SECONDARY ION MASS SPECTROMETRY
Applications in Materials Characterization

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Secondary Ions Mass Spectrometry

- Basic principles
- Instrument design
- Examples of applications in materials characterization

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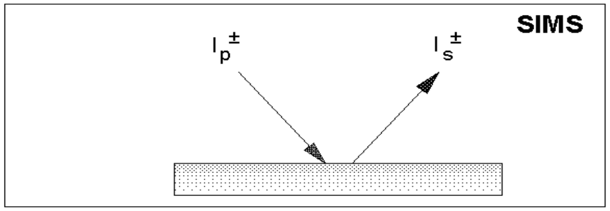
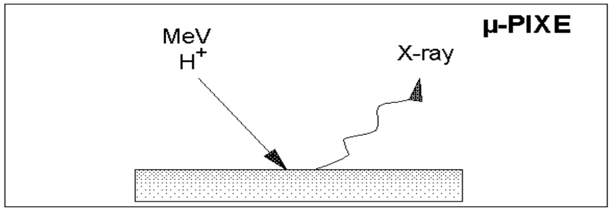
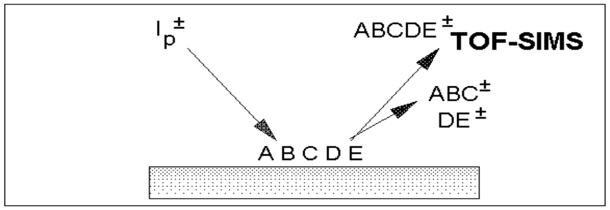


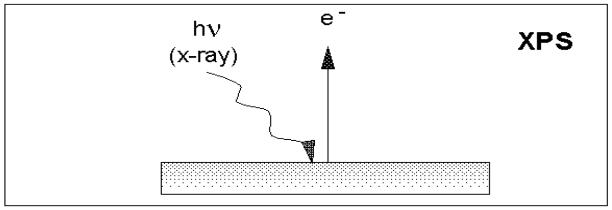
Operated in a dynamic SIMS mode, an energetic primary ion beam is used to sputter atoms from the sample surface. Secondary ions emitted are mass analyzed in electrostatic magnetic sector instrument. Very high sensitivity and quantitative analysis are key features. Depth profiling and imaging capabilities.



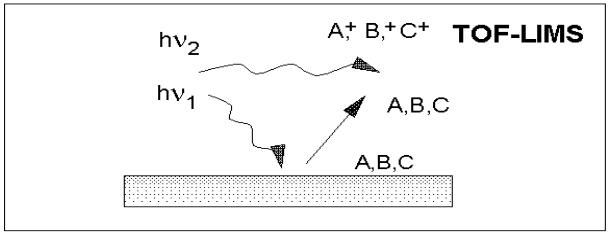
A high energy proton beam is focused on a mineral particle to generate characteristic X-rays for elemental detection. Simultaneous multielemental detection and mapping of trace elements.



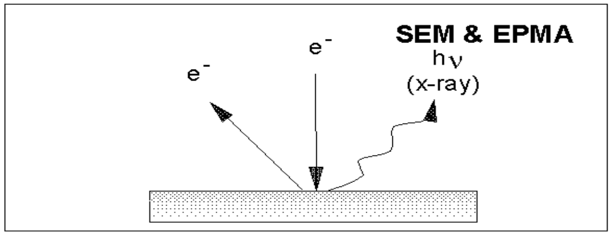
TOF-SIMS generally operates in a static SIMS mode whereby the top monolayers of the sample surface are analyzed. A pulsed ion beam is used and secondary ions emitted from compounds and molecules are mass analyzed and imaged.



When the surface of a sample is excited with X-rays, high-resolution energy analysis of photoelectrons emitted from atoms near the surface can be used to characterize a variety of inorganic and organic materials. Chemical bonding information may be determined from the chemical shift of atomic transitions.



A focused laser beam ablates neutral particles from the sample surface that are indiscriminately ionized by a second powerful laser source using the process of nonresonant multiphoton ionization (NRMPI). Surface analysis of inorganic species with high elemental and surface sensitivity.

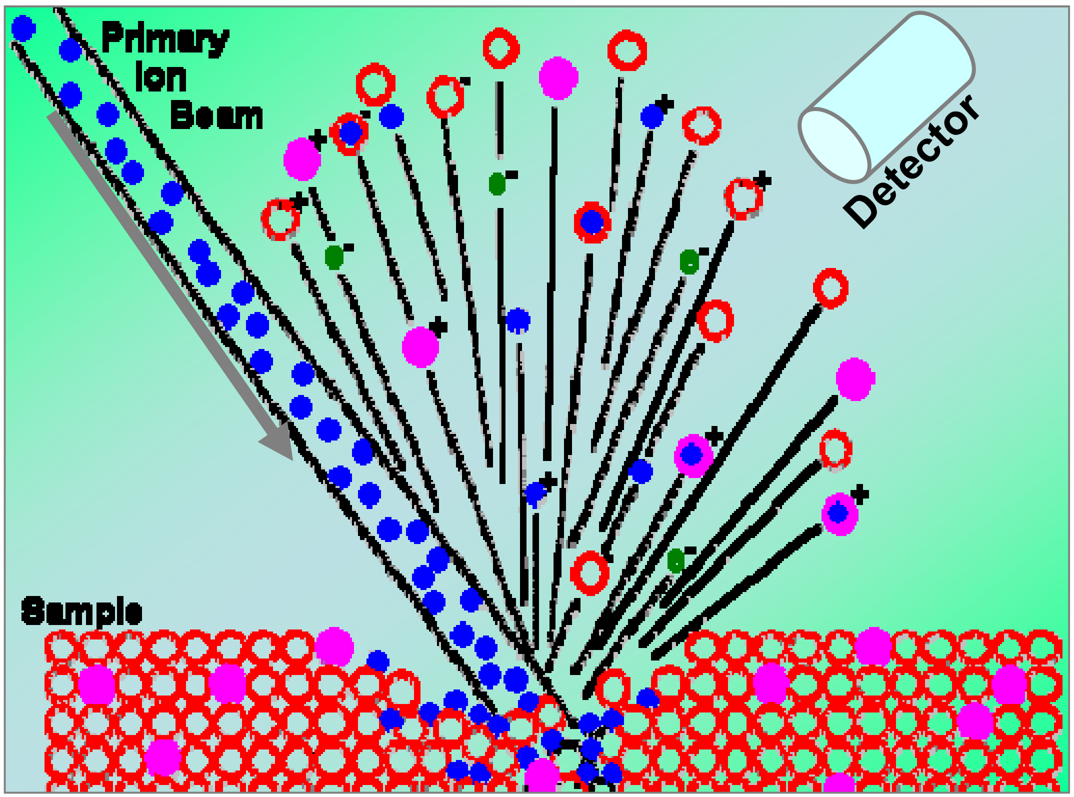


. A finely focused electron beam is rastered over the sample's surface from which an image is formed from the particles produced (e.g. secondary/backscattered electron and photon emission). Combined with energy dispersive X-ray (EDX) spectroscopy elemental quantification is possible. Wavelength dispersive X-ray (WDX) spectroscopy offers improved sensitivity.

Ion beam based micro-beam analytical techniques

Collisional ionization

Primary ion beam based SIMS is a method of analyzing the mass/charge ratio of ionized particles produced from the sample upon bombardment of an energetic (25 keV) primary ion beam (Bi^+, Cs^+, C_{60}^+).



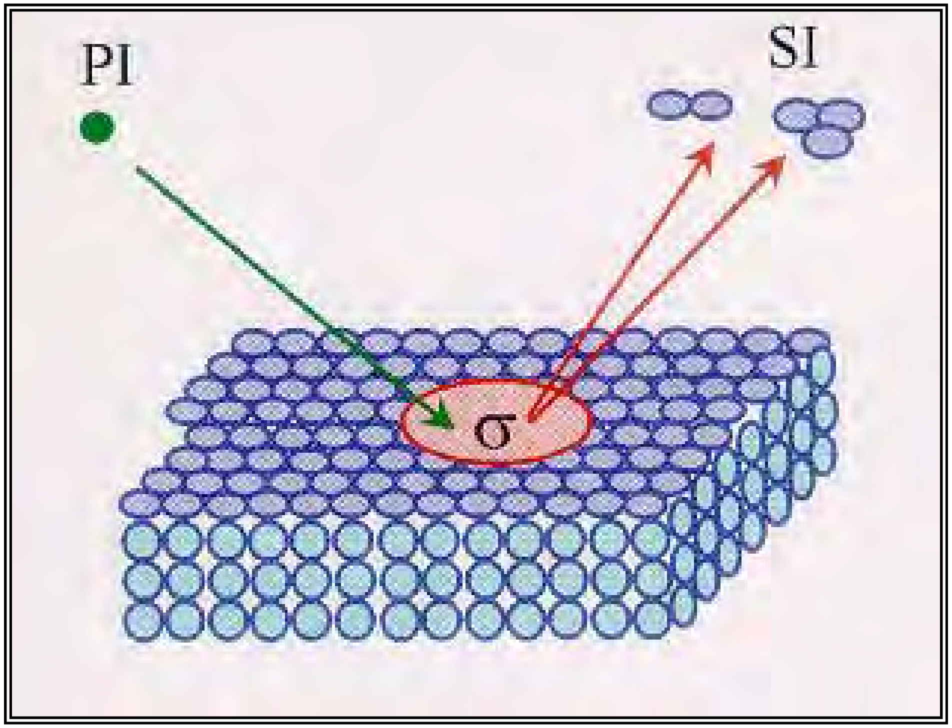
Neutral particles

Ions

Electrons

Ion beam based micro-beam analytical techniques

Collisional ionization

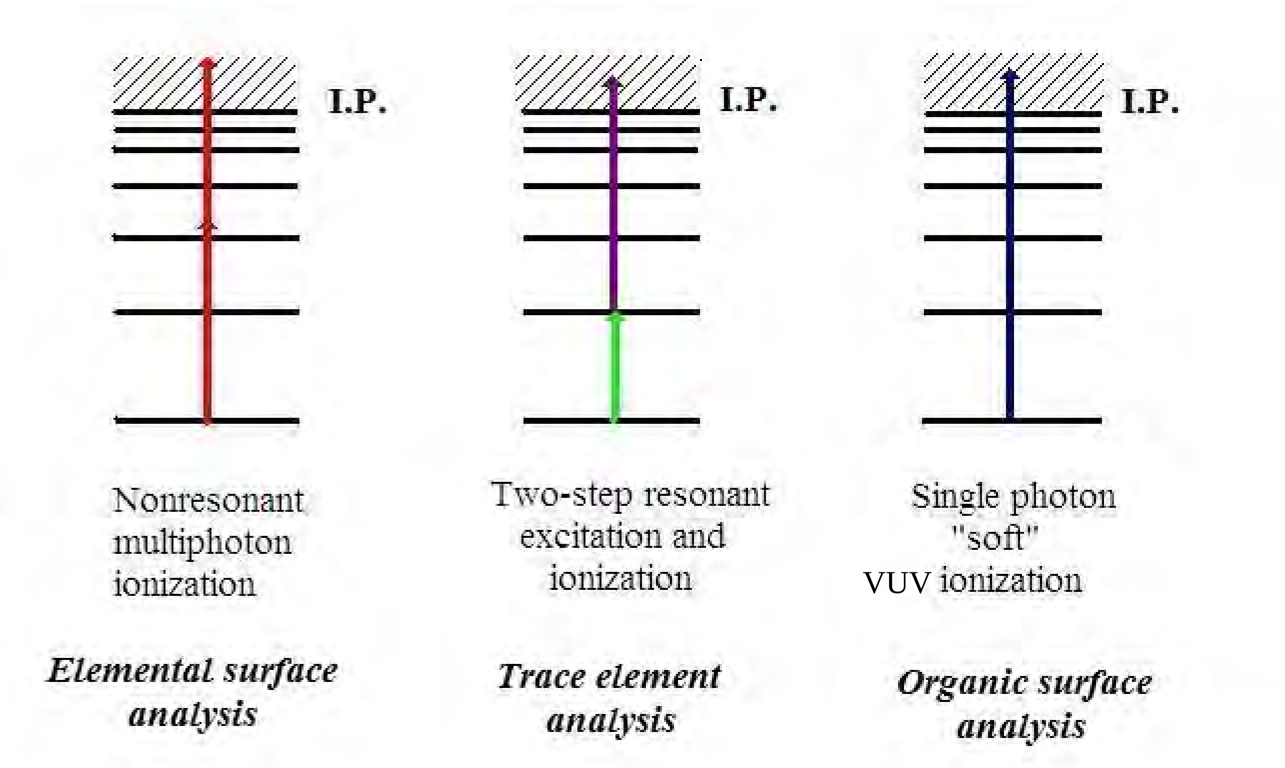


- The SIMS process is destructive – one sacrifices the surface particles that are analyzed by the mass spectrometer.

- ***Static SIMS*** (TOF SIMS): secondary ion emission from damaged areas is negligible. **Analytical depth *is limited to top monolayers***.
- ***Dynamic SIMS***: truly destructive, high primary ion beam fluence.

Laser based micro-beam analytical techniques

Optical ionization



TOF-LIMS

TOF-RIMS

VUV SALI TOF-SIMS
VUV TOF-LIMS

Instrument Design

Key performance characteristics

- Destructive/non-destructive analysis
- Elemental/ molecular analysis
- Surface sensitivity/depth profiling
- Imaging capacity
- Mass resolution
- Detection limits

Key factors

- Primary ionization source
- Mass spectrometer type

Instrument Design

Choice of mass spectrometer type

- Quadrupole type mass spectrometer
- Magnetic sector type mass spectrometer
- Time-of-flight type mass spectrometer

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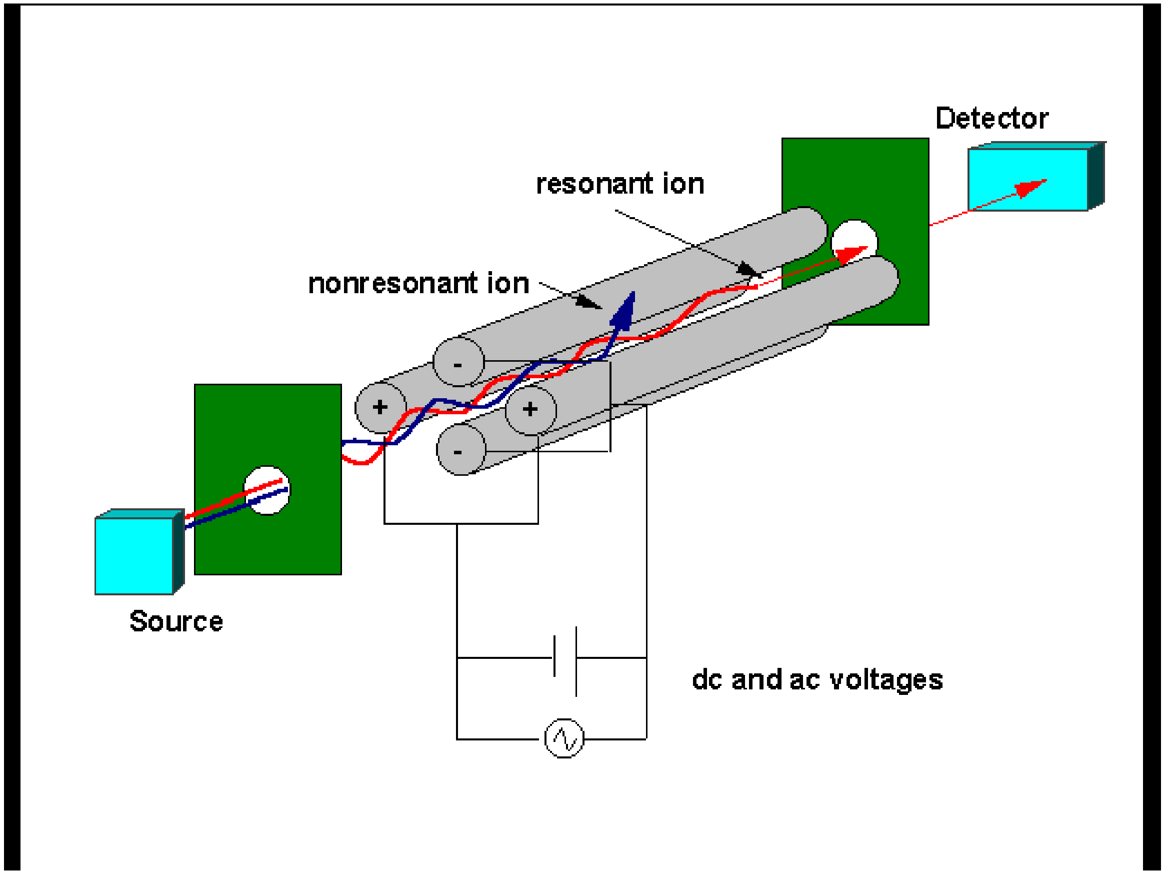
Quadrupole Mass Spectrometer



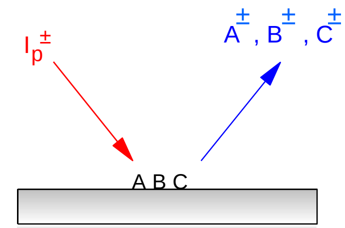
Mass spectrometers separate ions according to their mass-to-charge ratio (m/z)

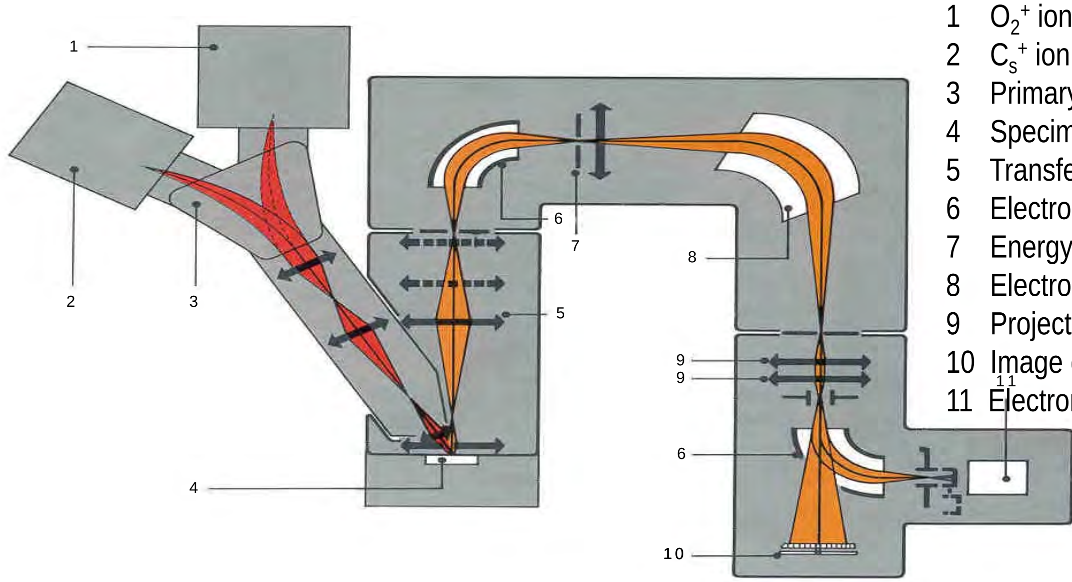
Features:

- **Good reproducibility**
- **Relatively small and low cost systems**
- **Limited resolution and ion transmission in the range of $10^{-3} – 10^{-4}$**
- **Benchtop GC/MS and LC/MS systems**
- **Triple quadrupole MS systems**

Dynamic SIMS

Magnetic sector mass spectrometer
CAMECA SIMS instrument





1 O_2^+ ion source
2 C_s^+ ion source
3 Primary beam mass filter
4 Specimen
5 Transfer optics
6 Electrostatic analyzer
7 Energy slit
8 Electromagnet
9 Projection lenses
10 Image detector
11 Electron multiplier

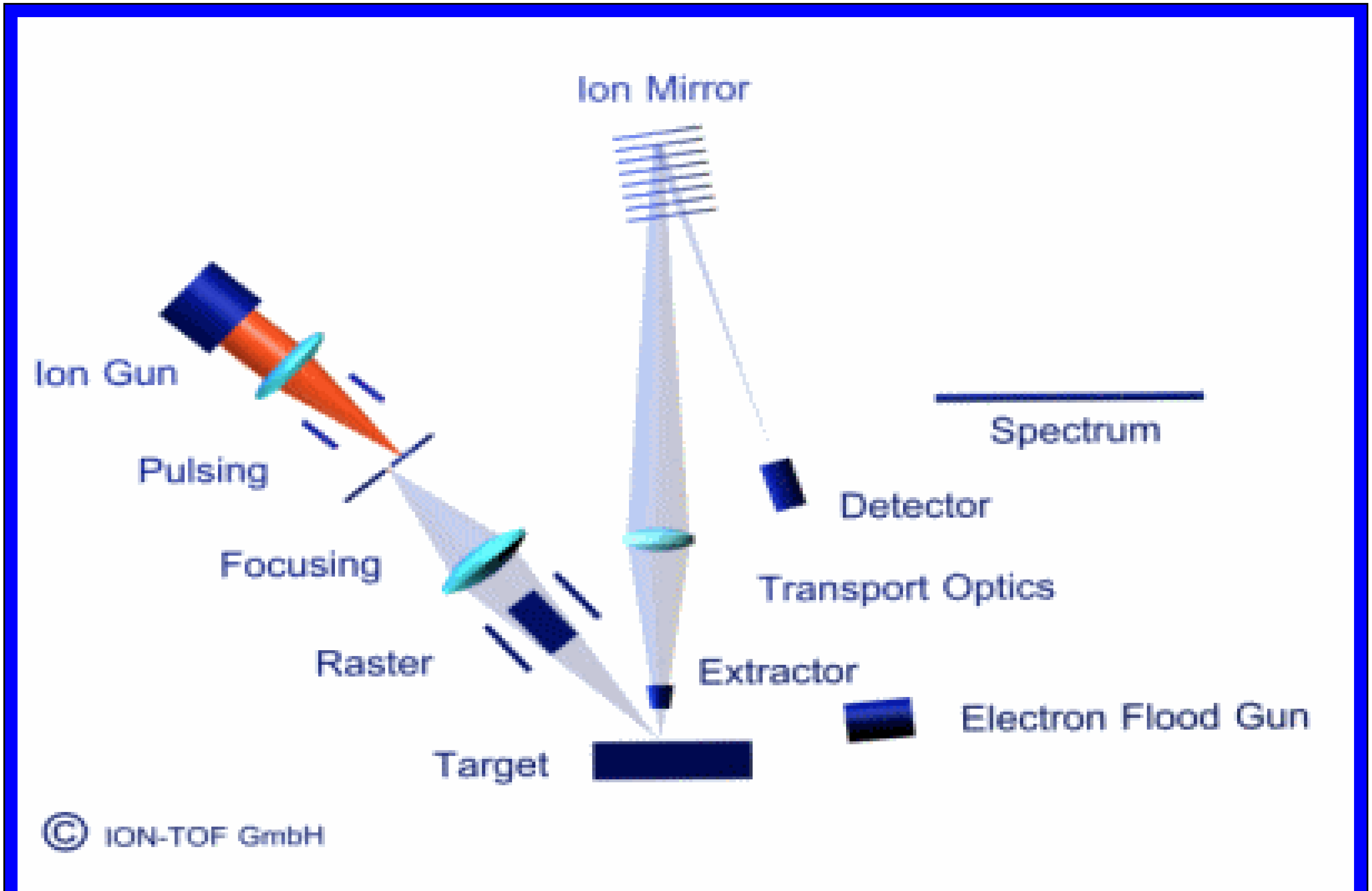
High performance mass spectrometer

- ■ **Very high reproducibility**
- ■ **Best quantitative performance**
- ■ **High mass resolution**
- ■ **High sensitivity**
- ■ **High dynamic range**
- ■ **Imaging capabilities; 1µm lateral resolution**

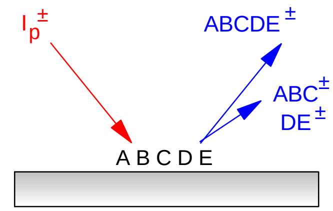
D-SIMS System Capabilities:

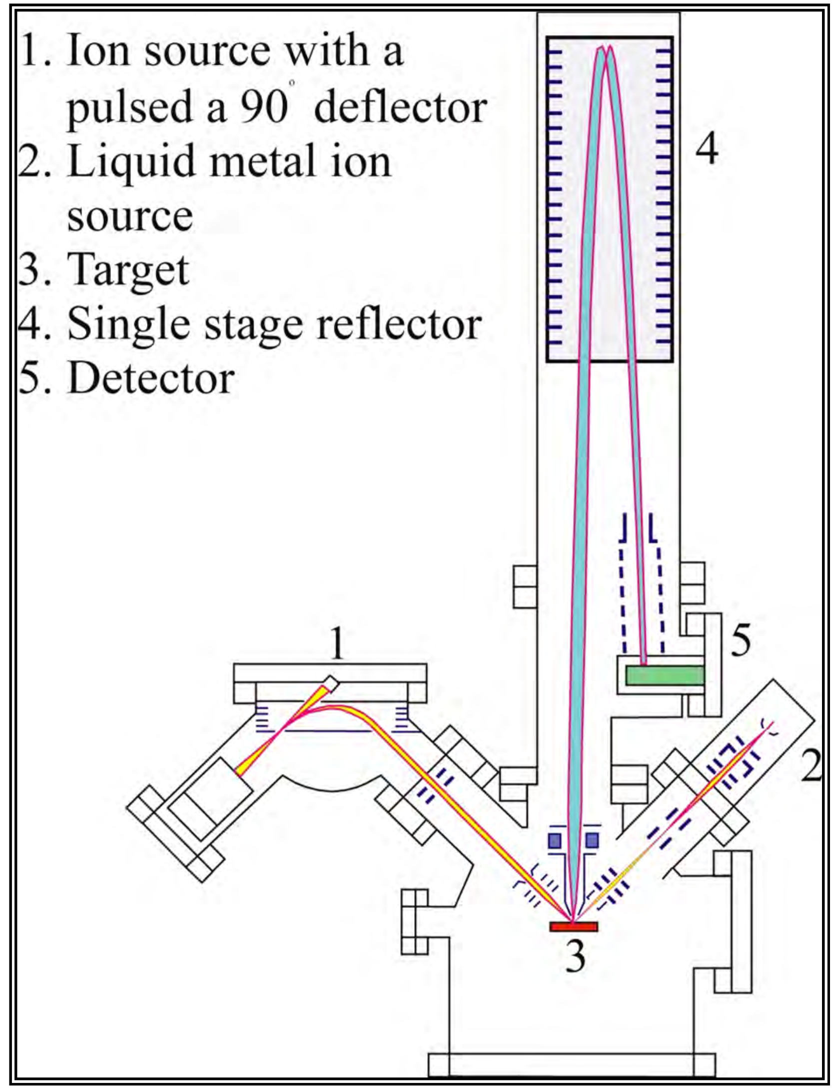
- ■ **Elemental and isotopic survey analysis covering the entire periodic table**
- ■ **Quantitative microanalysis;MDL100 ppb**
- ■ **Elemental depth profiling**
- ■ **Imaging**

Time-of-Flight Mass Spectrometer
TOF-MS



Time-of-Flight Secondary Ions Mass Spectrometry (TOF SIMS)





ION TOF IV TOF SIMS instrument
This mass spectrometer is able to analyze an unlimited mass range with high sensitivity and parallel detection of all secondary ions collected by the mass spectrometer.

TOF-SIMS Technique

Last generation instrument
ION TOF IV TOF-SIMS equipped with Cs, C_{60} and Bi ion cluster guns

STATIC SIMS mode of operation
System capabilities:

- **Non destructive elemental and molecular compound analysis**
- **High mass range (above 10,000 Daltons) and high mass resolution: M/ΔM >2,000-10,000**
- **Detection limits in the low ppm/ppb range**
- **Imaging with spatial resolution down to 0.3µm**
- **Depth profiling with depth resolution of less than 10A**
- **Retrospective analysis**

Relevance:

Benchmark technique for elemental and molecular surface analysis

Secondary Ion Mass Spectrometry Techniques

Primary source	Mass Spectrometer	Technique	Area of application			
			Surface analysis	Depth profiling	Trace element analysis	Imaging
VIS/UV laser	TOF MS Quadrupole MS	TOF-LIMS LA ICPMS	√ Elemental		√ Elemental	√ Elemental
Tunable laser	TOF MS	TOF-RIMS			√ Elemental	
VUV laser	TOF MS	VUV TOF-LIMS	√ Molecular			
Pulsed Cs, O_2 ion sources	TOF MS	TOF-SIMS	√ Elemental	√		√ Elemental
Ion cluster sources: Bi^{n+},Au^{n+},C60	TOF MS	TOF-SIMS	√ Elemental & Molecular	√		√ Elemental & Molecular
DC Cs, O_2 ion sources	Magnetic Sector MS	Dynamic SIMS		√	√ Elemental	√ Elemental

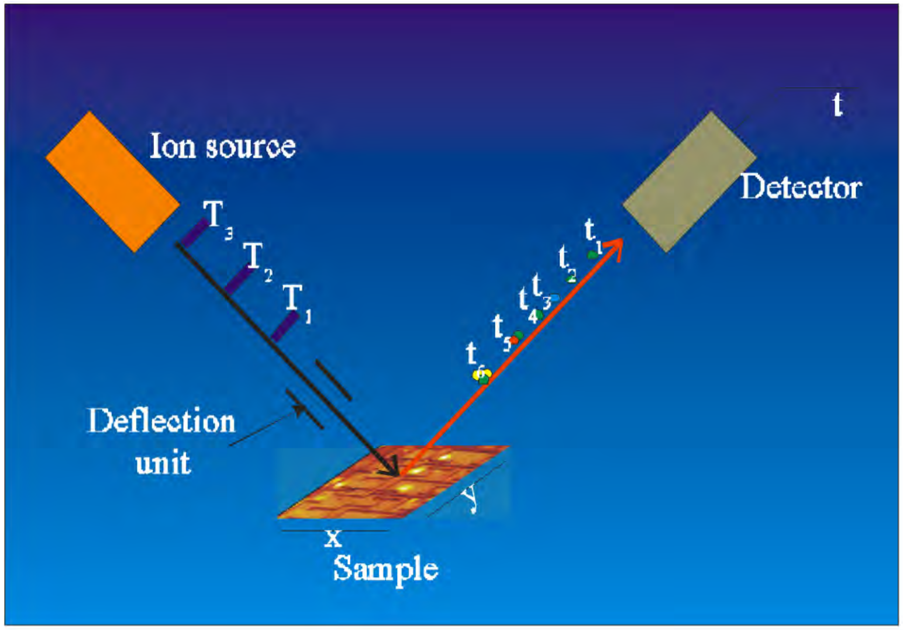
TOF-SIMS Retrospective Analysis

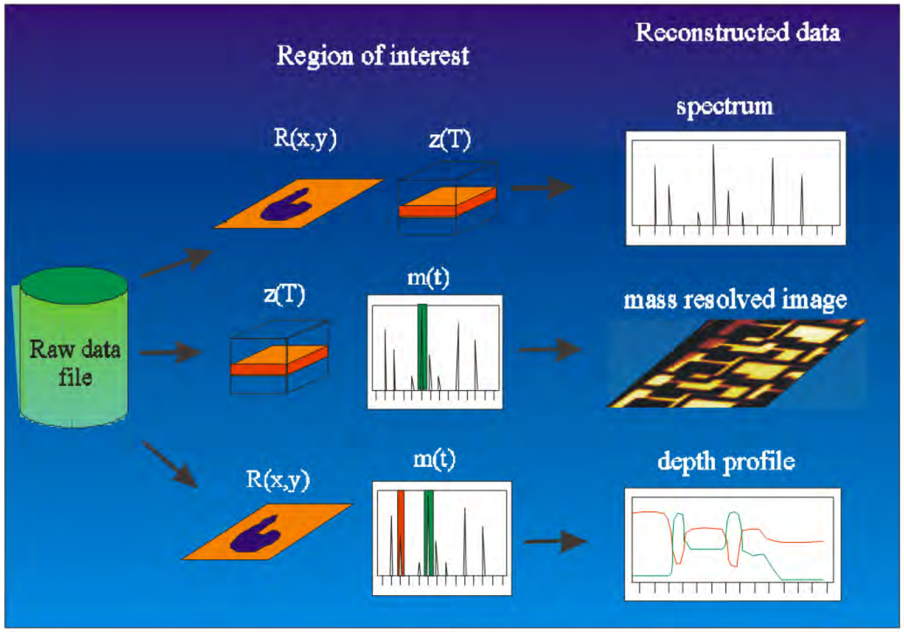
Acquisition of raw data

Storage: time-of-flight (t), position (x,y) and measurement time (T) for each SI

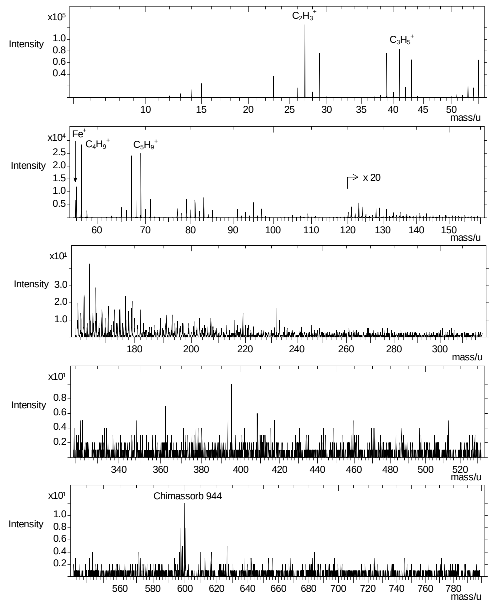
Retrospective Analysis

4D raw data file with (x,y,z,m) for each SI detected allows to reconstruct spectra, profiles and images

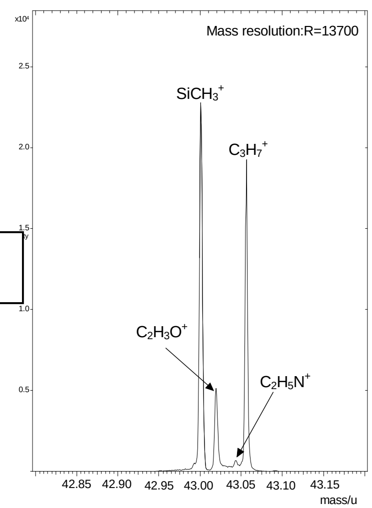




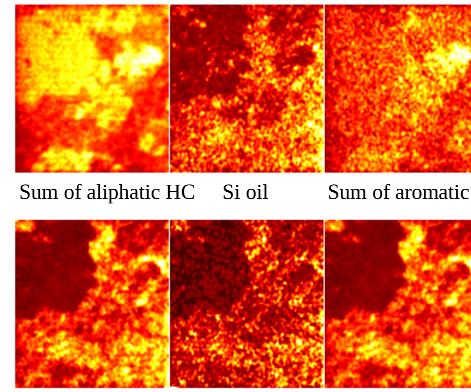
SIMS



Surface Mass Spectrometry



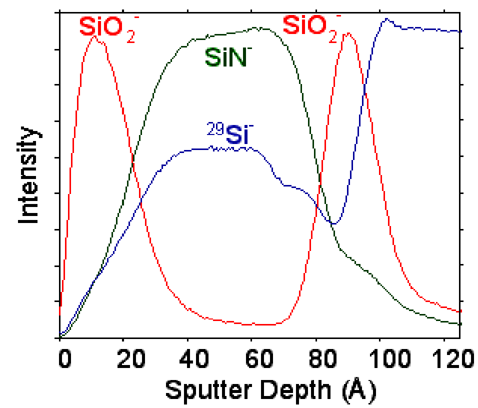
High Resolution MS



Sum of aliphatic HC Si oil Sum of aromatic HC

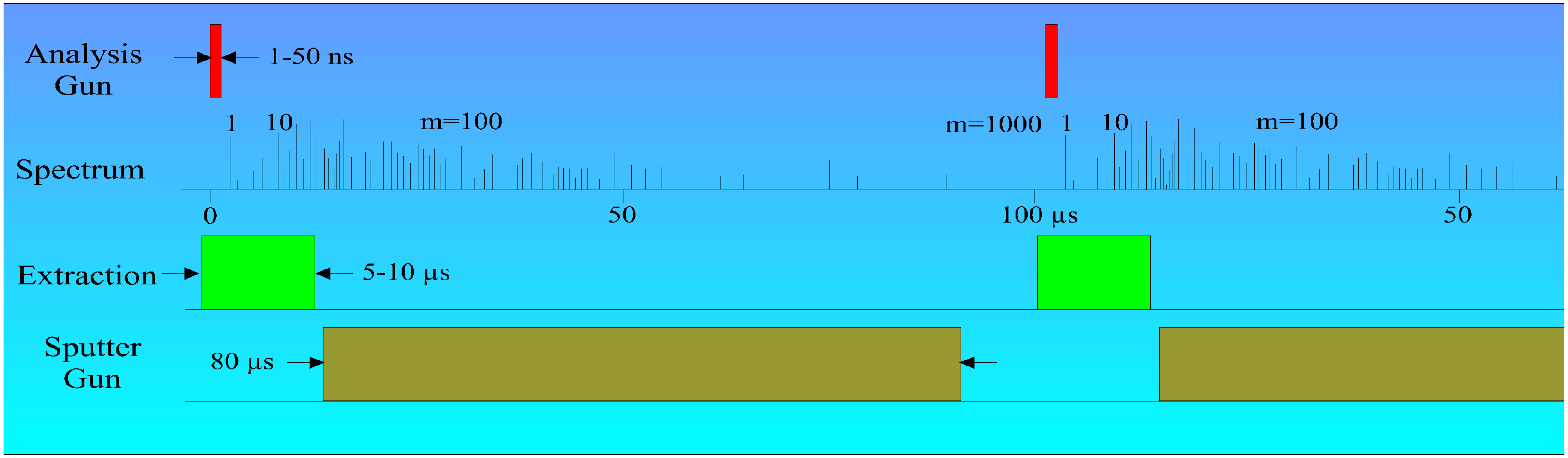
Mass 58 (C_3H_8N) Mass 124 ($C_8H_{14}N$) Sum of Chimassorb

Selected Ion Imaging



Depth Profiling

Dual beam depth profiling

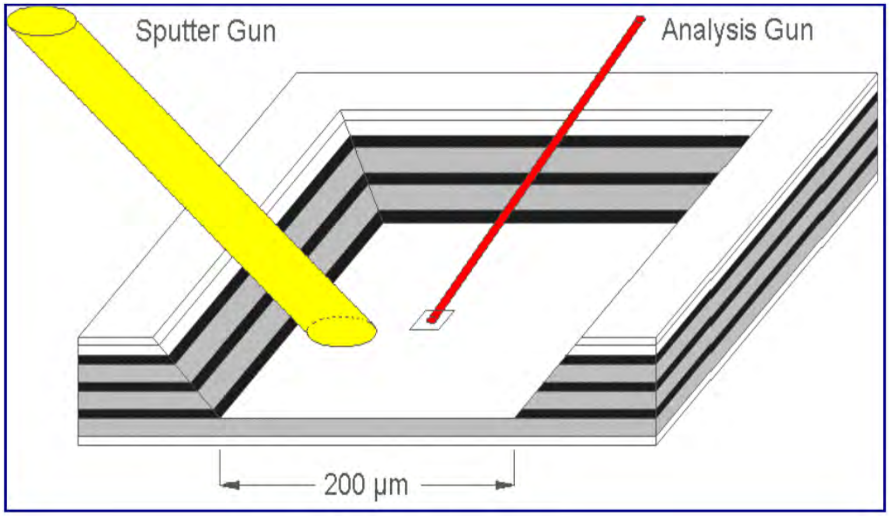


Analysis:
- high energy beam

⇒ high lateral resolution

Sputtering:
- low energy beam
- free choice of ion species

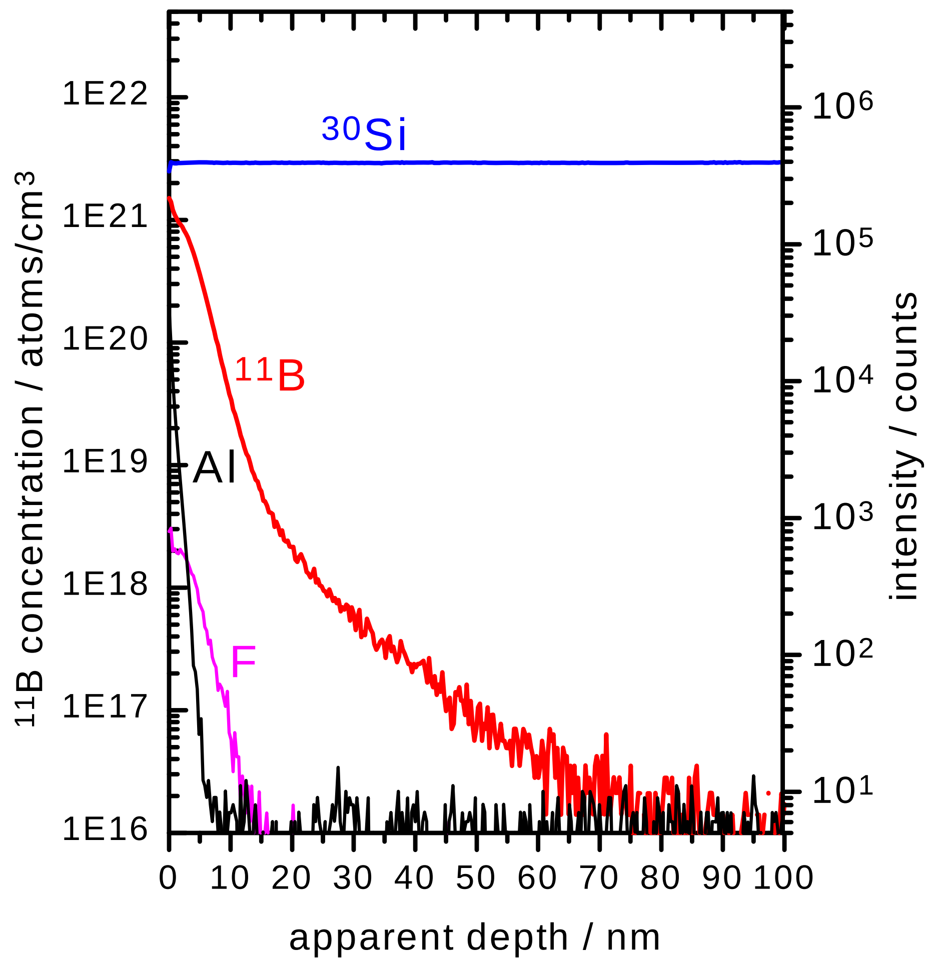
⇒ high depth resolution



Ultra Shallow Implants

Example:
BF_2 Implant in Silicon

- **High Sensitivity**
  (detection limit ^{11}B: 1E16 at./cm^3)
- **High Depth Resolution**
  (decay length Al: 0.77 nm)
- **Parallel Mass Detection**
  (contaminant screening)



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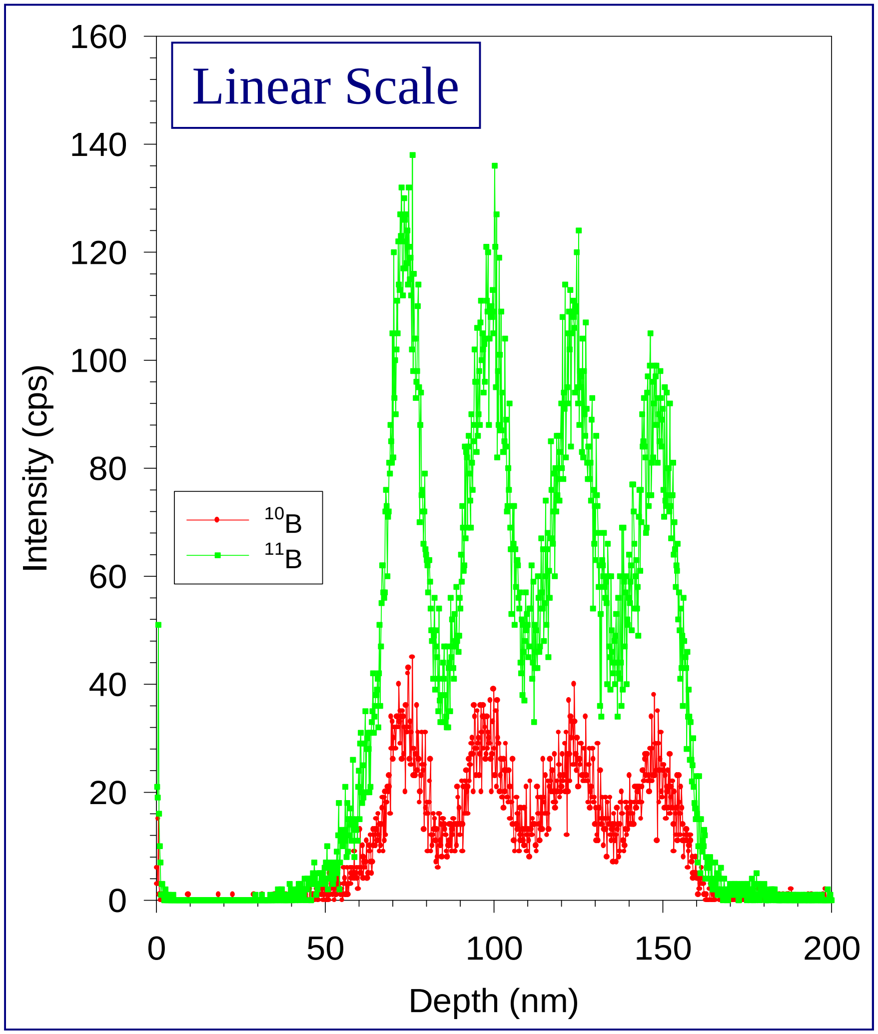
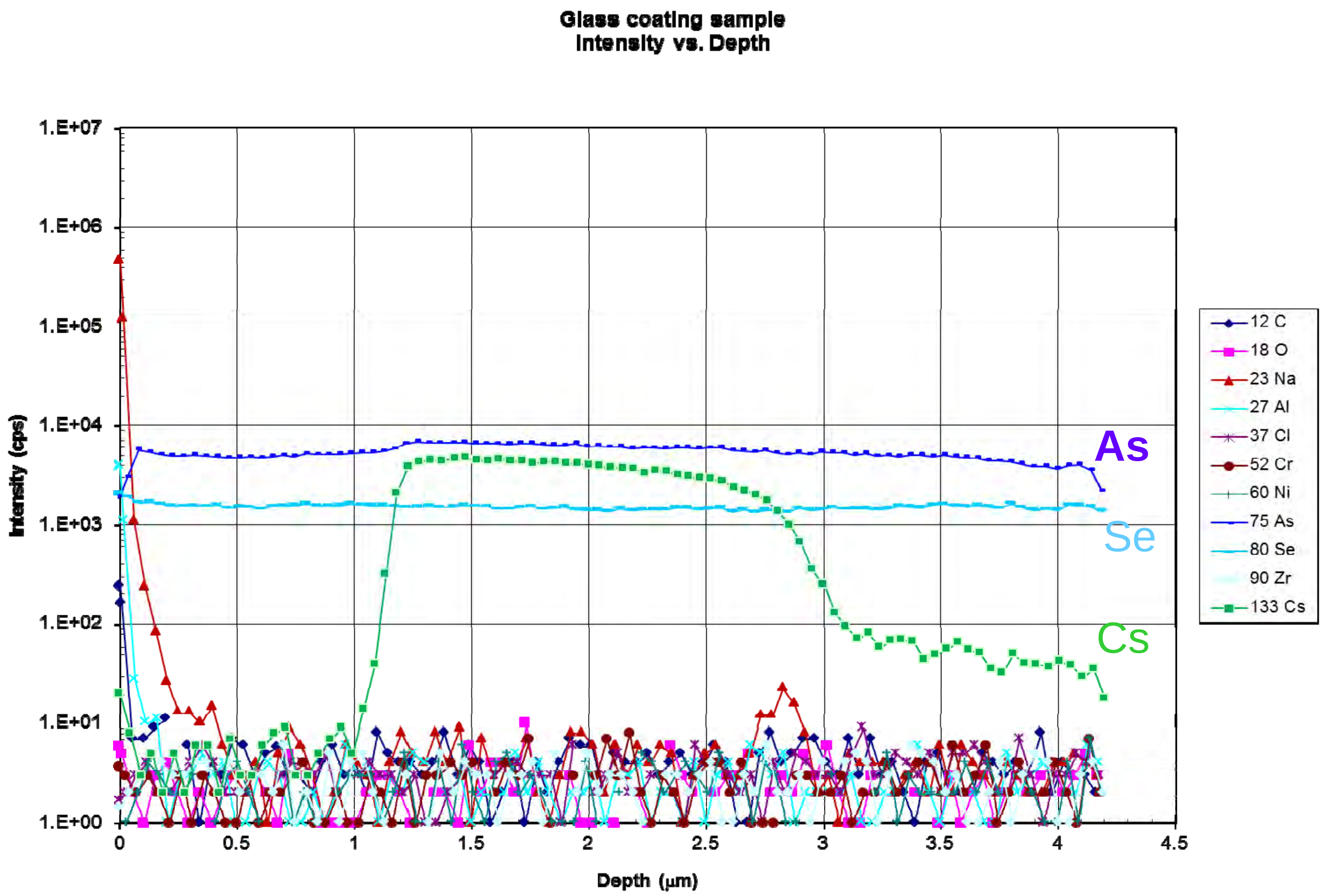
Ultra-Shallow Depth Profiles of B implants in Si wafer

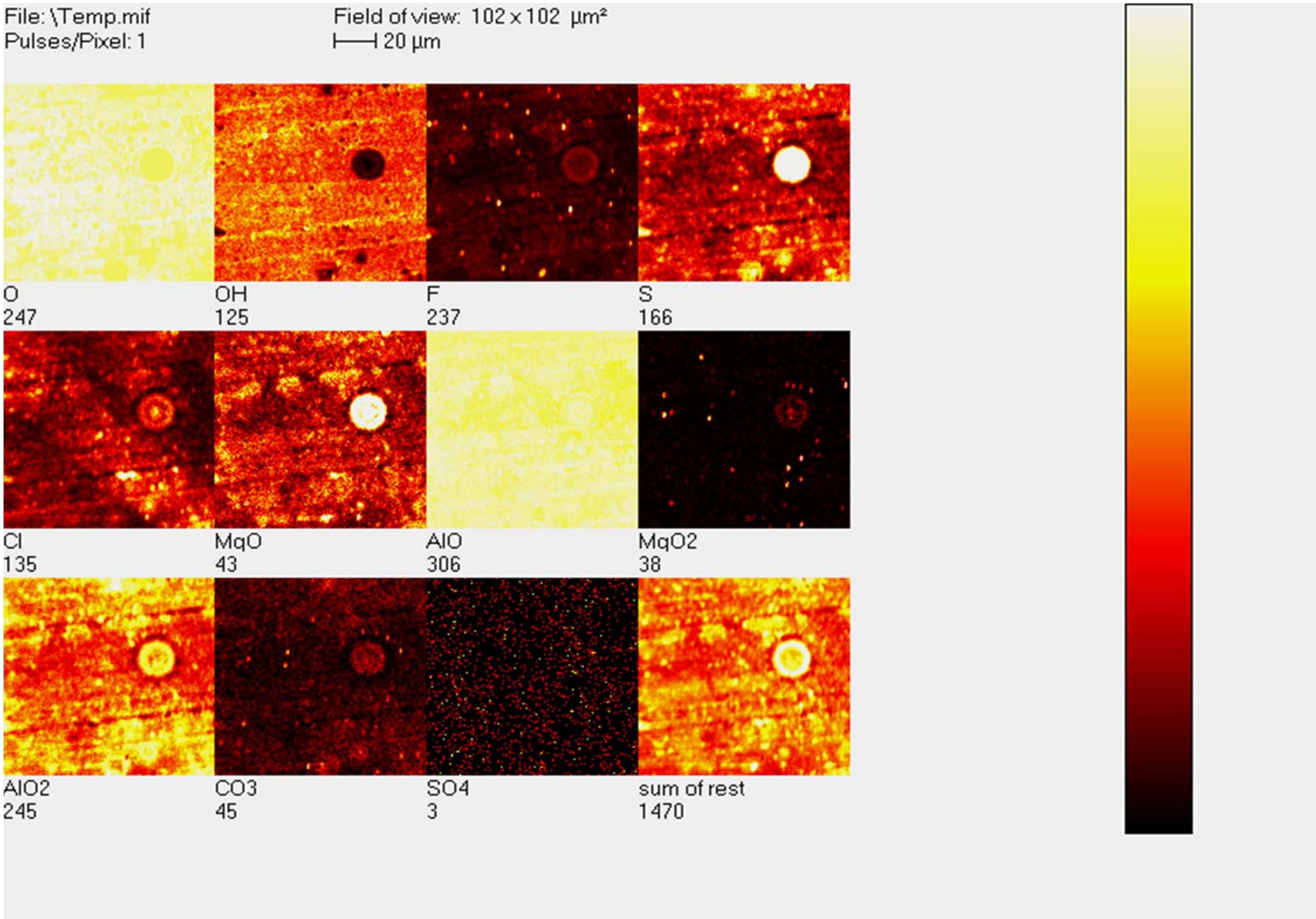
4 × (100A 5×10^{19} B/cm^{3})



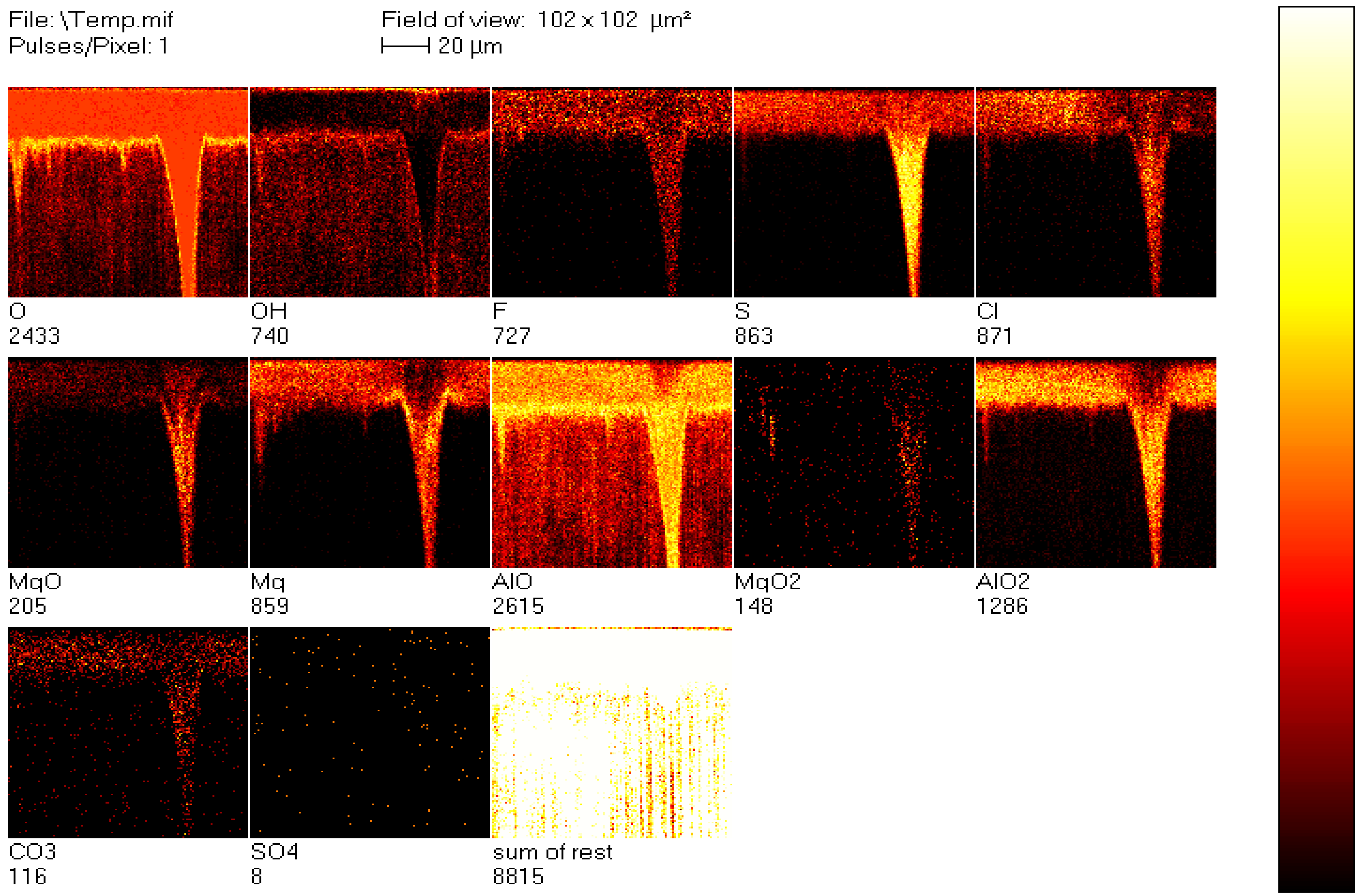
D-SIMS depth profile of Cs in Arsenic rich layer used in X-ray detector



Corrosion on Al sample, Plan View



3-D Cross Section Reconstructed from Raw Data



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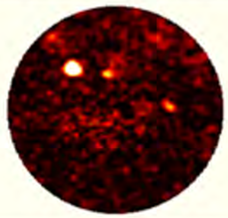
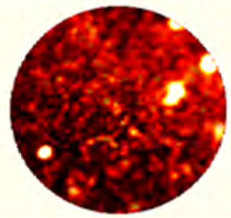
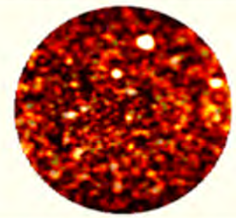
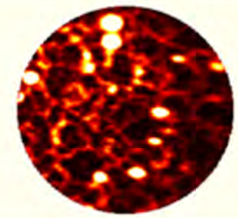
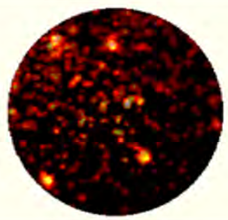
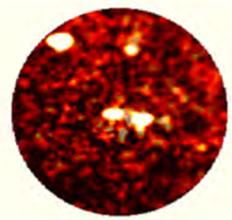
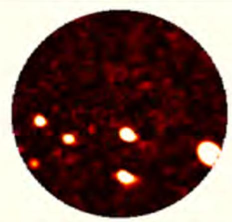
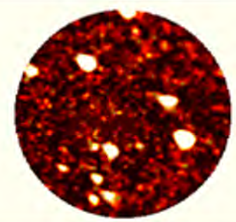
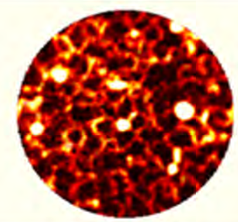
Corrosion studies: D-SIMS study on aging of tubing used in nuclear stations

- Steam Generator tubing from four Canadian nuclear stations examined (in service from 1.5 to 26 years).
- Steam Generator tubing may experience measurable aging (change in composition/microstructure) after many years of service.
- Precipitation of some elements had occurred.

Area\Tube ID	D4 SG3 R54C76 2 Yrs of Service	D4 SG1 R49C61 10 Yrs of Service	G2 SG3 X69Y54 25.5 Yrs of Service	PLGS SG3 R32C65 26.8 Yrs of Service
OD Edge				
ID Edge				
Mid-Section				

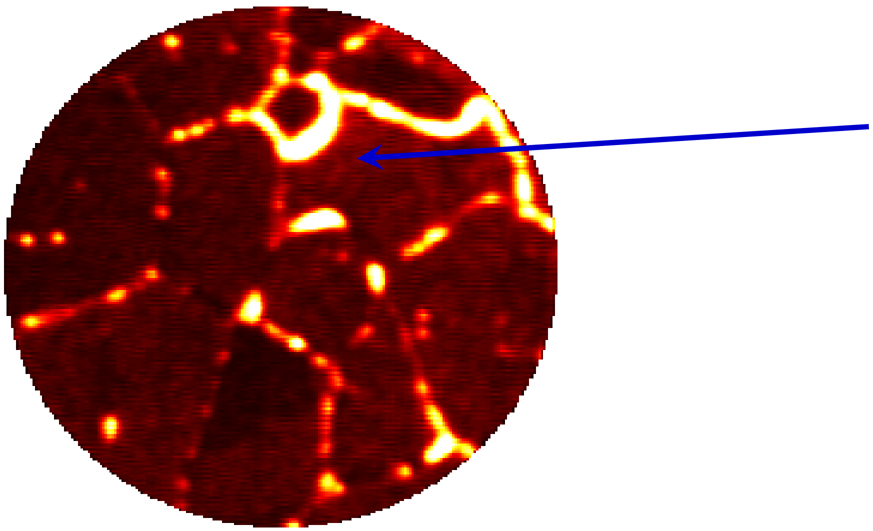
- Increased B (as BO) precipitation as a function of # of years in service.

Corrosion studies: D-SIMS study on aging of tubing used in nuclear stations

- Impurity precipitation at the metal grain boundaries can result in preferential corrosion along the grain boundaries.
- Intergranular attack (IGA) was observed on Alloy 800 steam generator (SG) tubing removed from service in a nuclear power station.
- Alloy 800 composition: 30-35%Ni, 19-23% Cr, 39.5% Fe (max), 0.10 C (max), 0.15-0.6 Al, 0.15-0.6 Ti, 0.3-1.2 Al+Ti (max).
- B is an impurity present at levels well below that of the major alloying elements.
- Secondary Ion Mass Spectrometry (SIMS) imaging was employed to determine grain boundary precipitation:
  - SIMS can detect all elements from hydrogen to uranium.
  - Dynamic SIMS has very low detection limits, of the order of ppm and even ppb for some elements.
  - SIMS depth profiling can be used to determine the composition distribution within layers up to 10-20 µm deep in a reasonable period of analysis time (4-5 hours).

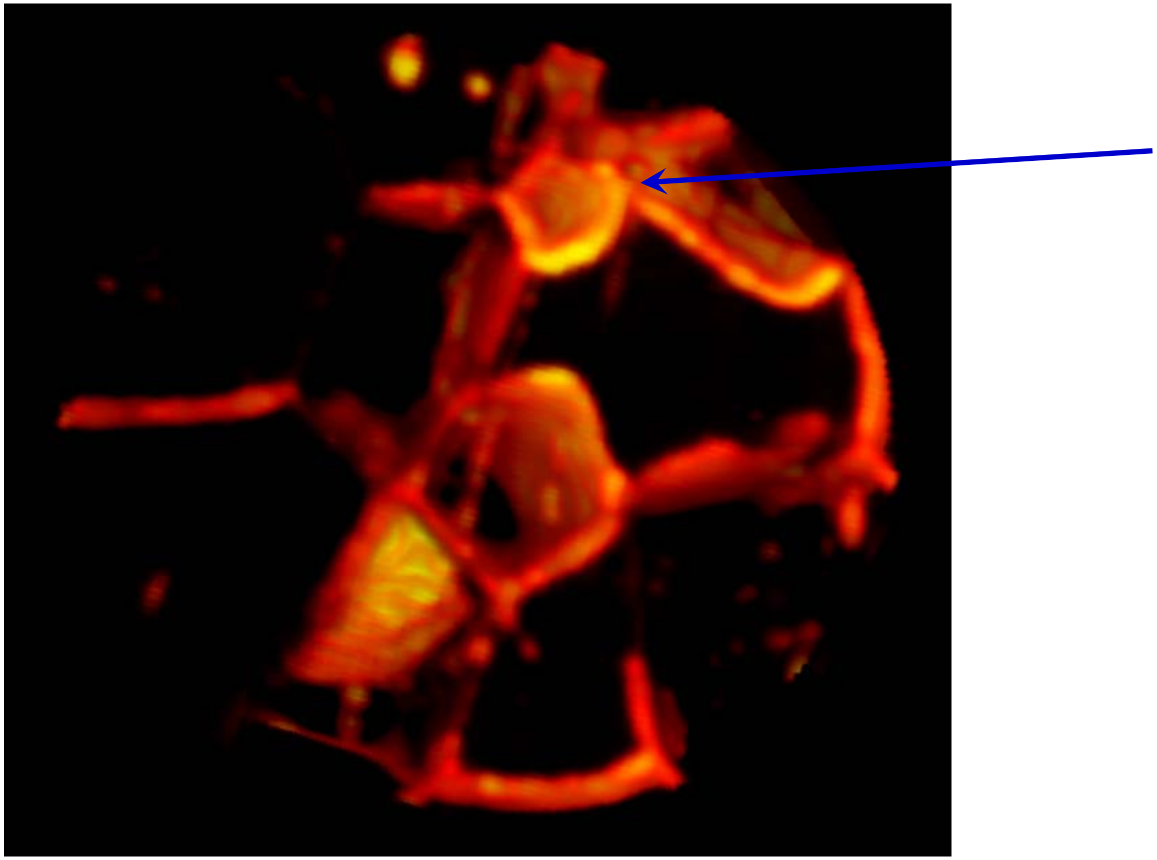
Corrosion studies: D-SIMS study on aging of tubing used in nuclear stations

Intergranular attack (IGA)



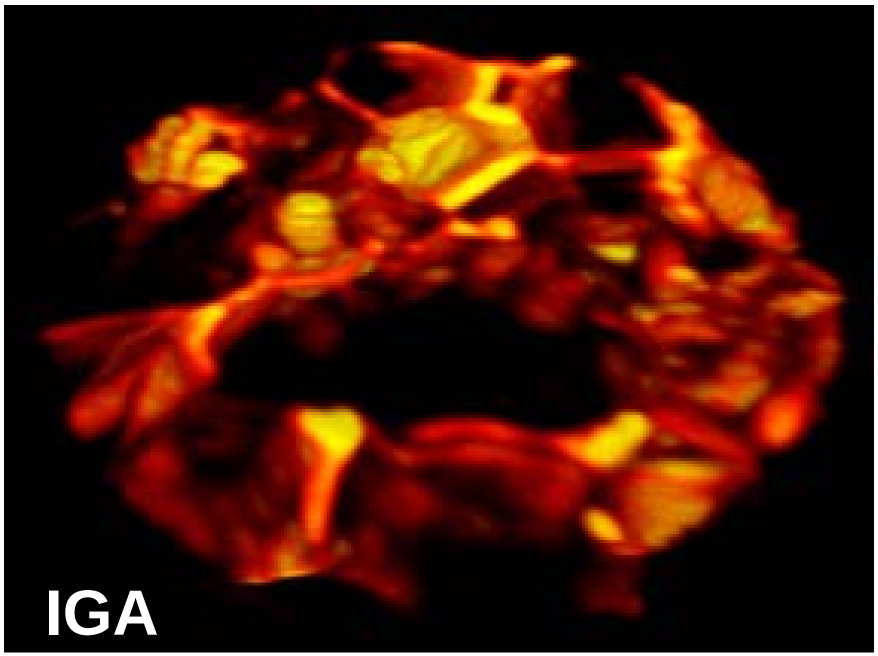
- One slice of ^{27}BO image.
- Precipitation of B along the grain boundaries can be seen in this image.

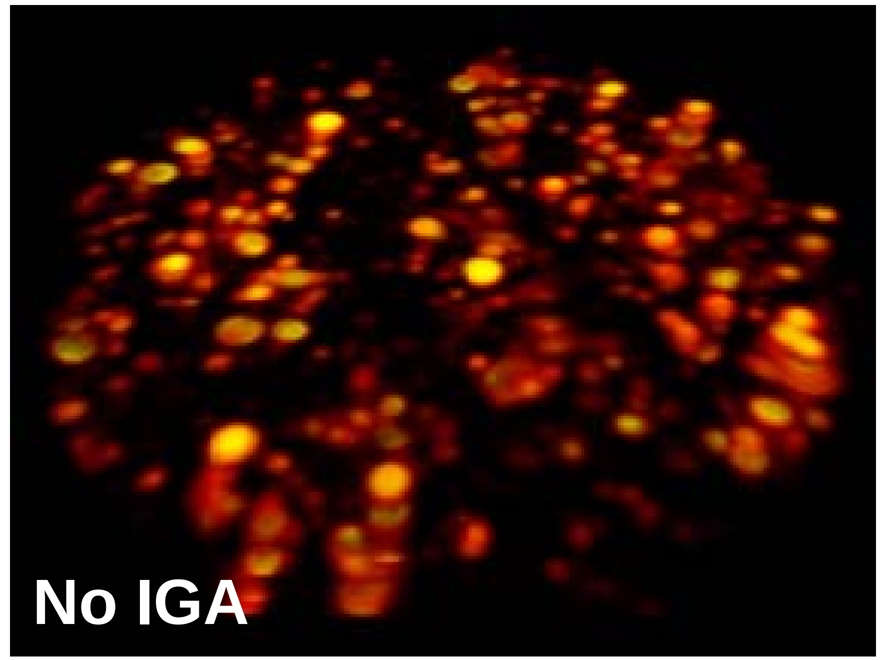
Corrosion studies: D-SIMS study on aging of tubing used in nuclear stations



- 3D image of the same volume slide shown in the previous slide.
- ^{27}BO precipitation along the grain boundaries can be clearly seen.
- The grain pointed by the blue arrow is the same one as in the previous slide.

Corrosion studies: D-SIMS study on aging of tubing used in nuclear stations

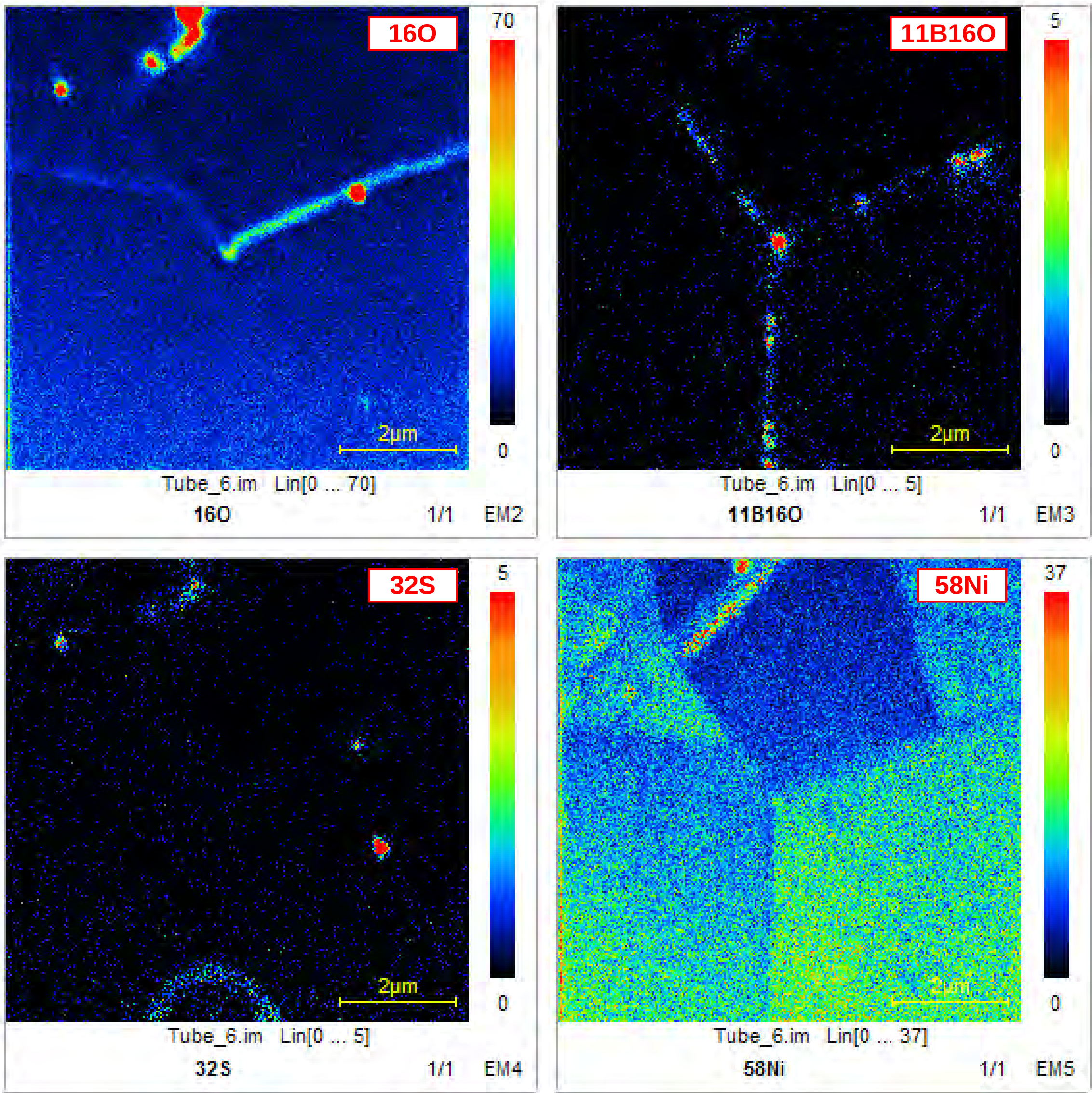




- 3D images of ^{27}BO distribution at the grain boundaries on regions exhibiting IGA and no IGA.

Nano-SIMS Imaging

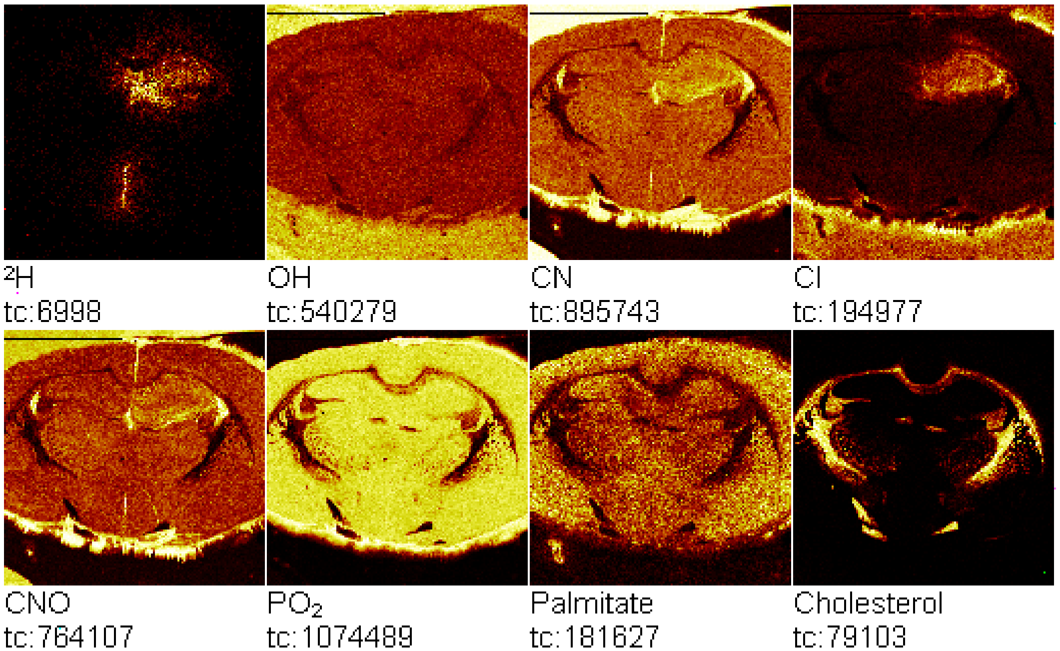
Nano-SIMS can image features as small as 50 nm



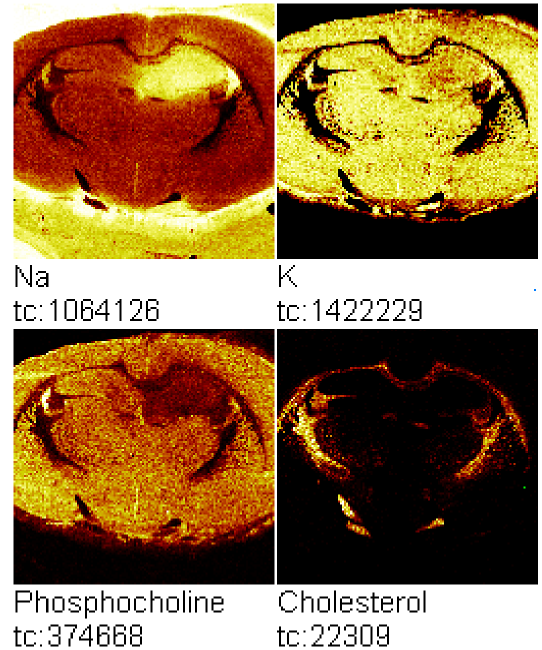
- Negative secondary ions, Cs^+ primary ion source
- ^{58}Ni describes the grain structure
- ^{27}BO, ^{16}O and ^{32}S are corrosion related impurities.

Ion images of a sectioned rat brain

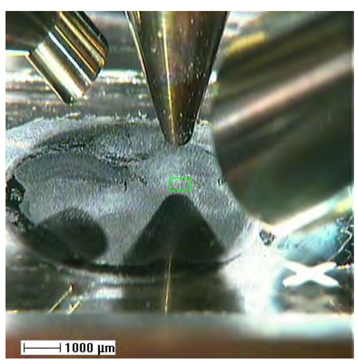
Field of view: 12000.0 x 12000.0 µm²



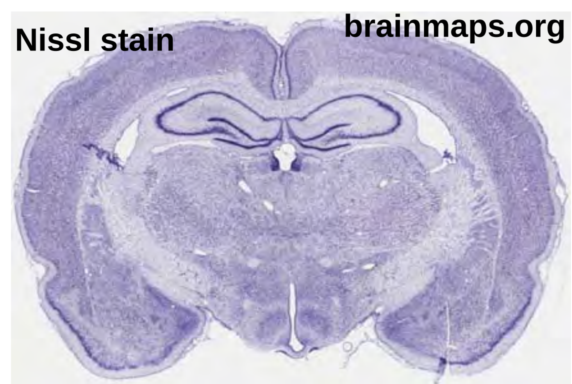
Field of view: 12000.0 x 12000.0 µm²



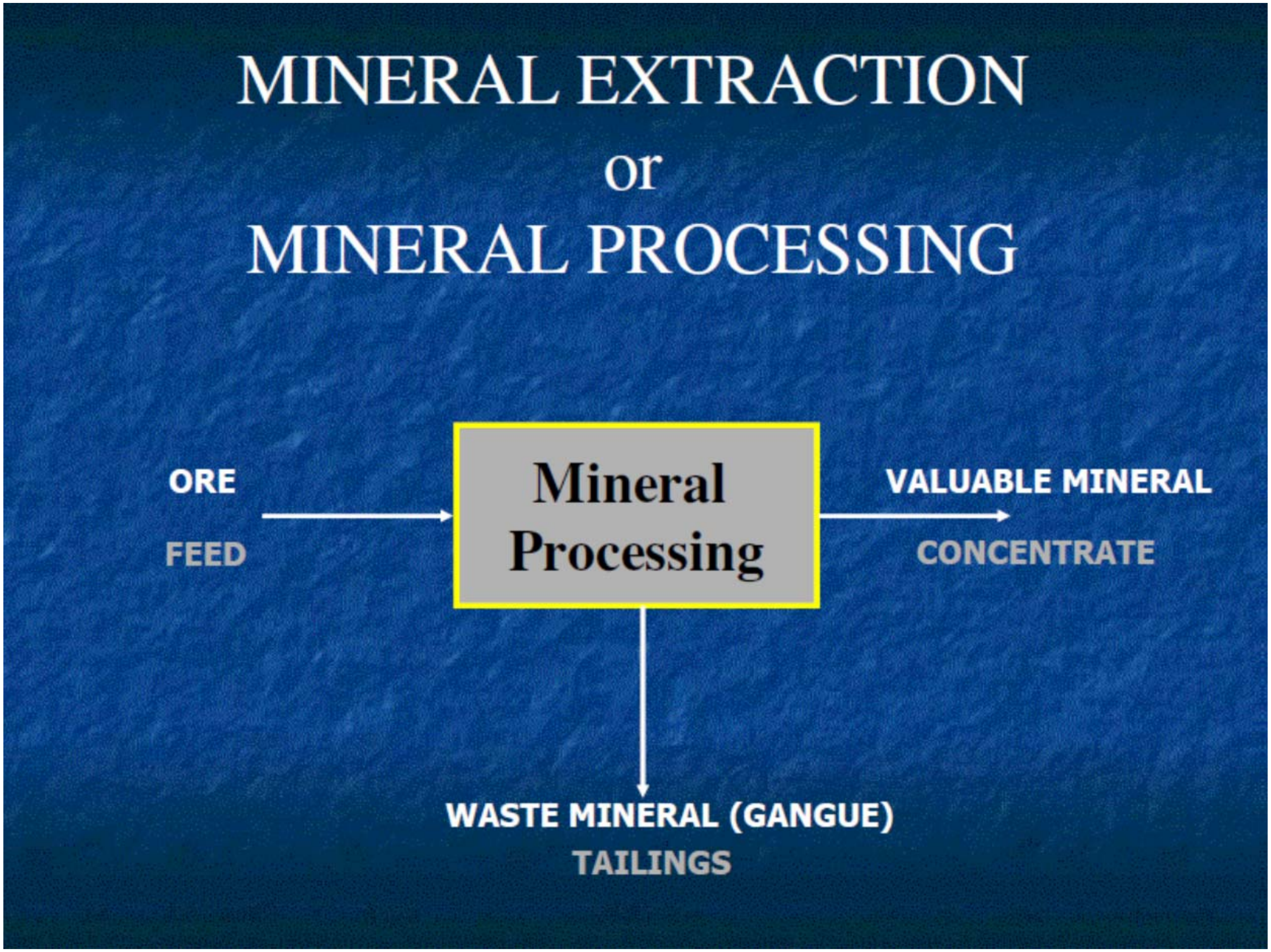
Optical image showing the setup



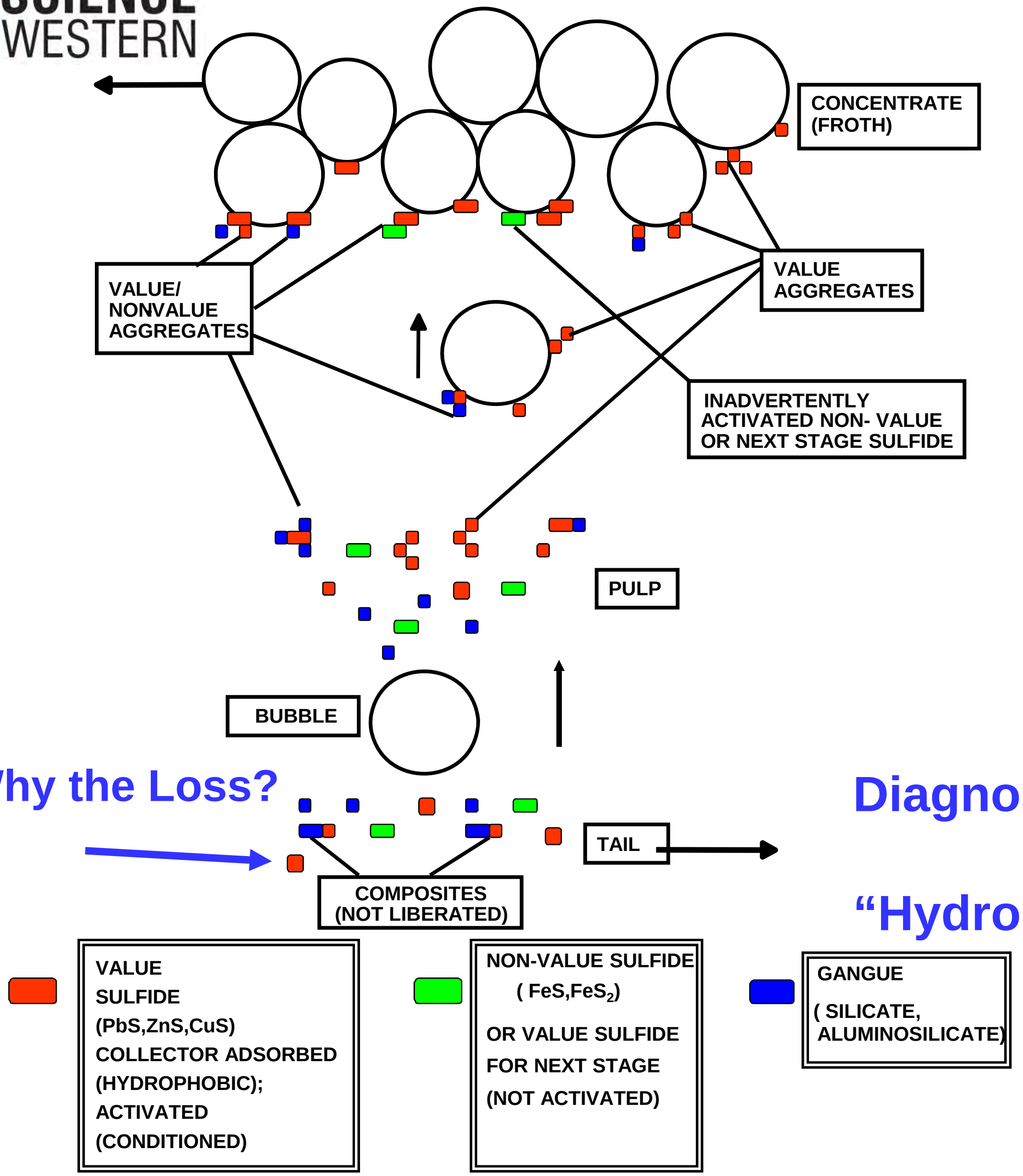
Nissl stain with Cresyl Violet
Staining Nissl body (ER) with aniline containing dye



Froth flotation



Flotation Separation

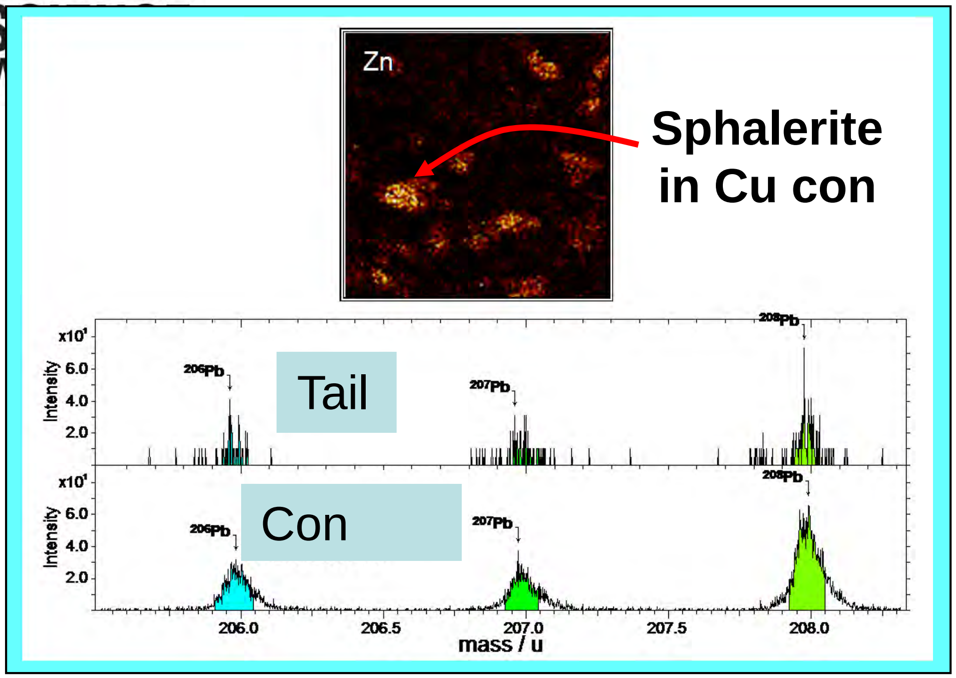


Why the Loss?

FLOTATION PROCESS:

Diagnosis of the surface chemistry

“Hydrophobic/Hydrophillic balance”



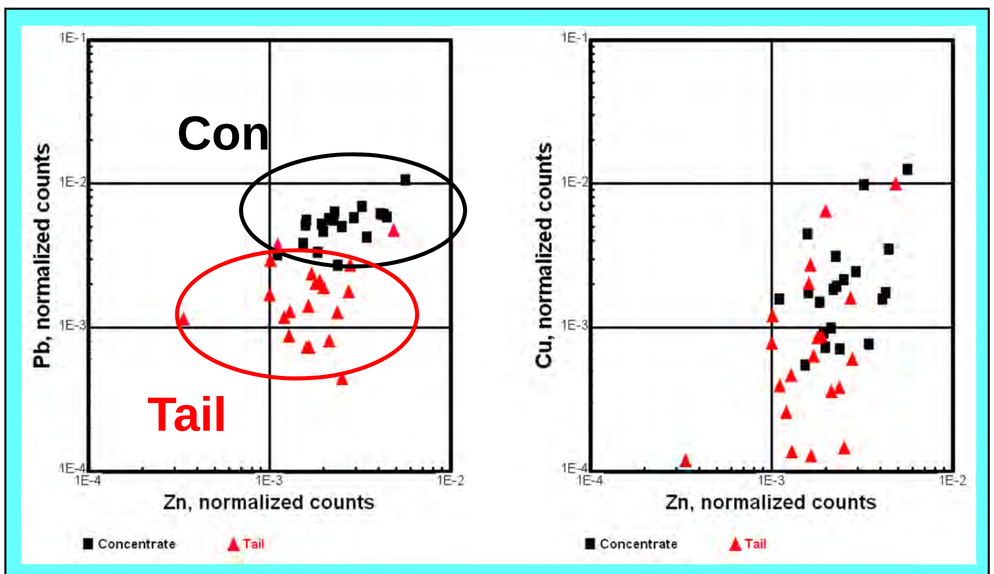
Surface analysis applied to mineral processing: Case #1

Flotation products

Inadvertent activation

ToF-SIMS Spectra:

- **Pb on surface of sphalerite grain in concentrate and tail samples**



Concentrate versus tail scatter plots showing the distribution for Pb and Cu versus Zn on sphalerite surfaces

Gold deportment studies and optimized gold recovery process by SIMS

Facts:

- Very high capital cost in developing of a gold mine: x$100millions
- Typical gold content in a commercially viable gold deposit: 1-2g/t
- Projected gold recovery : >85%

Objectives:

- To determine all forms and carriers of Au in the ore sample
- Establishing complete and quantitative Au mineralogical balances
- Identification of specific causes for gold losses in the process stream products

Relevance:

- Process mineralogical mapping
- Process selection and optimization

Dynamic SIMS applications in gold deportment studies

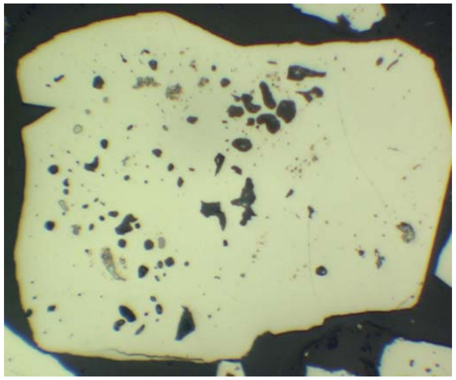
Information derived from D-SIMS analysis:

- **Characterization of the carriers and forms of sub-microscopic (invisible) gold:**
  - **i) quantitative analysis**
  - **ii) forms of sub-microscopic gold: colloidal type and solid solution type gold**
  - **iii) imaging of the sub-microscopic gold distribution**
- **Establishing complete and quantitative Au mineralogical balances**
- **Identification of specific causes for gold losses in the process stream products**

Relevance:

- **Benchmark technique for analysis of sub-microscopic gold**
- **Effectively addresses the analytical gap between the electron microprobe (MDL≈200ppm) and bulk analytical techniques (MDL≈low ppb)**

Sub-microscopic gold



Pyrite (FeS_2)
Common carrier of sub-microscopic gold

■ **The sub-microscopic gold is refractory gold, i.e it is locked within the crystalline structure of the mineral phase (most often in sulphide minerals) and it can not be directly released by the cyanide leach process**

■ **Two forms of “invisible” sub-microscopic gold:**

i) solid solution within the sulphide mineral matrix

ii) colloidal size: finely disseminated colloidal size gold particles (<0.5μm)

■ **Refractory gold ores are becoming the most common gold ore deposits and they need a special treatment in order release the sub-microscopic gold**

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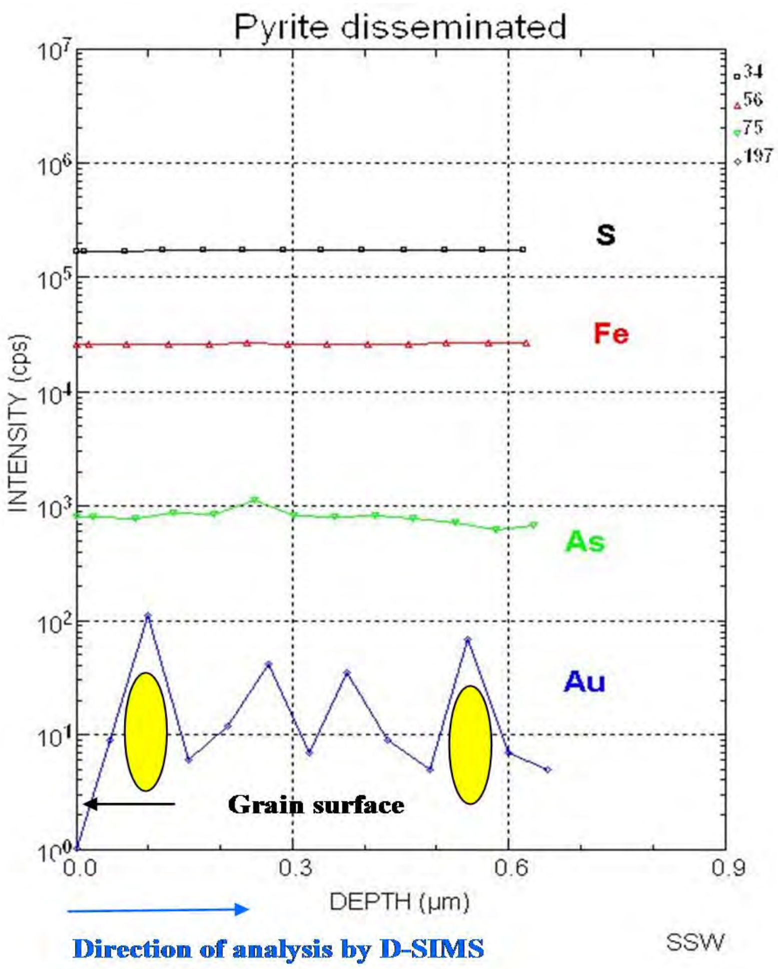
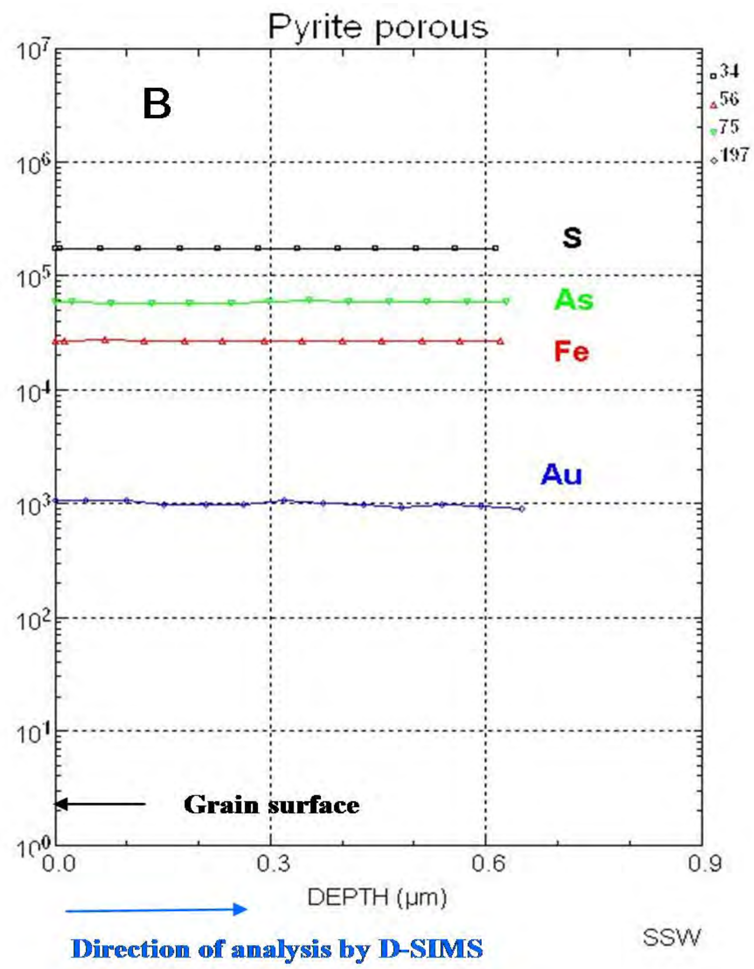
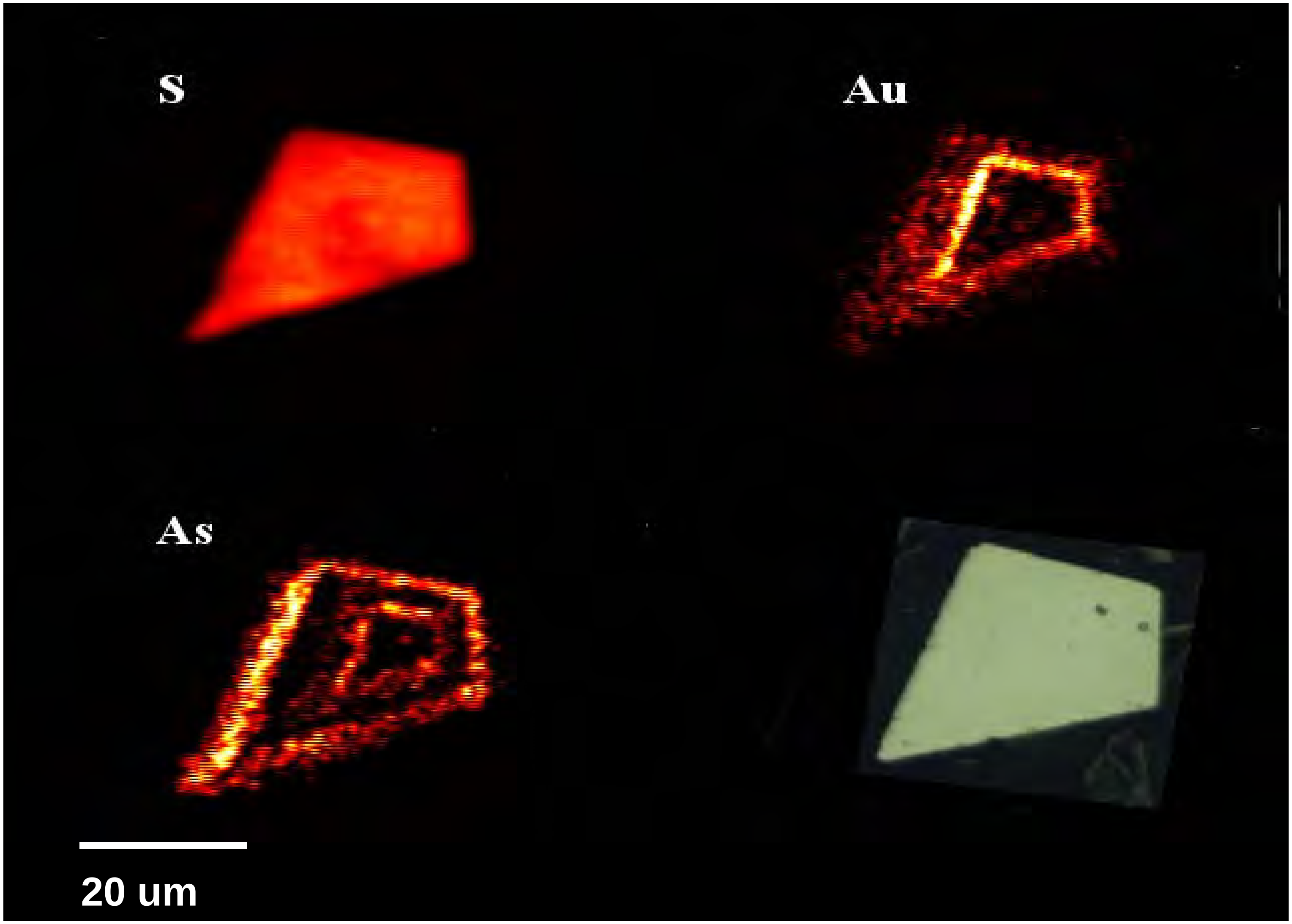
Colloidal size sub-microscopic gold in pyrite

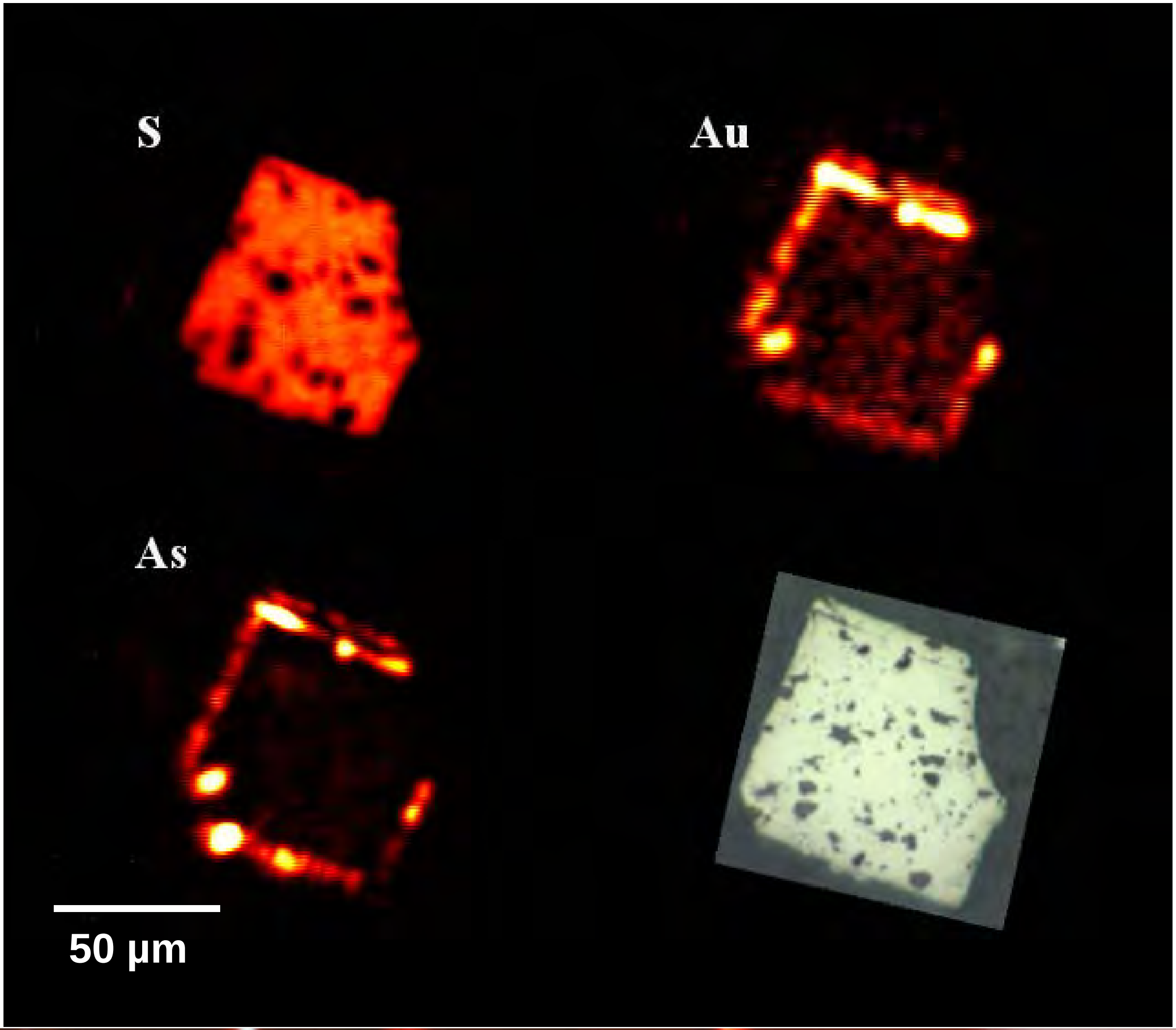


Solid solution type sub-microscopic gold in pyrite

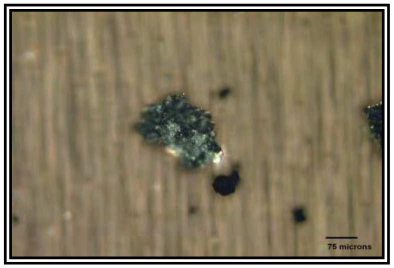


Dynamic SIMS images of gold and arsenic distribution in pyrite

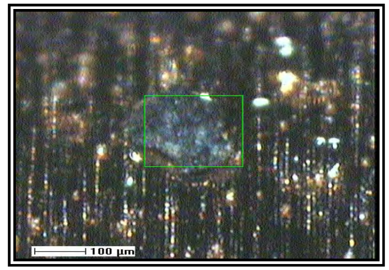



S
Au
As
50 µm

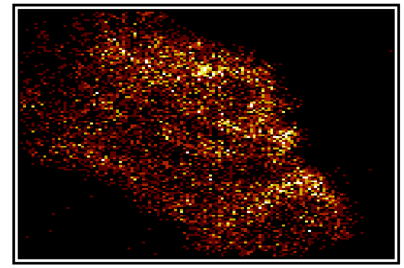
Optical images along with TOF-SIMS elemental and compositional maps for disseminated TCM grain from CIL residue



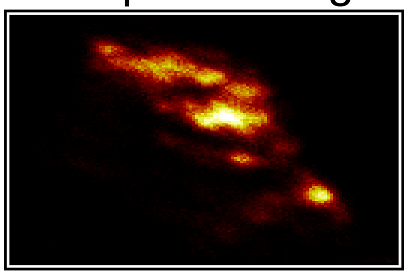
Optical Image



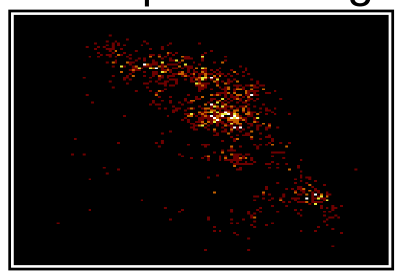
Optical Image



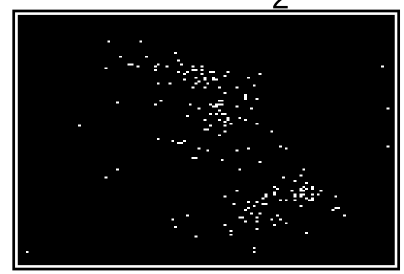
SiO_2



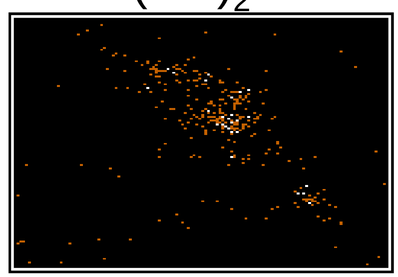
CN



$(CN)_2$



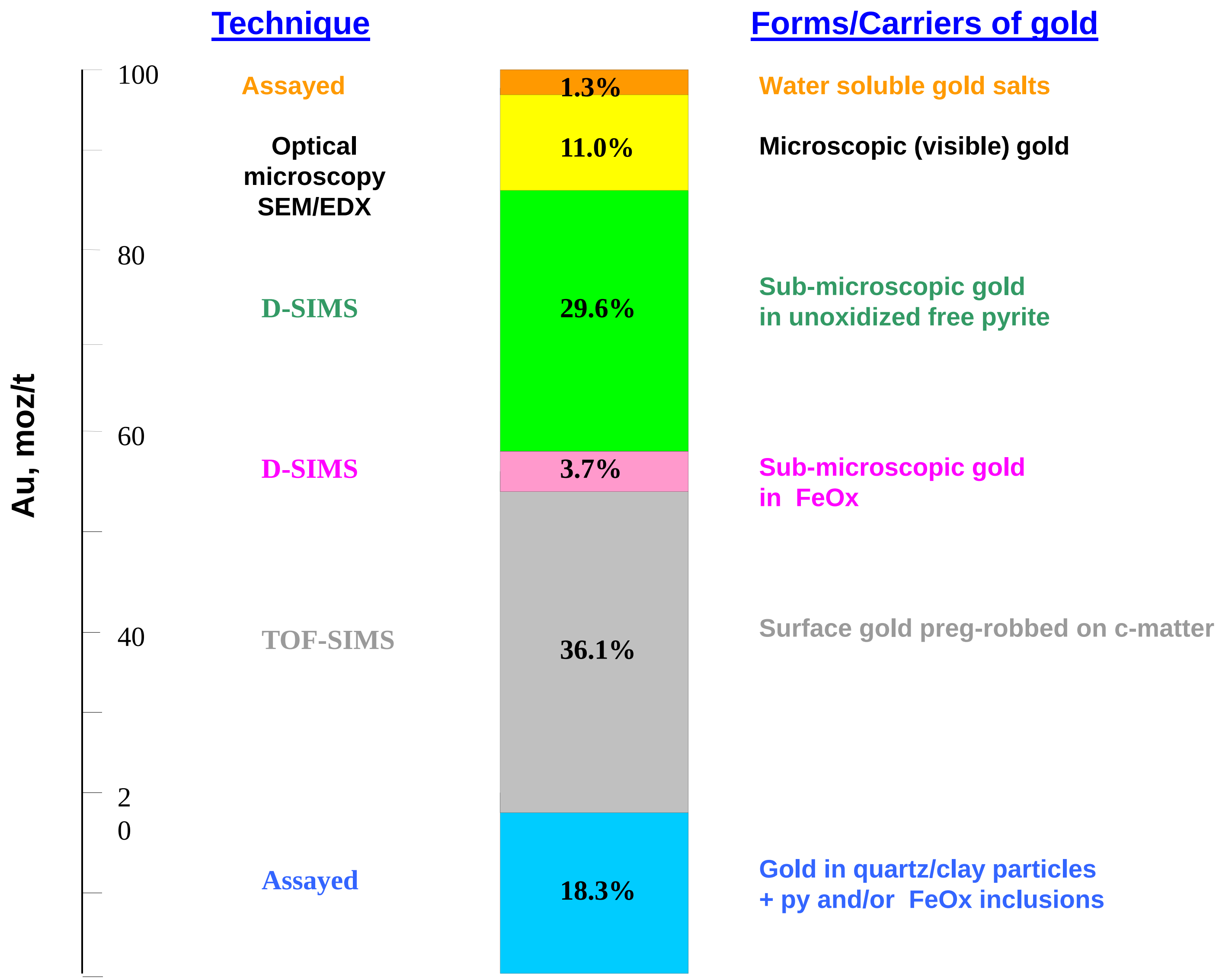
Au



$Au(CN)_2$

Calculated Au concentration based on Au and $Au(CN)_2$ components = 105 ppm

Gold deportment in CIL residue sample



Secondary Ion Mass Spectrometry

Large variety of ionization sources and mass spectrometer types facilitate instrument configurations with unique performance capabilities

- **Ultrahigh sensitivity to surface layers (TOF-SIMS)**
- **Detection limits in the low ppm/ppb range**
- **Elemental and molecular analysis**
- **Ultra-shallow depth profiles or depth profiles of tens of µm**
- **Imaging capabilities**
- **Retrospective analysis of raw data streams (TOF-SIMS)**
- **Universal applicability to practically all types of solid materials and sample forms**

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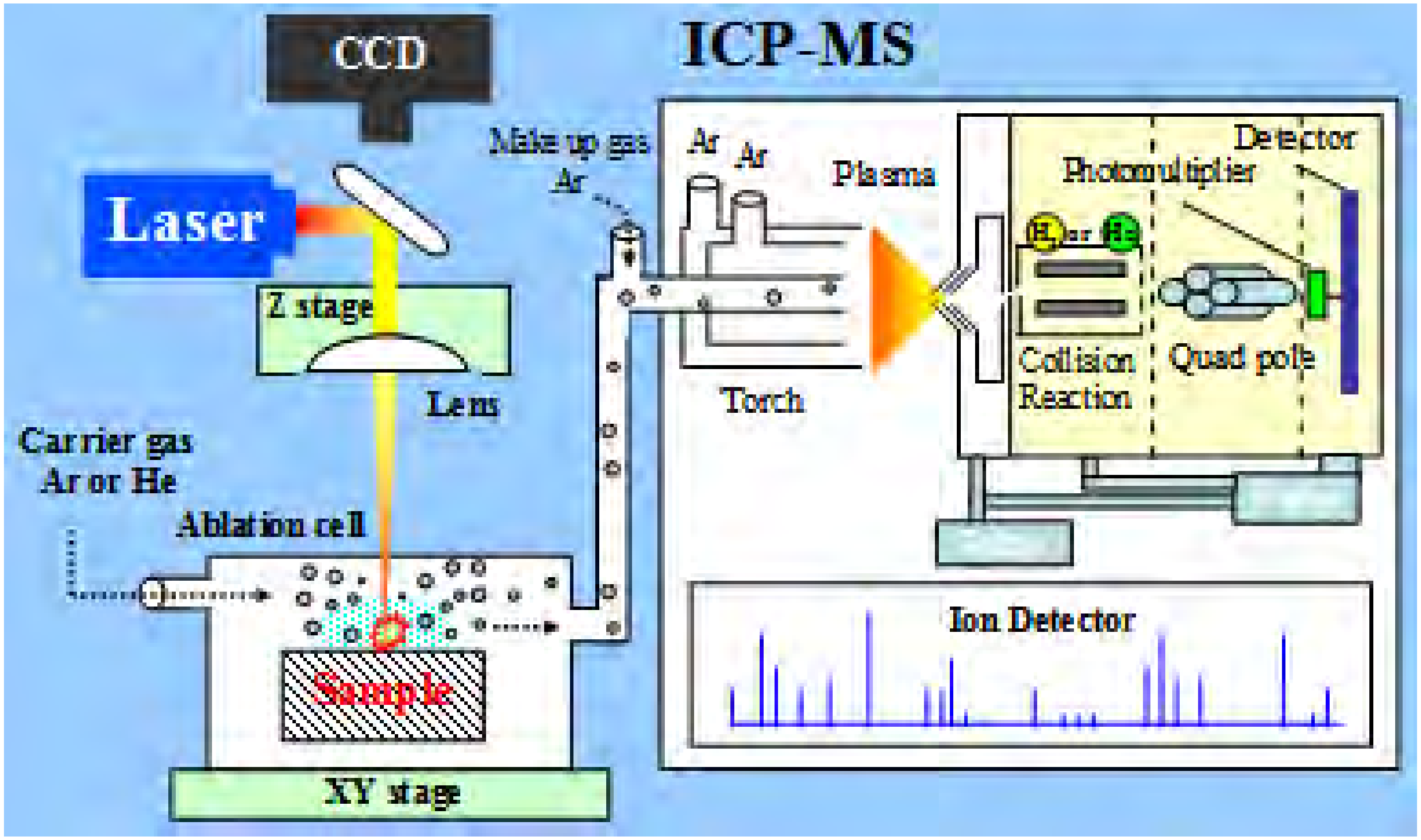
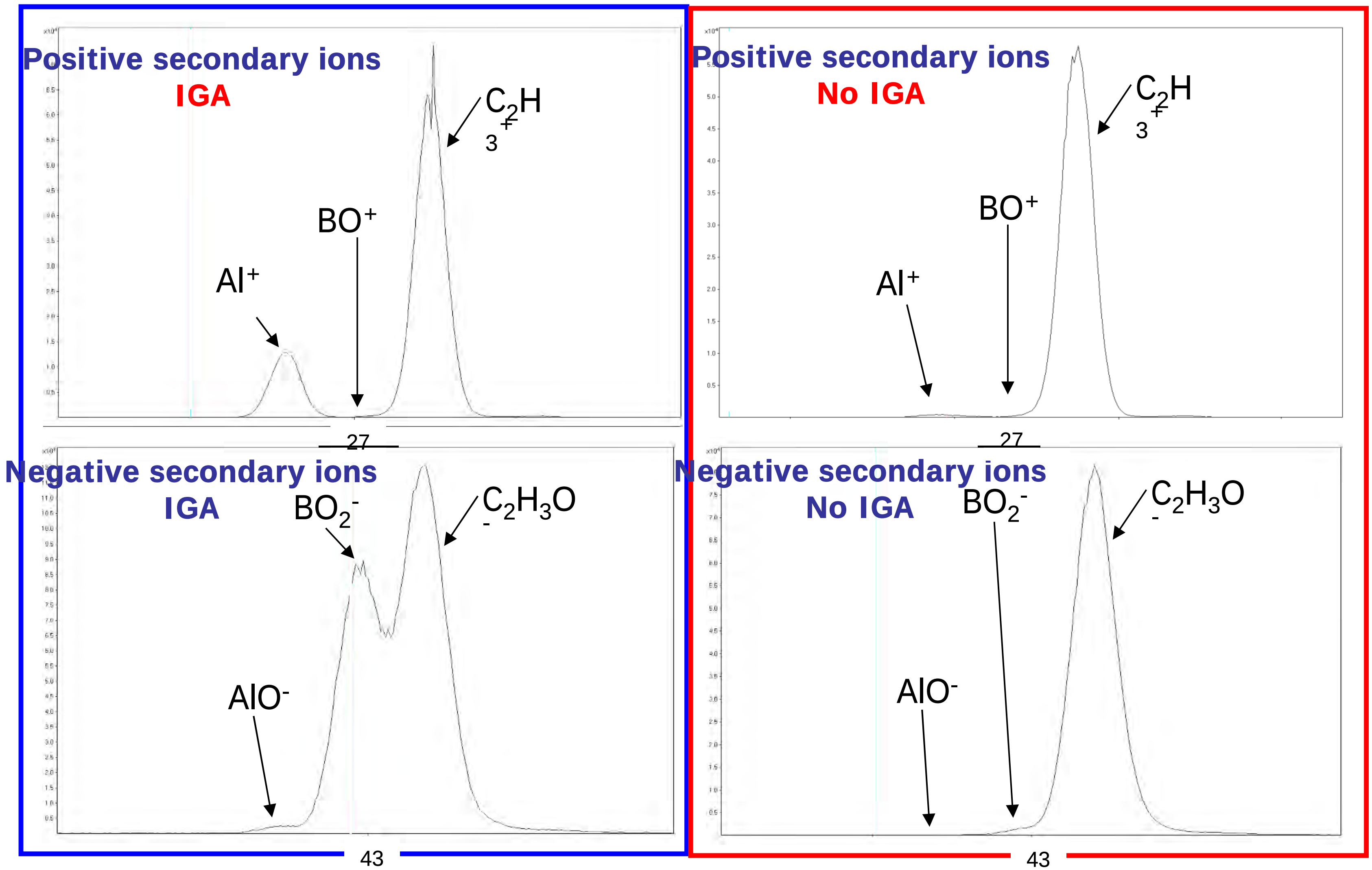


Methodology:

- Dynamic secondary ion mass spectrometry (SIMS) analyses were performed using a Cameca IMS-3f SIMS instrument.
- The SIMS analyses were performed using 400 nA, 5.5 keV Cs^+ primary ion beam that was rastered over a 250 x 250 μm^2 area on the specimen surface.
- Negative secondary ions were collected from a 150 µm area within this sputtered area.
- A micro-channel plate was employed for collecting the SIMS images.
- SIMS images were collected for the mass number ^{27}BO after each sputter cycle.
- Intensity of ^{27}BO was monitored instead of ^{11}B because of the intensity enhancement by the presence of oxygen – improves the detection limit.
- SIMS images have been presented on a thermal scale, i.e. brighter areas qualitatively represent the presence of greater amounts of the element of interest in that area.
- The collected SIMS images were stacked together to create a three-dimensional image.


Positive secondary ions
IGA
$C_2H_3^+$
BO^+
Al^+
27
Negative secondary ions
IGA
BO_2^-
$C_2H_3O^-$
AlO^-
43
Positive secondary ions
No IGA
$C_2H_3^+$
BO^+
Al^+
27
Negative secondary ions
No IGA
BO_2^-
$C_2H_3O^-$
AlO^-
43