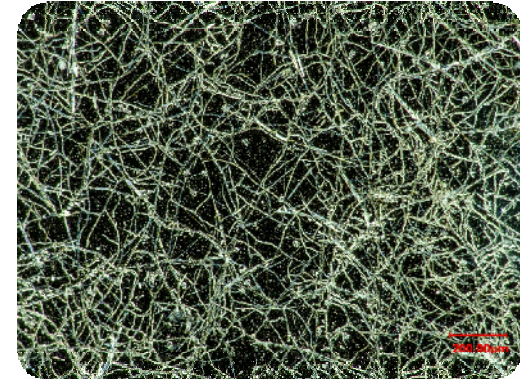
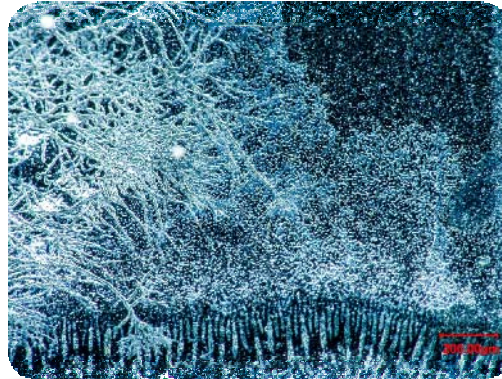
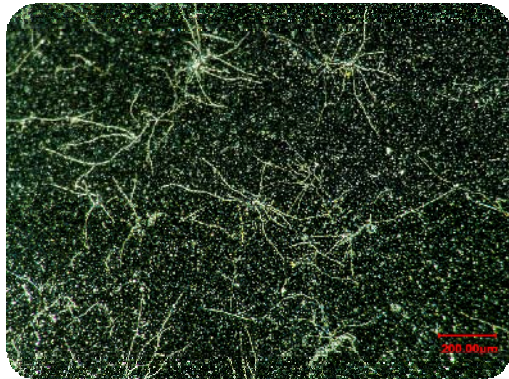


UNDERSTANDING VOLMEUR ARTWORK WITH OPTICAL AND ELECTRON MICROSCOPY



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CERN R&D Engineer in Material Science
elisa.garcia-tabares.valdivieso@cern.ch

Outline

- **CERN: a brief introduction**
- **Context**
- **Experimental**
- **Results**
- **Summary & Conclusions**

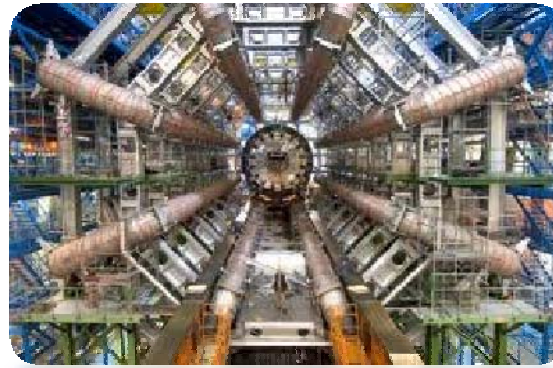
CERN: A BRIEF INTRODUCTION

- CERN = the European Organization for Nuclear Research
- Intergovernmental organization, founded in 1954
- 22 Member States, 10 000 staff members+associates
- Located on both sides of the French-Swiss border closed to Geneva

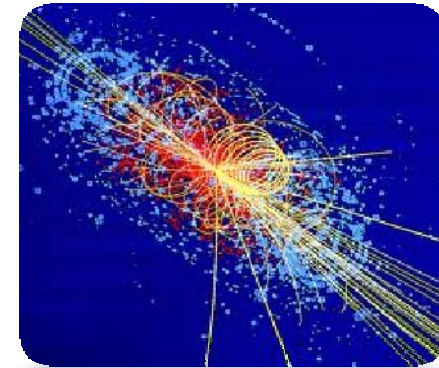
Overview of CMS detector



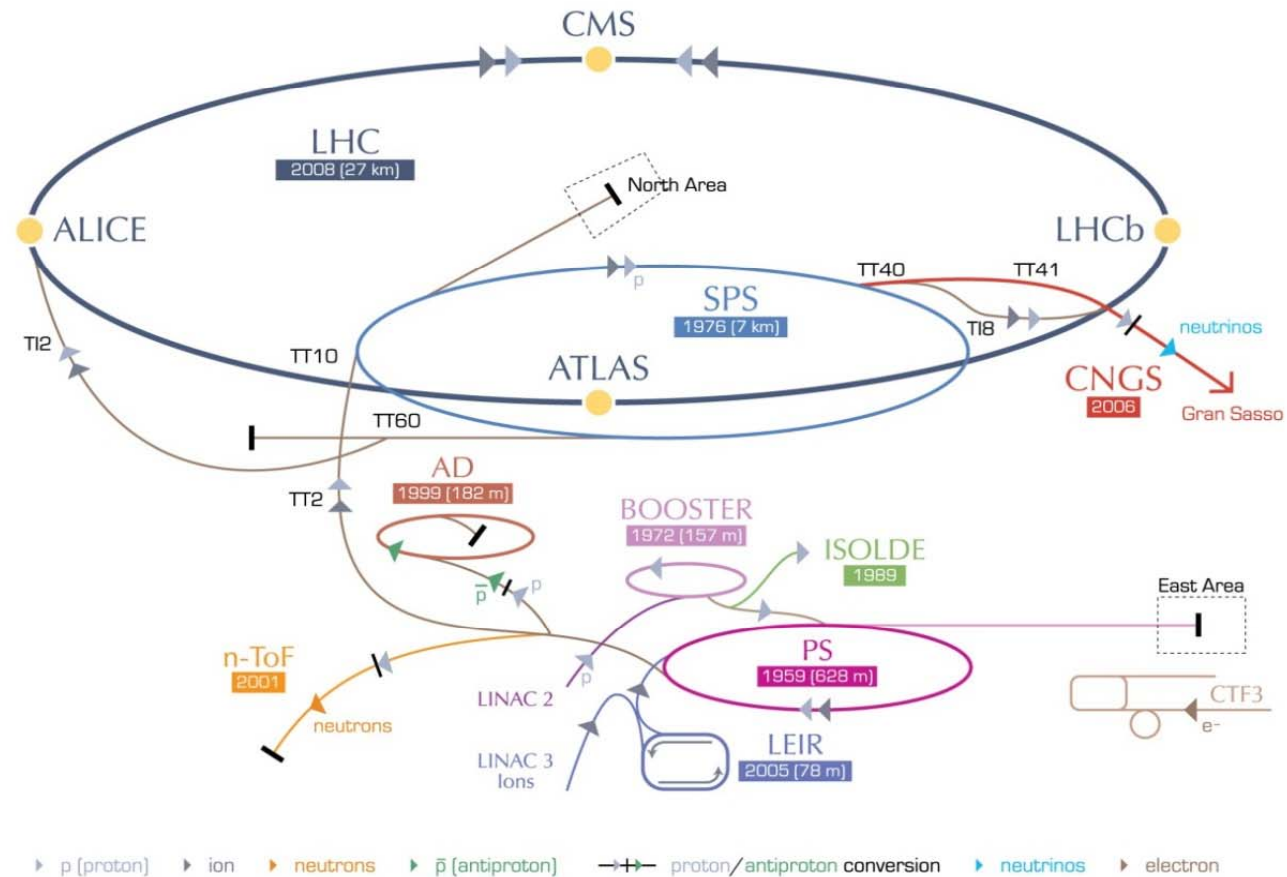
Overview of ATLAS detector



Simulation from CMS of protons colliding



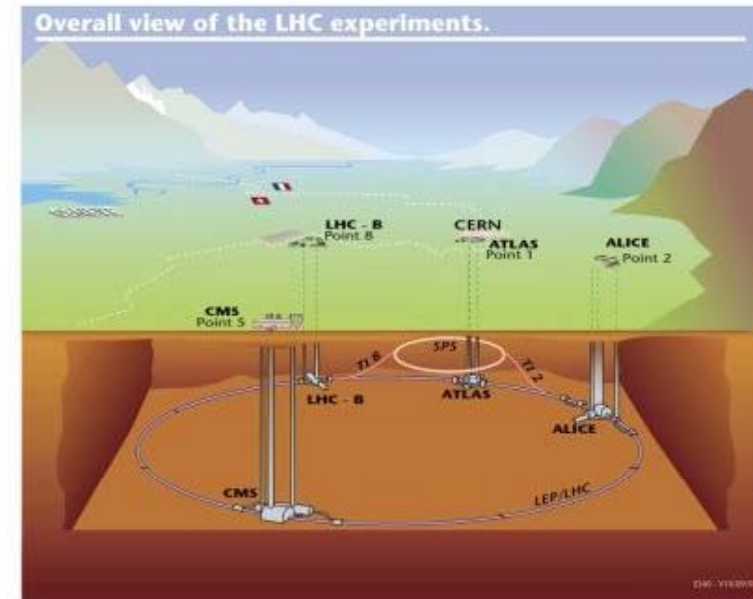
CERN: A BRIEF INTRODUCTION



LHC Large Hadron Collider SPS Super Proton Synchrotron PS Proton Synchrotron
 AD Antiproton Decelerator CTF3 Clic Test Facility CNGS Cern Neutrinos to Gran Sasso ISOLDE Isotope Separator OnLine DEvice
 LEIR Low Energy Ion Ring LINAC LINear ACcelerator n-ToF Neutrons Time Of Flight

CERN: A BRIEF INTRODUCTION

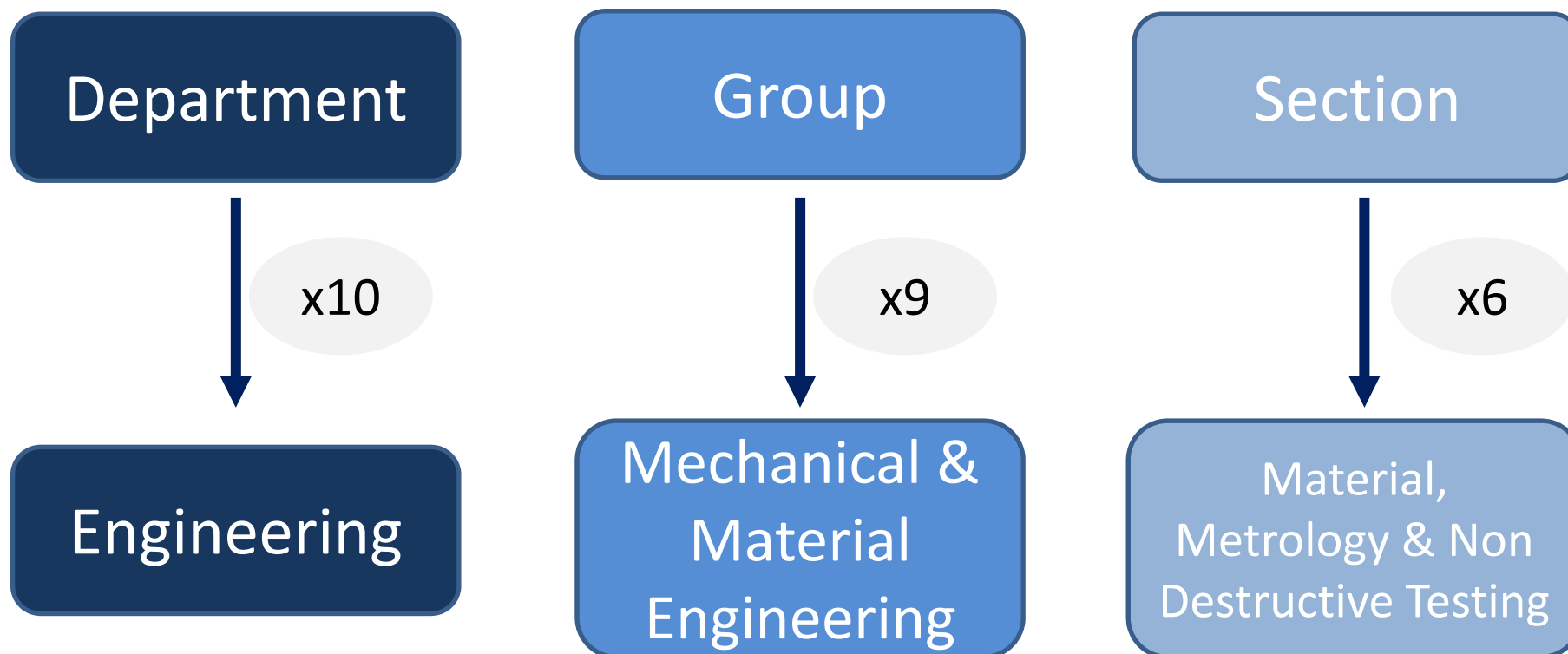
→ The world's most powerful particle accelerators





CERN: A BRIEF INTRODUCTION

CERN structure





CERN: A BRIEF INTRODUCTION

EN-MME-MM

- Development
 - Selection & Specification
 - Characterization & Analysis
- } Metals and alloys, composites, ceramics and thin films
- Quality control of materials and components
 - Non-destructive testing and dimensional controls
 - Failure analyses
 - Mechanical tests
 - Development of new materials

CERN: A BRIEF INTRODUCTION

EN-MME-MM



Materials



Ignacio Avilés
599 R-027



Pilar Fernández
599 R-011



Ewelina Muszalska
599 R-024



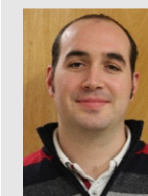
Pablo Ortega
599 R-024



Adrià Gallifa
599 R-023



Josep Busom
599 R-005



Enrique Rodríguez
599 R-023



Karolina Bagdanowicz
599 R-024

Metrology



Ahmed Cherif
72 R-005



Jean-Philippe Rigaud
72 R-009



Didier Glaude
100 R-023



Dominique Pognat
72 R-013



Patrice Francon
72 R-009



Bartosz Bulat
72 R-013

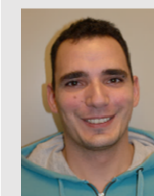
NDT



Gonzalo Arnau
112 2-018



Aline Piquet
112 2-021



Alexandre Porret
112 2-021



Simon Garner
112 2-022



Mariusz Jedrychowski
112 2-022

CONTEXT





CONTEXT

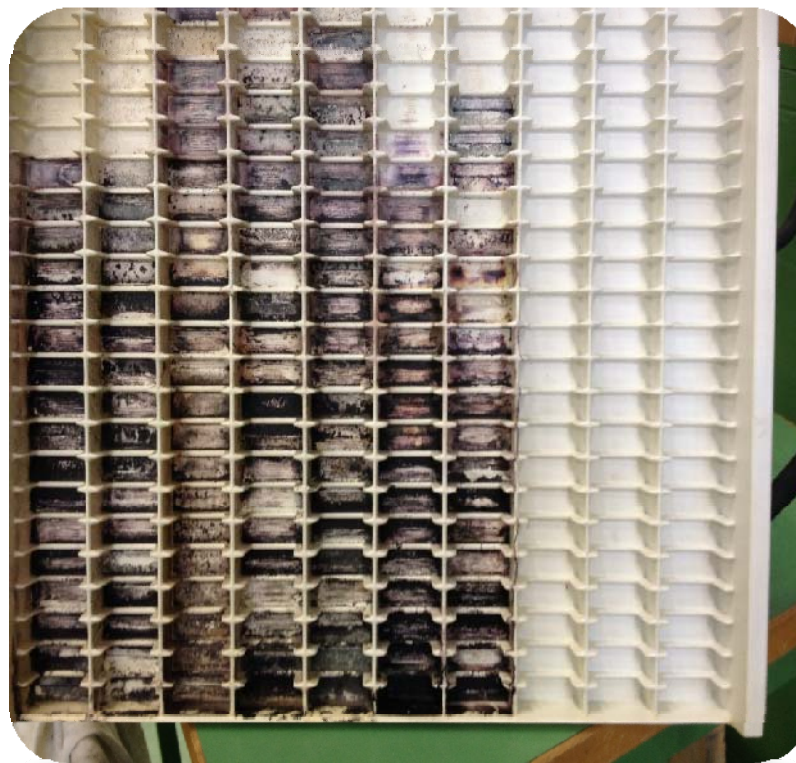
- Slides were stored in an open air storage system from ~1985 to ~ 2013. Then, moved to a different building in a clean and dry room.

CONTEXT

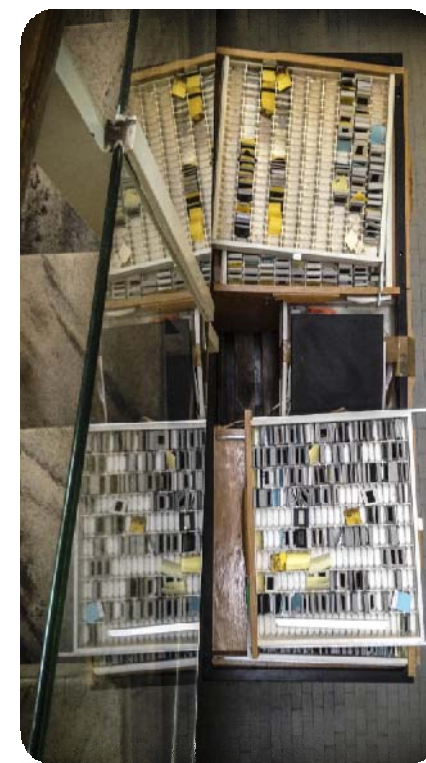
Appearance of the slides before the analysis





Appearance of the drawers where the slides were stored



“Open air” drawers



CONTEXT

	SAMPLE					
	1	2	3	4	5	6
SLIDE	Old	Old	Old	New	New	New
	Probably	Probably	Probably	No	Yes	Yes
	No	Yes	Half	No	No	Yes (artif.)*

* Some slides were treated ex-situ (water exposure and growth of artificial mold) to try to reproduce the lab conditions.

EXPERIMENTAL

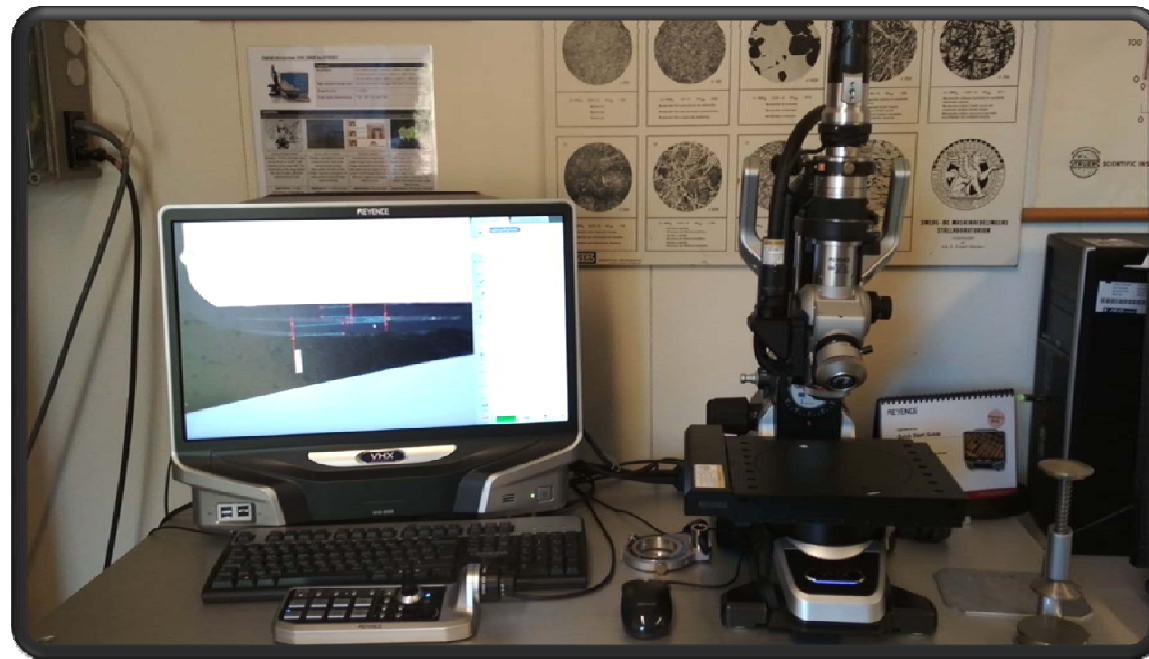


EXPERIMENTAL



Optical microscopy

- Optical Microscope Keyence 600
- Mag. 1- 1 000x



EXPERIMENTAL



Scanning Electron Microscopy

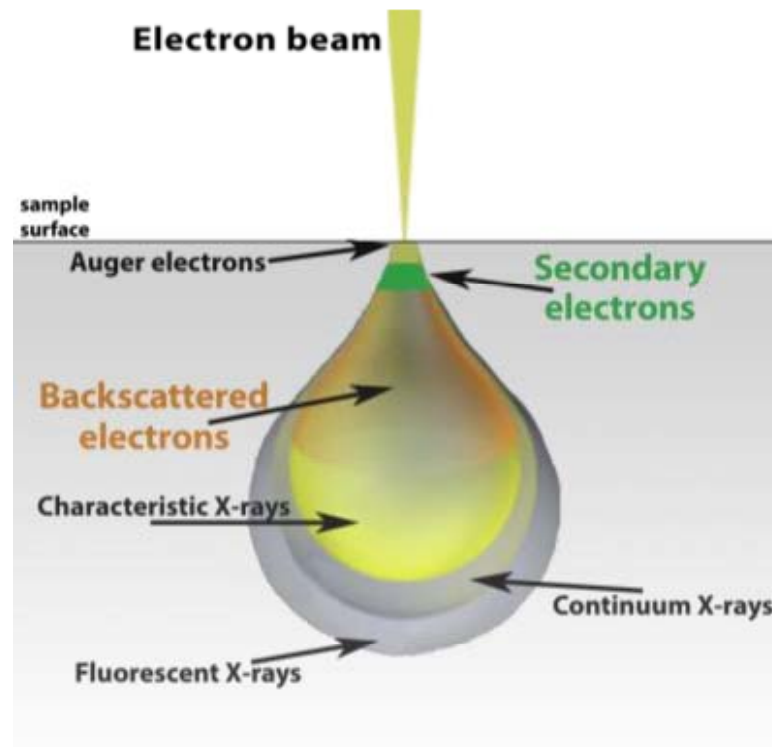


- Field Emission Gun (FEG)
- InLens, SE2, AsB detectors for imaging
- Oxford 50 mm² X Max EDS detector
- Mag. 12- 500 000x

EXPERIMENTAL



Scanning Electron Microscopy



Secondary electron (SE):

Imaging, topography contrast

Back scattered electron (BSE):

Imaging, Chemical contrast

Energy Dispersive Spectroscopy (EDS):

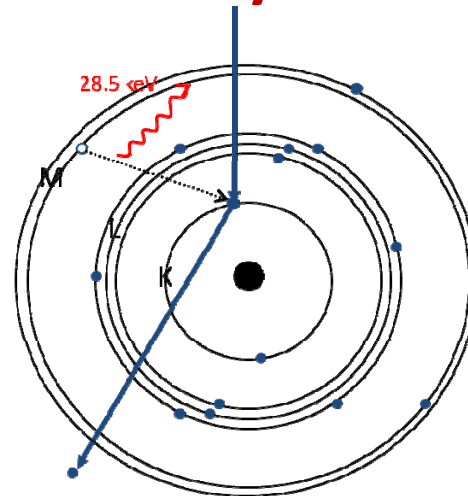
Semi-quantitative chemical information

EXPERIMENTAL



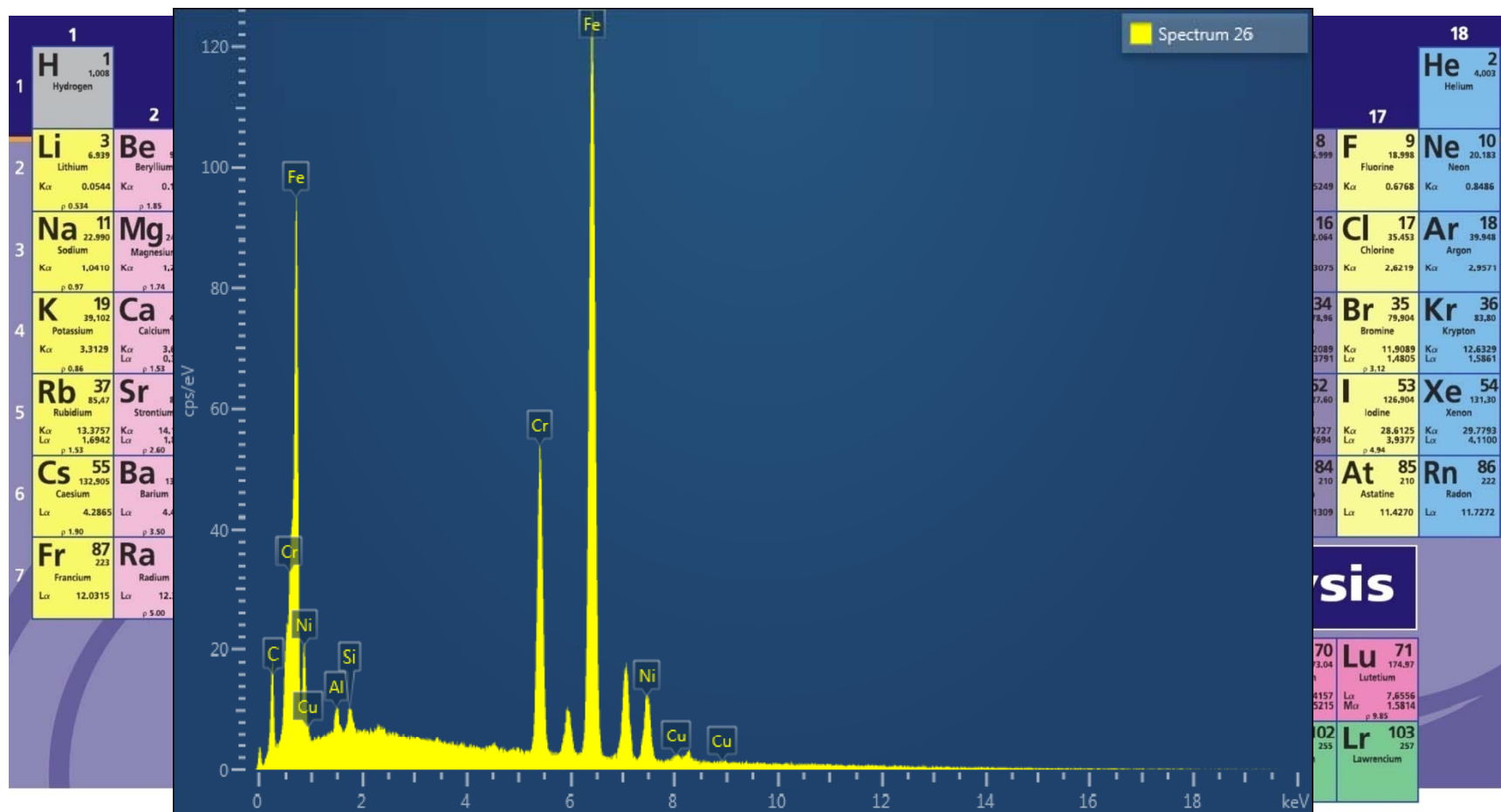
Energy Dispersive X-Ray Spectroscopy

- Analysis of X-rays emitted by the matter in response to being hit with charged particles
- Each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from one another.
- Allow the **elemental analysis** or **chemical characterization**



EXPERIMENTAL

Energy Dispersive X-Ray Spectroscopy



EXPERIMENTAL

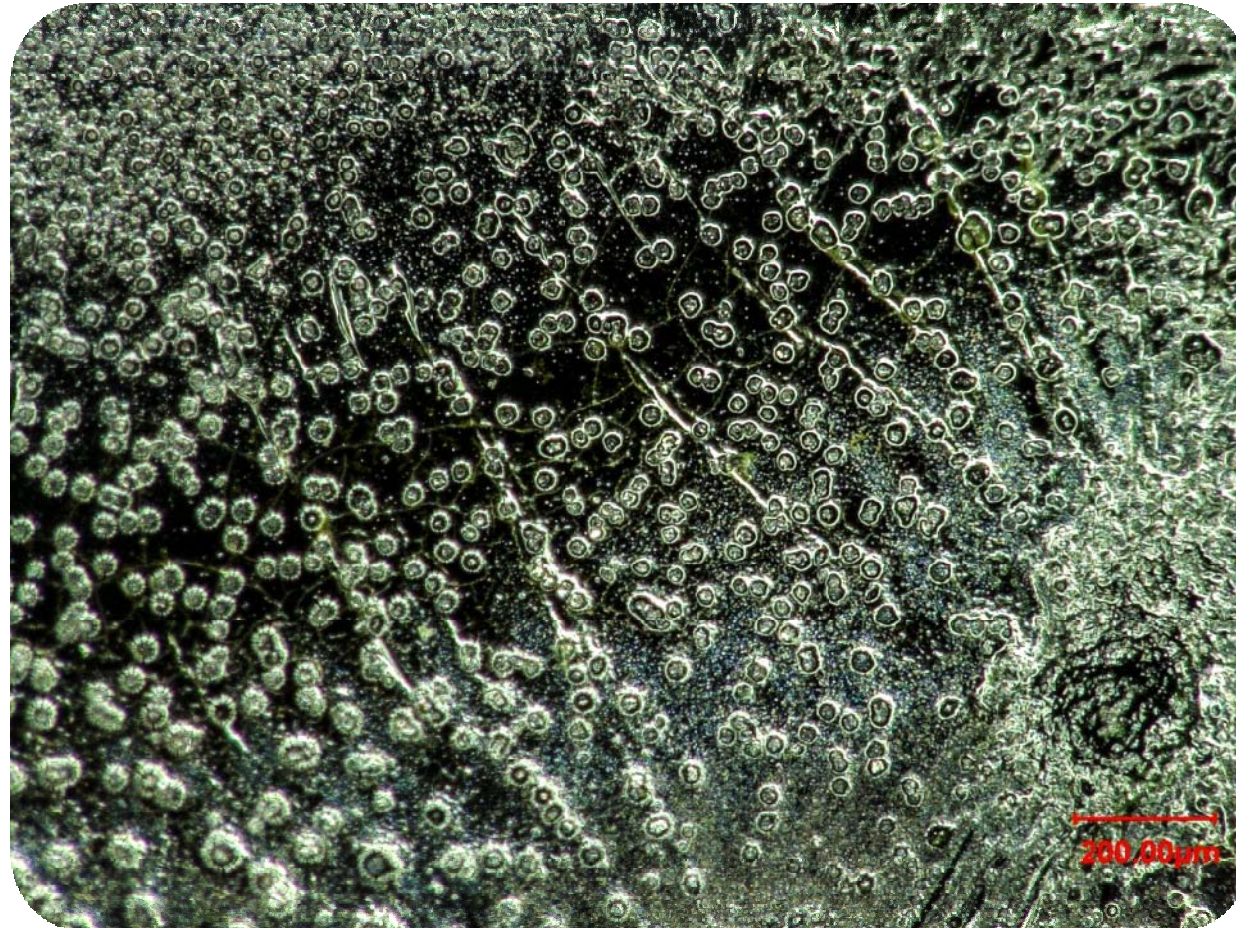


Energy Dispersive X-Ray Spectroscopy

- What can we analyse?
 - Identification of elements, for $Z \geq 4$ (Be)
 - Quantification
 - elements, for $Z > 9$ (F)
 - more than wt% 1 (depending on the element)
- What can we not or hardly analyse?
 - Elements with peaks overlapping ($\Delta E \leq 127$ eV)
 - Quantification is limited for
 - Light elements
 - Not perfectly flat samples
 - Not homogeneous samples





RESULTS



RESULTS

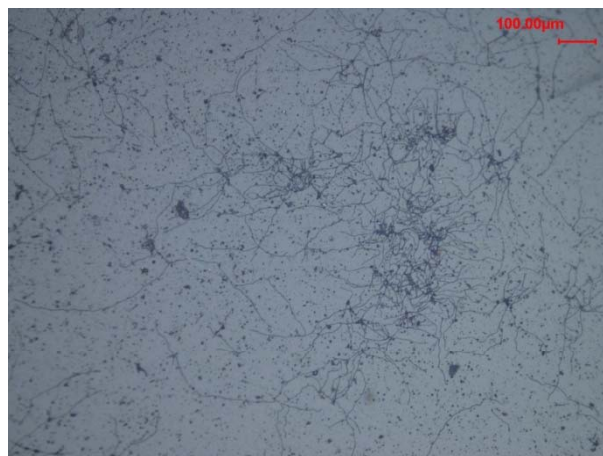
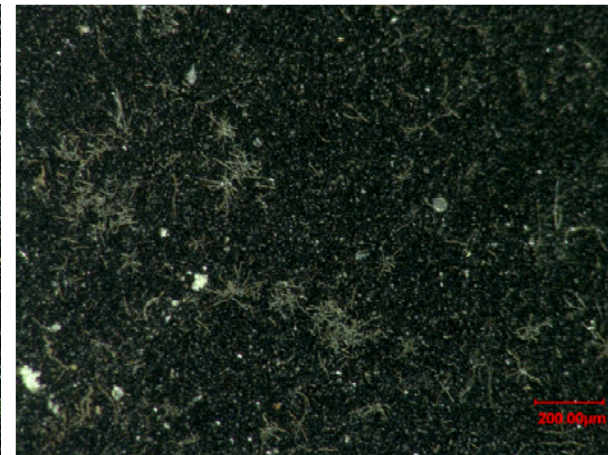
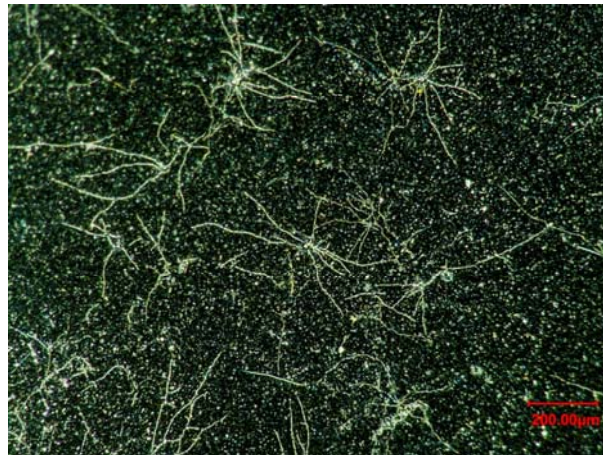


	SAMPLE					
	1	2	3	4	5	6
SLIDE	Old	Old	Old	New	New	New
	Probably	Probably	Probably	No	Yes	Yes
	No	Yes	Half	No	No	Yes (artif.)*

* Some slides were treated ex-situ (water exposure and growth of artificial mold) to try to reproduce the lab conditions.

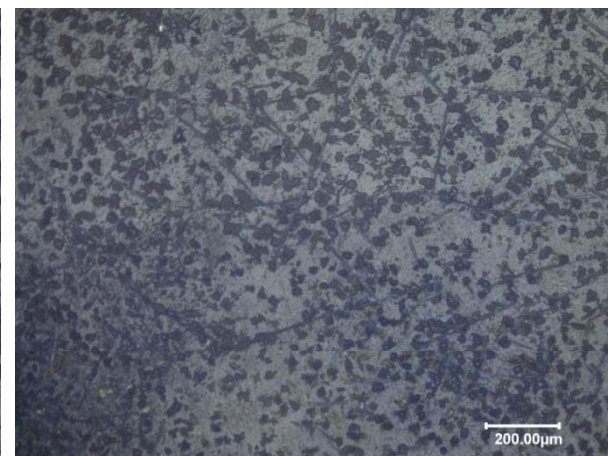
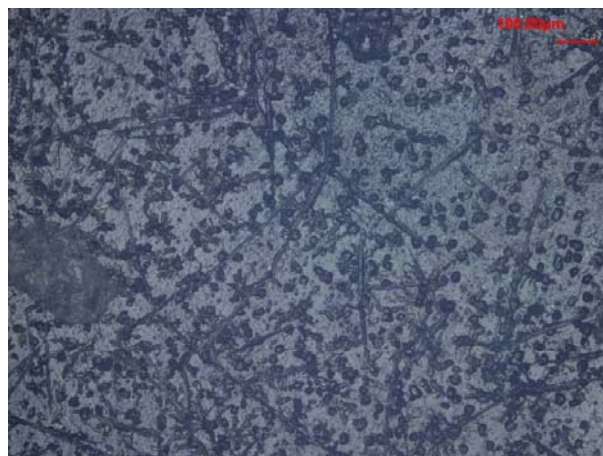
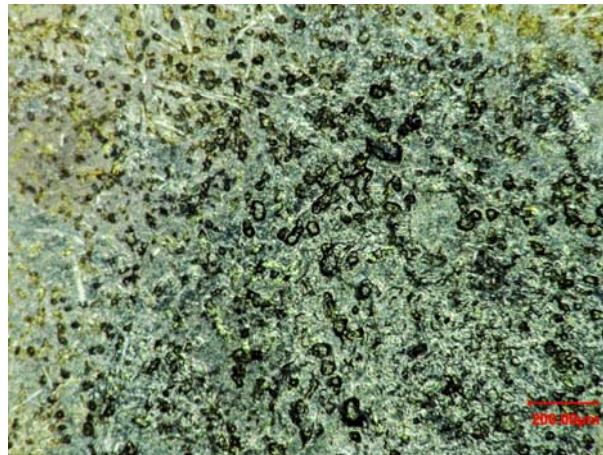
Results: Optical microscopy

OLD
SLIDE



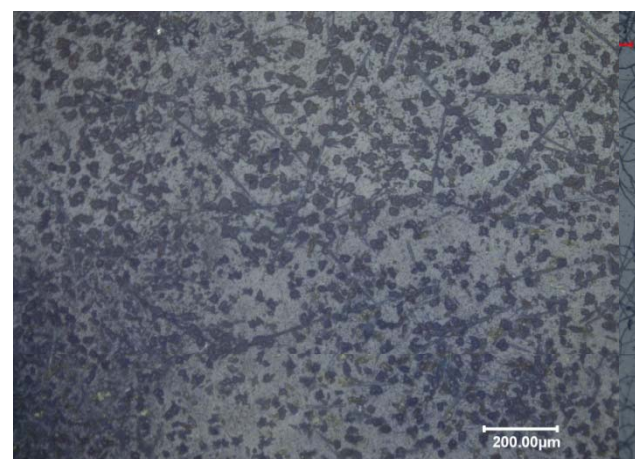
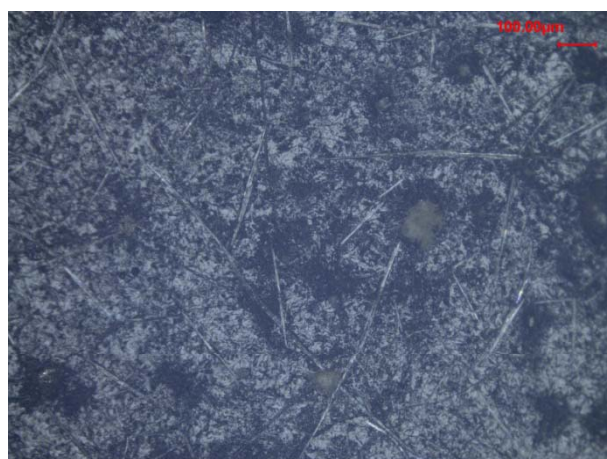
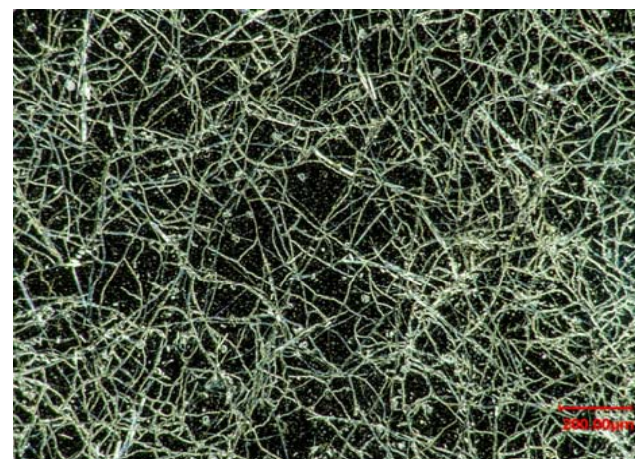
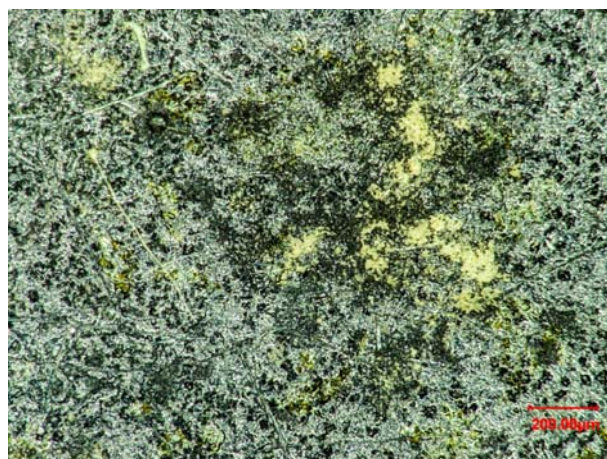
Results: Optical microscopy

OLD
SLIDE



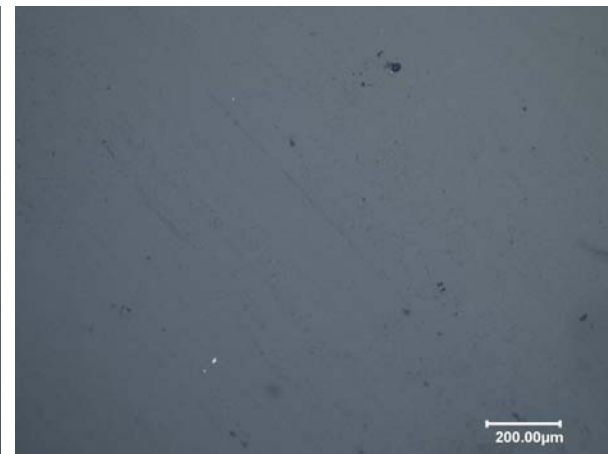
Results: Optical microscopy

OLD
SLIDE



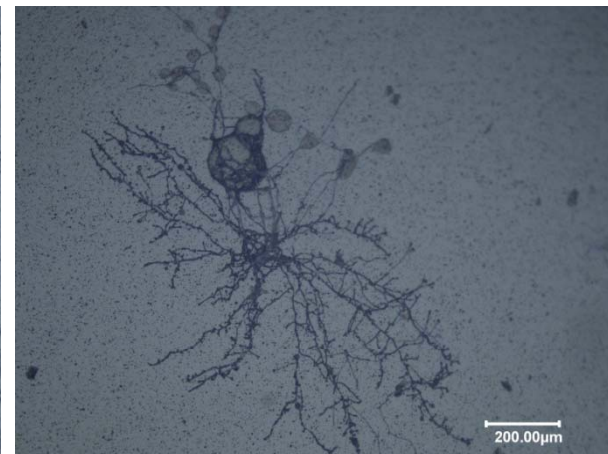
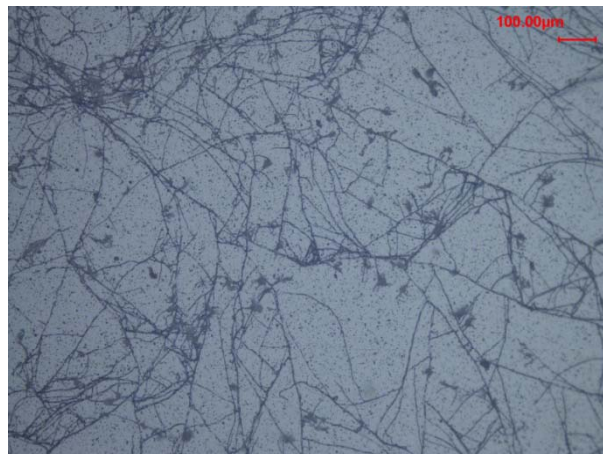
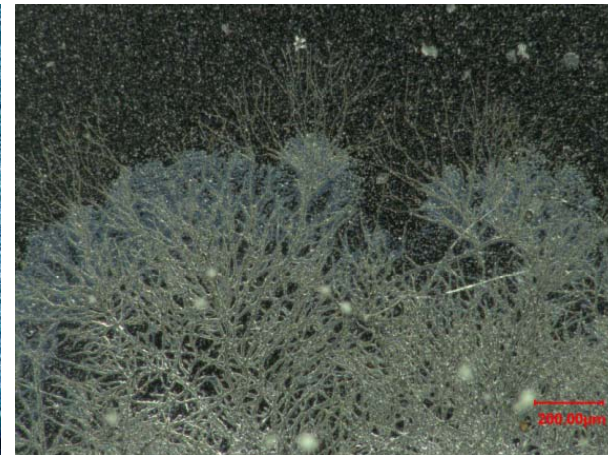
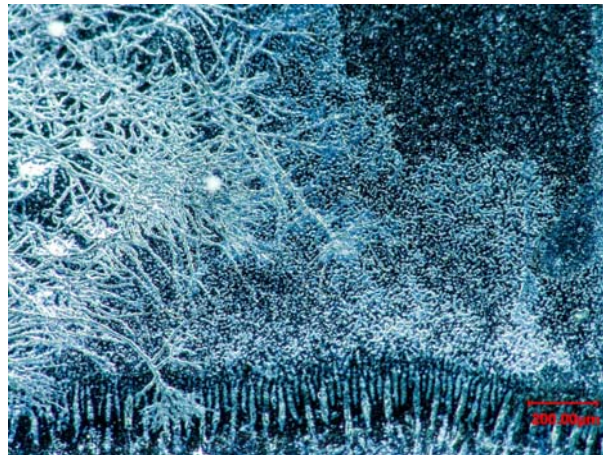
Results: Optical microscopy

NEW
SLIDE



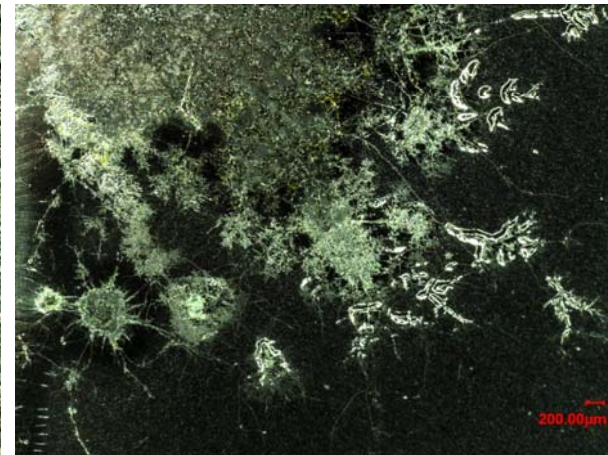
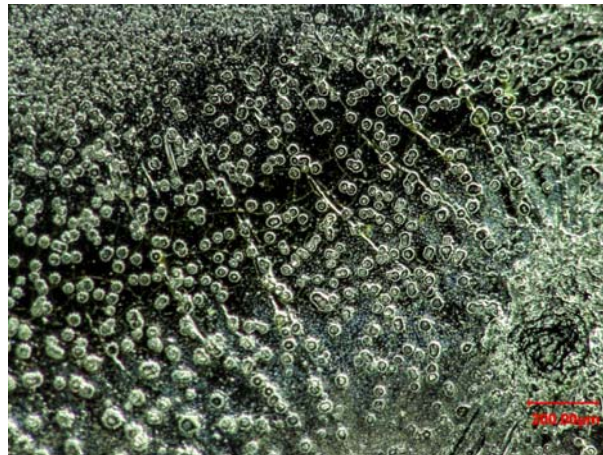
Results: Optical microscopy

NEW
SLIDE

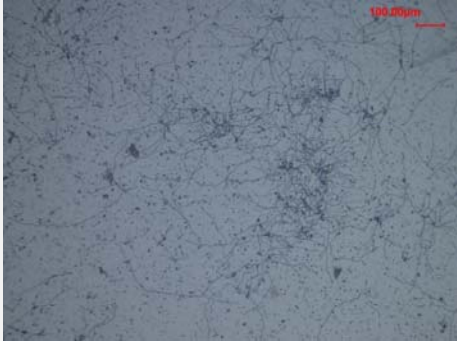
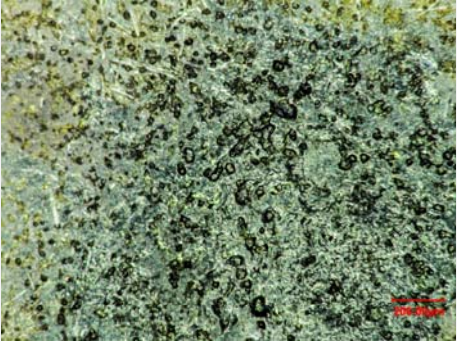
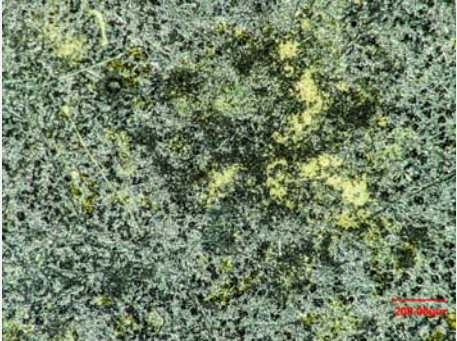

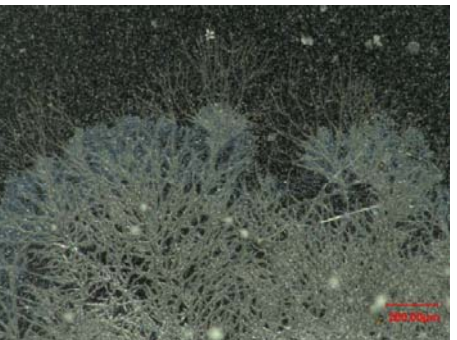



Results: Optical microscopy

NEW
SLIDE



Results: Comparison

Sample 1	Sample 2	Sample 3
		
Sample 4	Sample 5	Sample 6
		

Results: Electron Microscopy

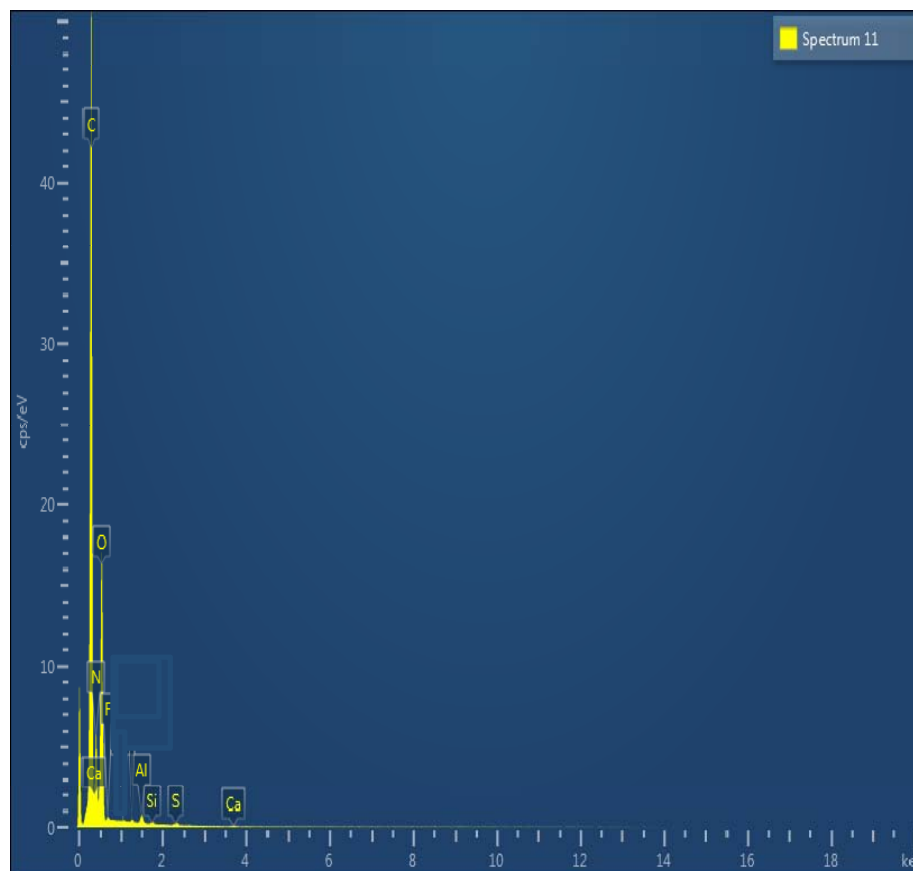


Some reminders...

- The composition of the slides is not known. Historically there have been three major types of film base in use: nitrocellulose, cellulose acetate and polyester. **All of them are based on C and O.**
- EDS makes impossible to detect presence of elements below around 0.2 wt %, or light elements.
- The following elements were found in all the samples: C, O, N, Al, S
- F, Na, Ca was detected in most of the cases but in a very low concentration (lower than the detection limit).

Results: Electron Microscopy

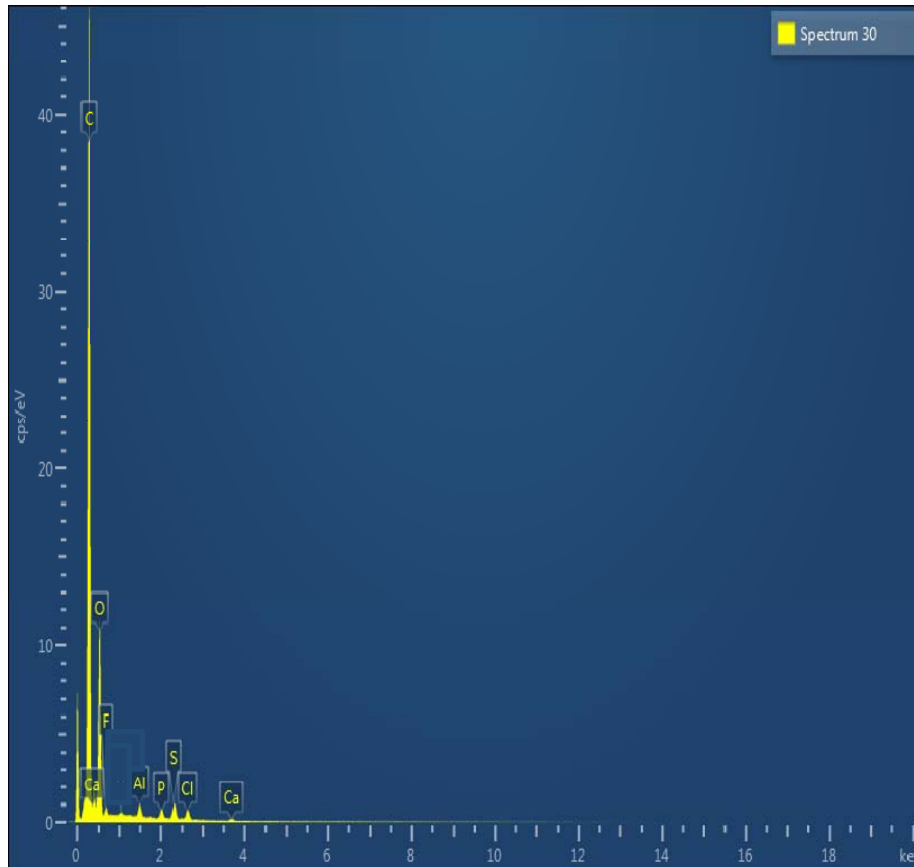
OLD
SLIDE



- C, O, N, Al, S, Ca
- Si

Results: Electron Microscopy

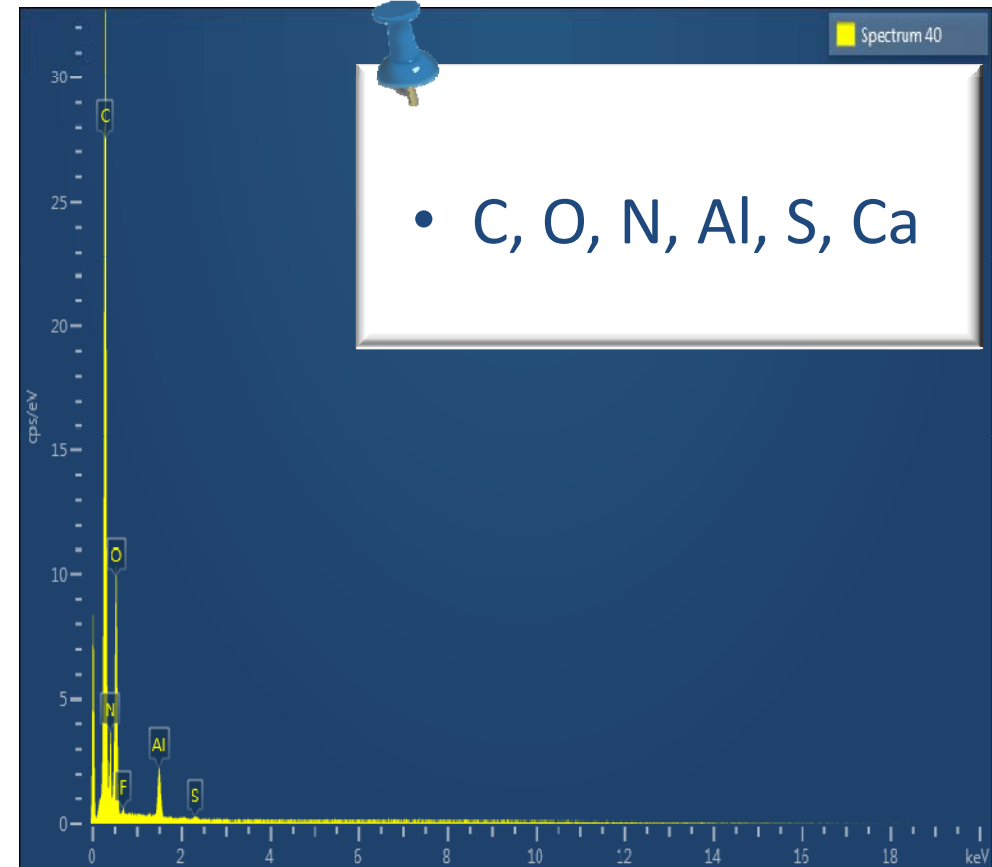
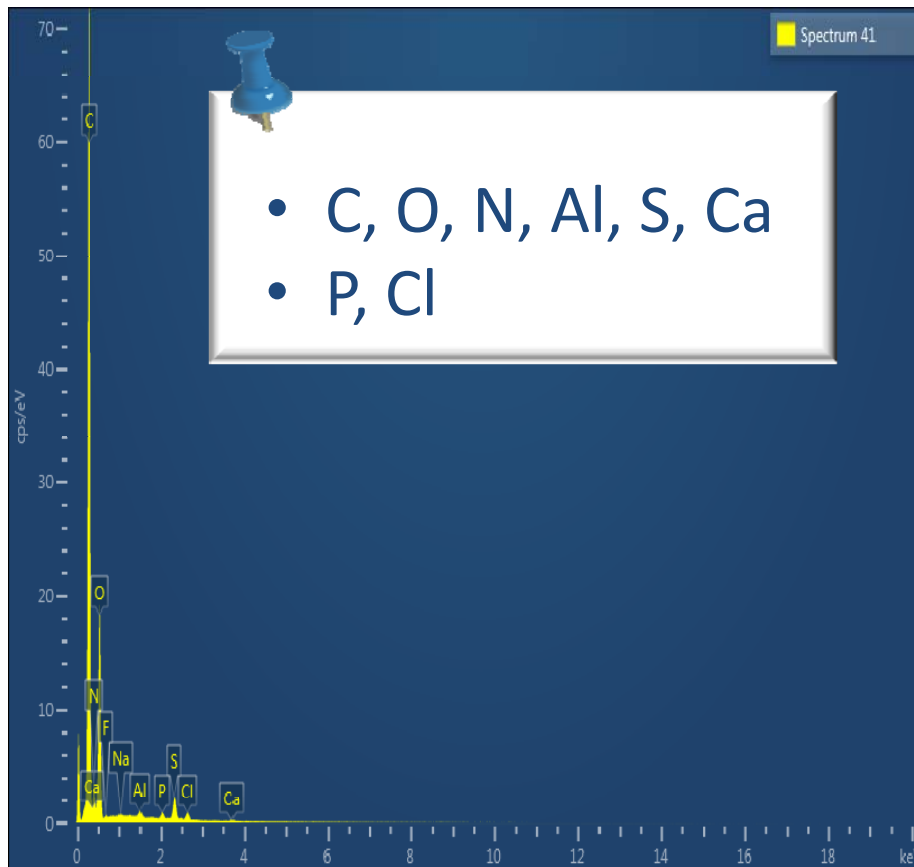
OLD
SLIDE



✓ C, O, N, Al, S, Ca
✓ P, Cl

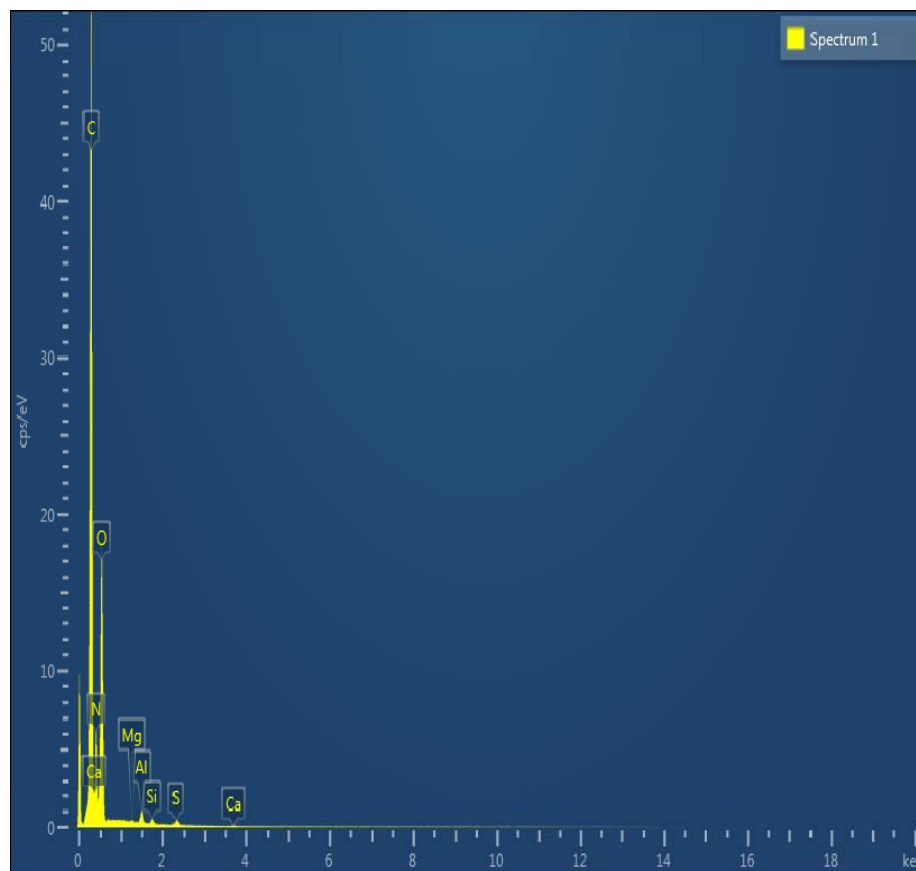
Results: Electron Microscopy

OLD
SLIDE



Results: Electron Microscopy

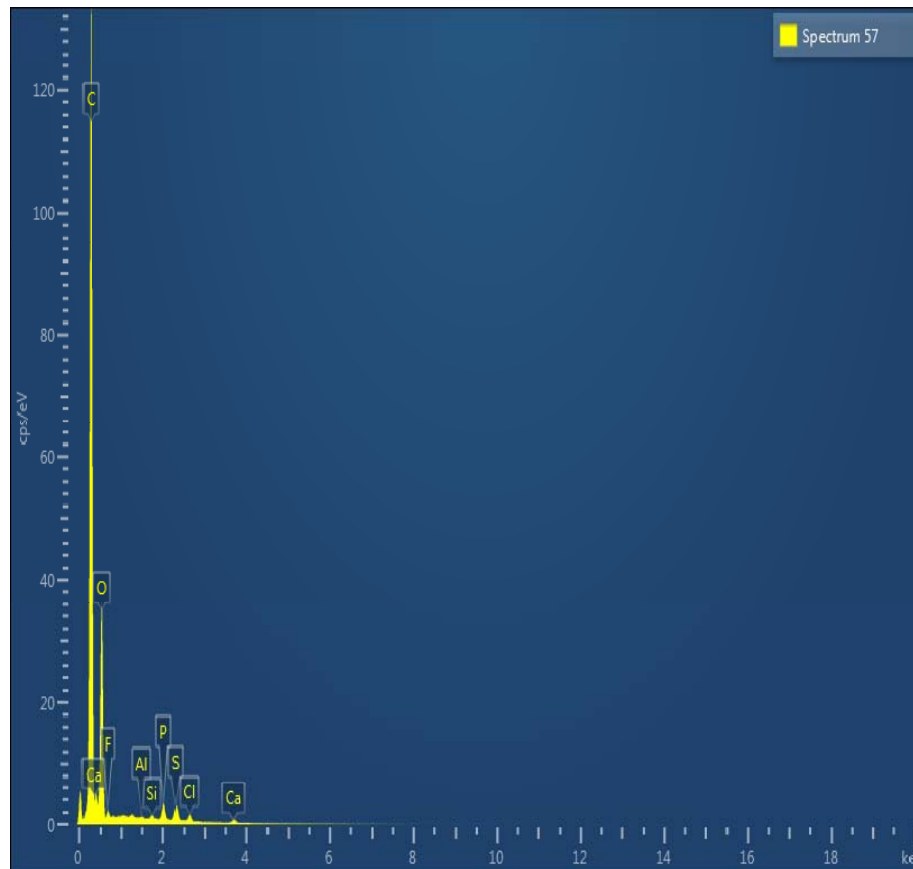
NEW
SLIDE



✓ C, O, N, Al, S, Ca
✓ Si

Results: Electron Microscopy

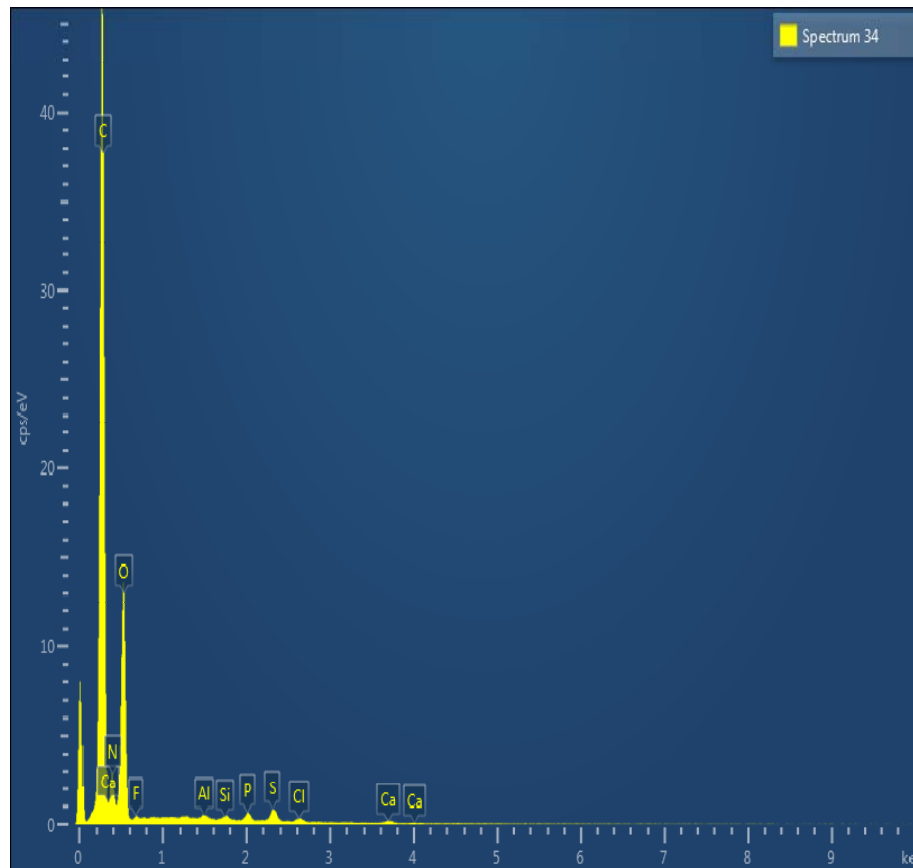
NEW
SLIDE



-
- ✓ C, O, N, Al, S, Ca
 - ✓ Si
 - ✓ P, Cl

Results: Electron Microscopy




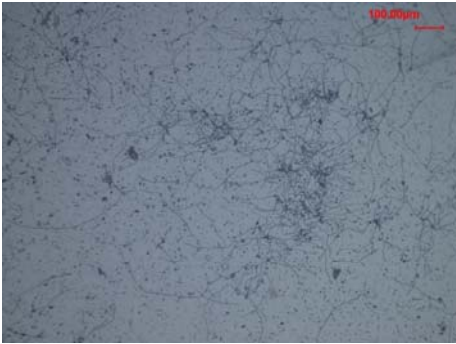
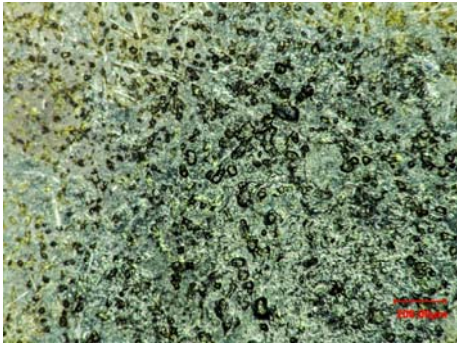
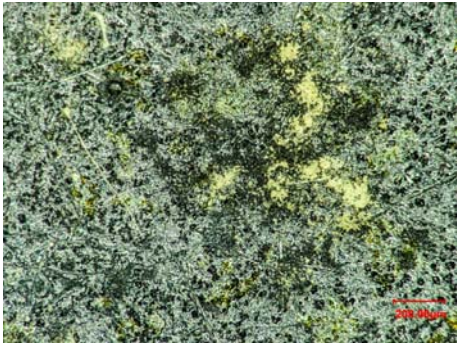
NEW
SLIDE







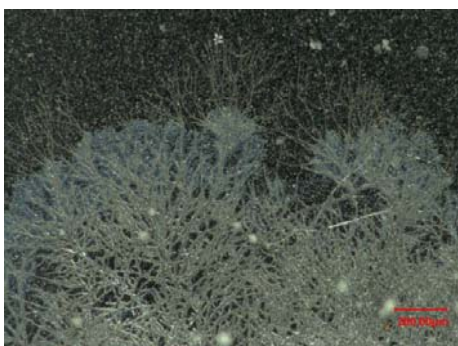
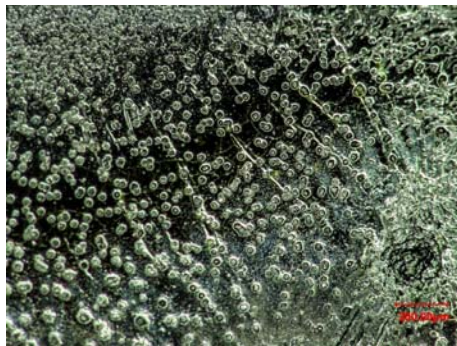
- ✓ C, O, N, Al, S, Ca
- ✓ Si
- ✓ P, Cl

No differences between
mold/no mold
→ same composition if
exposed to water

Results: Comparison

	Sample 1	Sample 2	Sample 3
	OLD SLIDES		
			
Si	Yes	-	-/ Yes
P	-	Yes	Yes/ -
Cl	-	Yes	Yes/ -
			

Results: Comparison

	Sample 4	Sample 5	Sample 6
	NEW SLIDES		
			
Si	Yes	Yes	Yes
P	-	Yes	Yes
Cl	-	Yes	Yes
			

SUMMARY & CONCLUSIONS

- ✓ Optical and Chemical analysis on slides submitted to different storage conditions.
- ✓ Comparison with new slides treated in a different ways to reproduce conditions.

- ✓ Slides are carbon-based thus difficult to differentiate with a mold.
- ✓ Limitations with the technique for quantifying light elements (C, O).

	Case 1	Case 2
	No degradation	Degraded
OM	Clean appearance	Surface covered surface with a relief material.
SEM	Chemical composition just based on C, O, Si and other traces.	P and Cl appear in the chemical composition of the slide.

SUMMARY & CONCLUSIONS

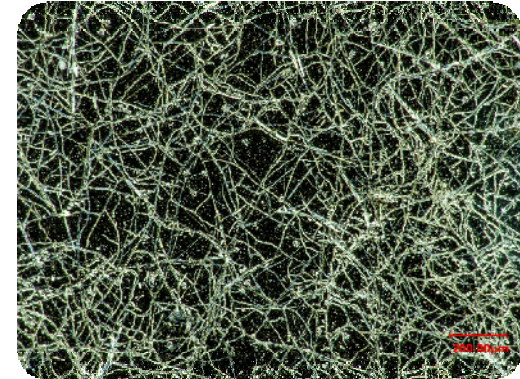
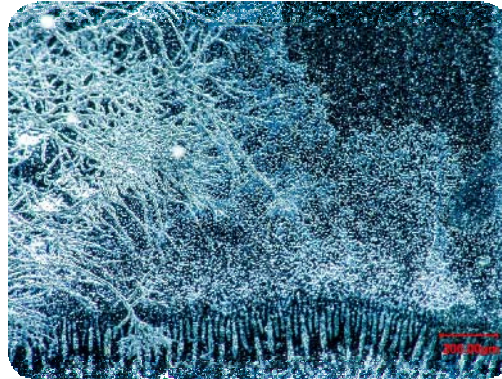
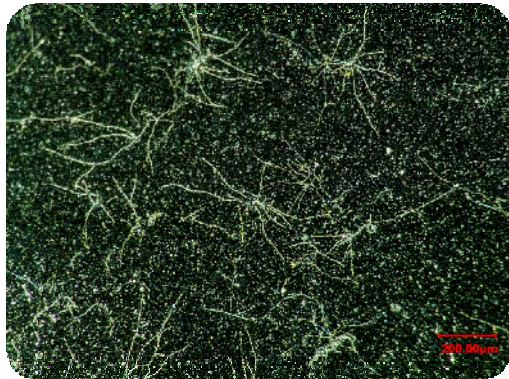
- ✓ Optical and Chemical analysis on slides submitted to different storage conditions.
- ✓ Comparison with new slides treated in a different ways to reproduce conditions.

- ✓ Slides are carbon-based thus difficult to differentiate with a mold.
- ✓ Limitations with the technique for quantifying light elements (C, O).

Under these circumstances, and considering the limitations of the technique:

- Confirmed the presence of an organic material on some slides.
- It is not possible to precise the nature of the substance (require a different technique – biology field)
- The appearance of this substance is related to the exposure of the slide to water. as a result, P and Cl appear in the EDS analysis.

UNDERSTANDING VOLMEUR ARTWORK WITH ELECTRON MICROSCOPY

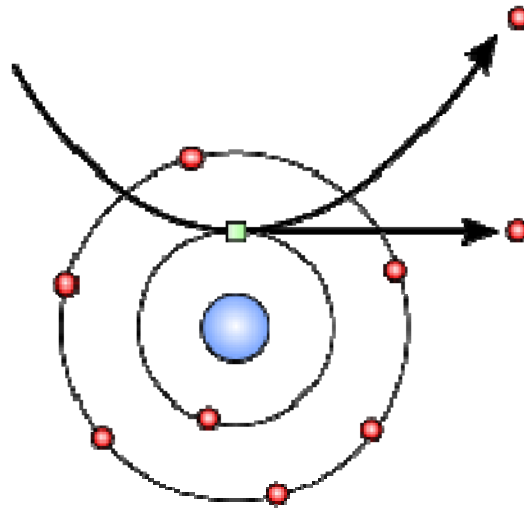


THANK YOU VERY MUCH FOR YOUR ATTENTION

elisa.garcia-tabares.valdivieso@cern.ch

Imaging - Secondary Electrons

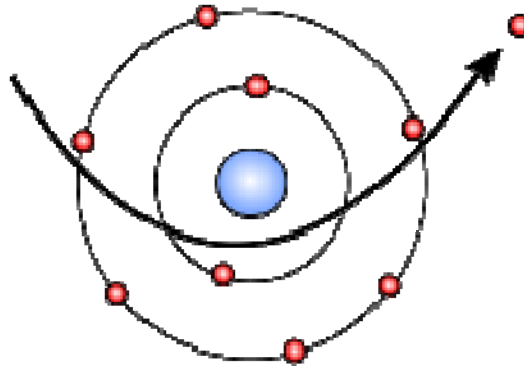
- Secondary Electrons (SE)
 - They are ejected from the k-orbitals of the specimen atoms by **inelastic scattering interactions** with beam electrons
 - They have a **low-energy (<50 eV)**



- Contrast given by topographic irregularities, roughness
 - SE quantity depends on the angle of the PE beam and the surface

Imaging - BackScattered Electrons

- Backscattered Electron (BSE)
 - Interaction between primary electrons from the beam and the nucleus of the atoms with a **low loss of energy** and a **quasi-elastic reaction**.



- Contrast given by Z
 - Heavy atoms emit more BSE than light atoms
 - The higher the Z , the brighter the image