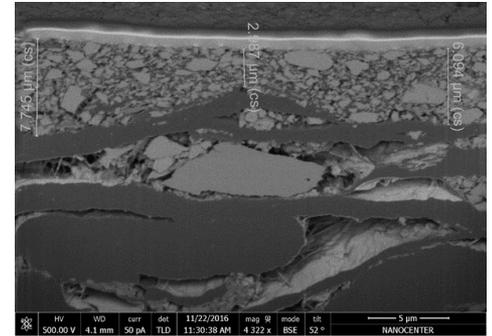
Calcium carbonate coating on top of filler

25µm

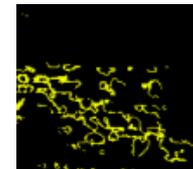
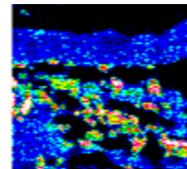
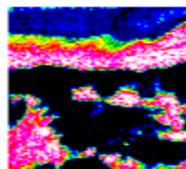
Summary



- FIB-SEM can be used for producing clean cross-sections of various paper materials while preserving their original form,
- In addition to SEM microscope, FIB-SEM provides surface and cross-sectional material analysis at the same time,
- Use of Low kV e-beam energies enables true-surface imaging of all present morphological forms within the paper material,
- Introduction of monochromator enables use of very low kV e-beam energies which eliminates beam damage and charging effects. It further provides UHR analytical imaging (Z-contrast),
- Combination of FIB-SEM and EDXS techniques offers elemental analysis of surface and cross-section of various paper materials (quantitative identification and distribution of any component),
- Use of advanced EDXS techniques such as spectrum imaging in addition provides detailed quantitative analysis and/or phase analysis of any present component within paper material.



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Department for Materials Chemistry



High end HR-SEM's and FIB-SEM instruments available to NIC



FE-SEM SUPRA 35 VP



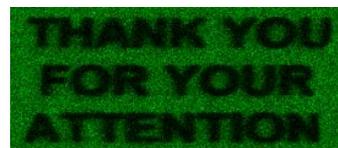
FE-SEM Ultra+



10µm



10µm



10µm

FIB Helios Nanolab 650i

