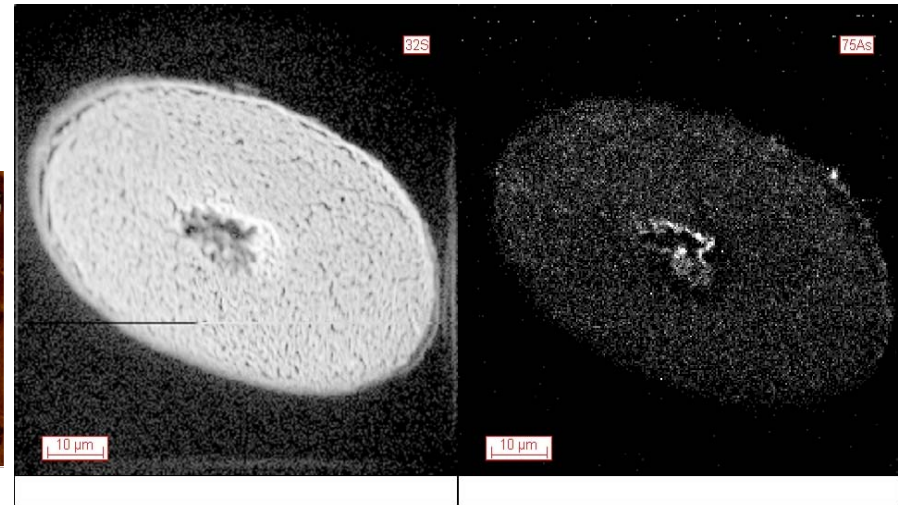


**La Spectrométrie de Masse d'Ions Secondaires  
(SIMS):  
un outil majeur pour l'étude de notre système  
solaire, les recherches biomédicales et le  
développement des nanomatériaux**

**Henri-Noël Migeon**

**Département "Science et Analyse des Matériaux"  
CRP-Gabriel Lippmann  
41, rue du Brill  
L-4422 Belvaux**

# The nanometer scale



← 100 microns →



Luxembourg/Nancy: 117 km

$$100 \text{ microns} / 100 \text{ km} = 10^{-9}$$

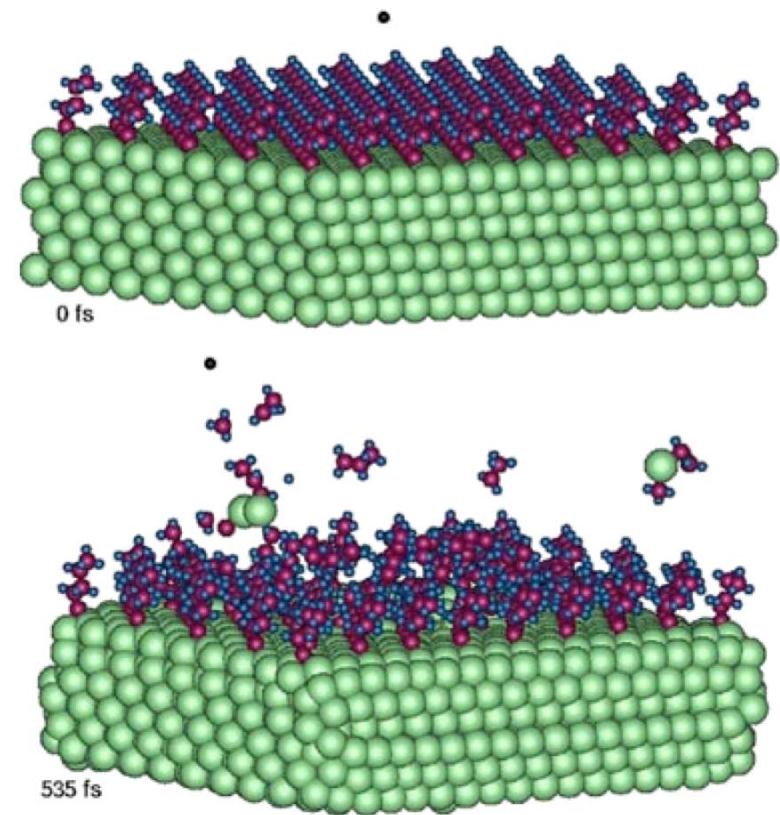
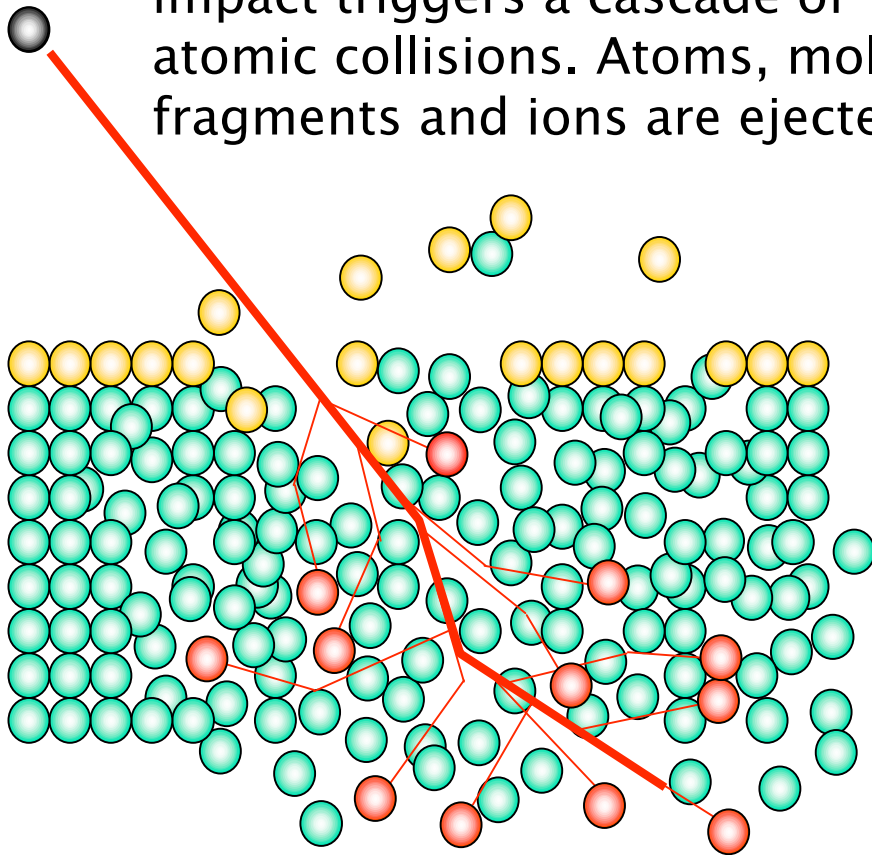
$$1 \text{ nm} / 1 \text{ m} = 10^{-9}$$

# Outline

1. Ion/matter interaction : impinging and outgoing particles
2. Instrumentation
3. General capabilities
  - Elemental range
  - Ion imaging
  - Depth profiling
  - 3D analysis
4. Applications
  - Geochronology
  - Biomed
  - Nanomaterials
5. Future developments

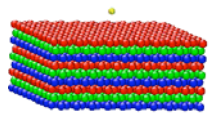


**Secondary Ion Mass Spectrometry (SIMS)** is based upon the sputtering of a few atomic layers from the surface of a sample induced by a “**primary ion**” bombardment. A primary ion impact triggers a cascade of atomic collisions. Atoms, molecule fragments and ions are ejected

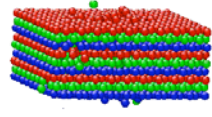


*Molecular Dynamics Simulations of Reactions Between Molecules: High Energy Particle Bombardment of Organic Films, R. S. Taylor and B. J. Garrison, Langmuir 11, 1220-1228 (1995).*

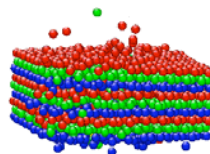
# C<sub>60</sub> bombardment - animation



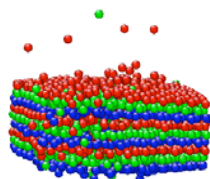
0 fs



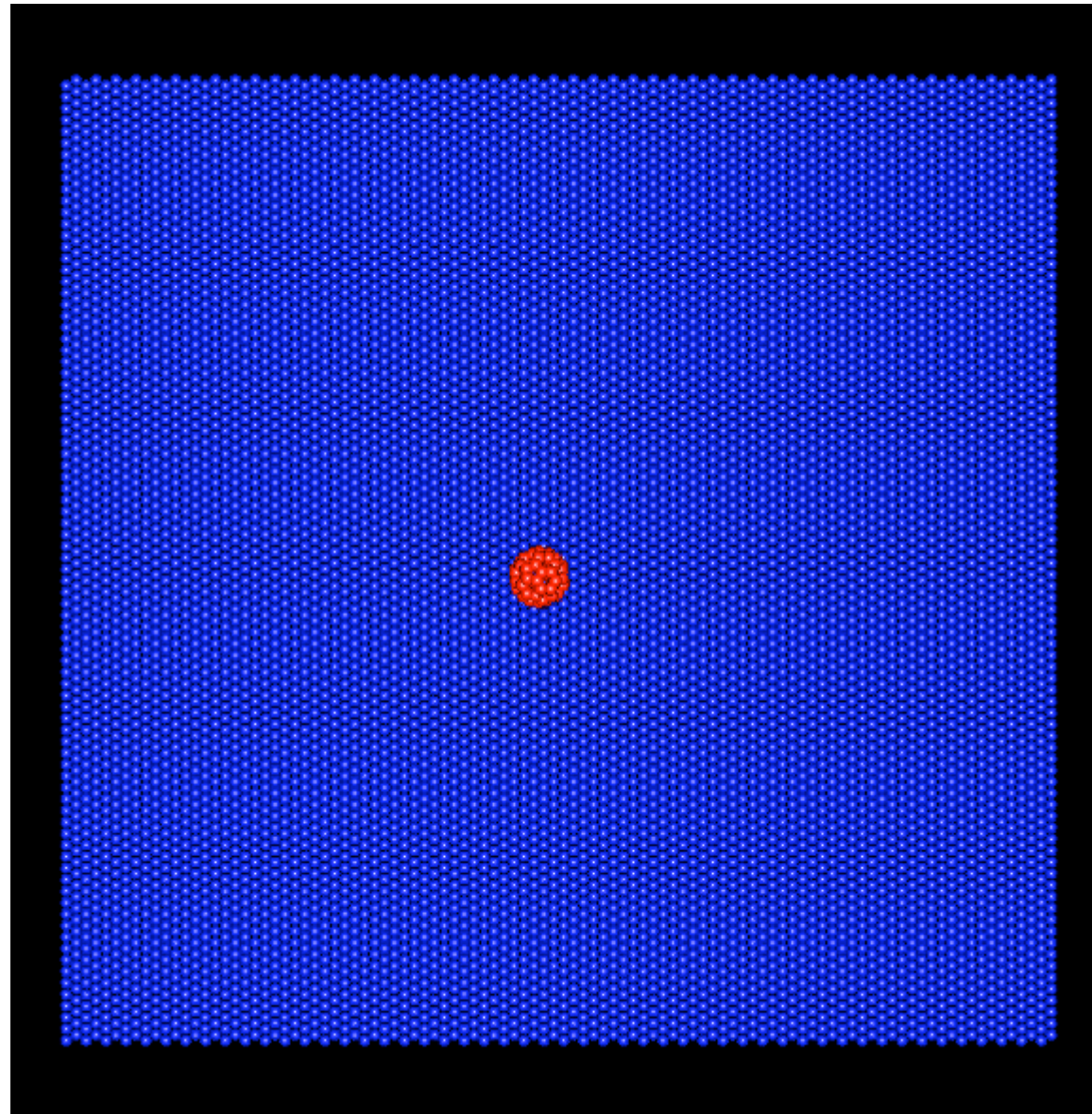
40 fs



80 fs



120 fs

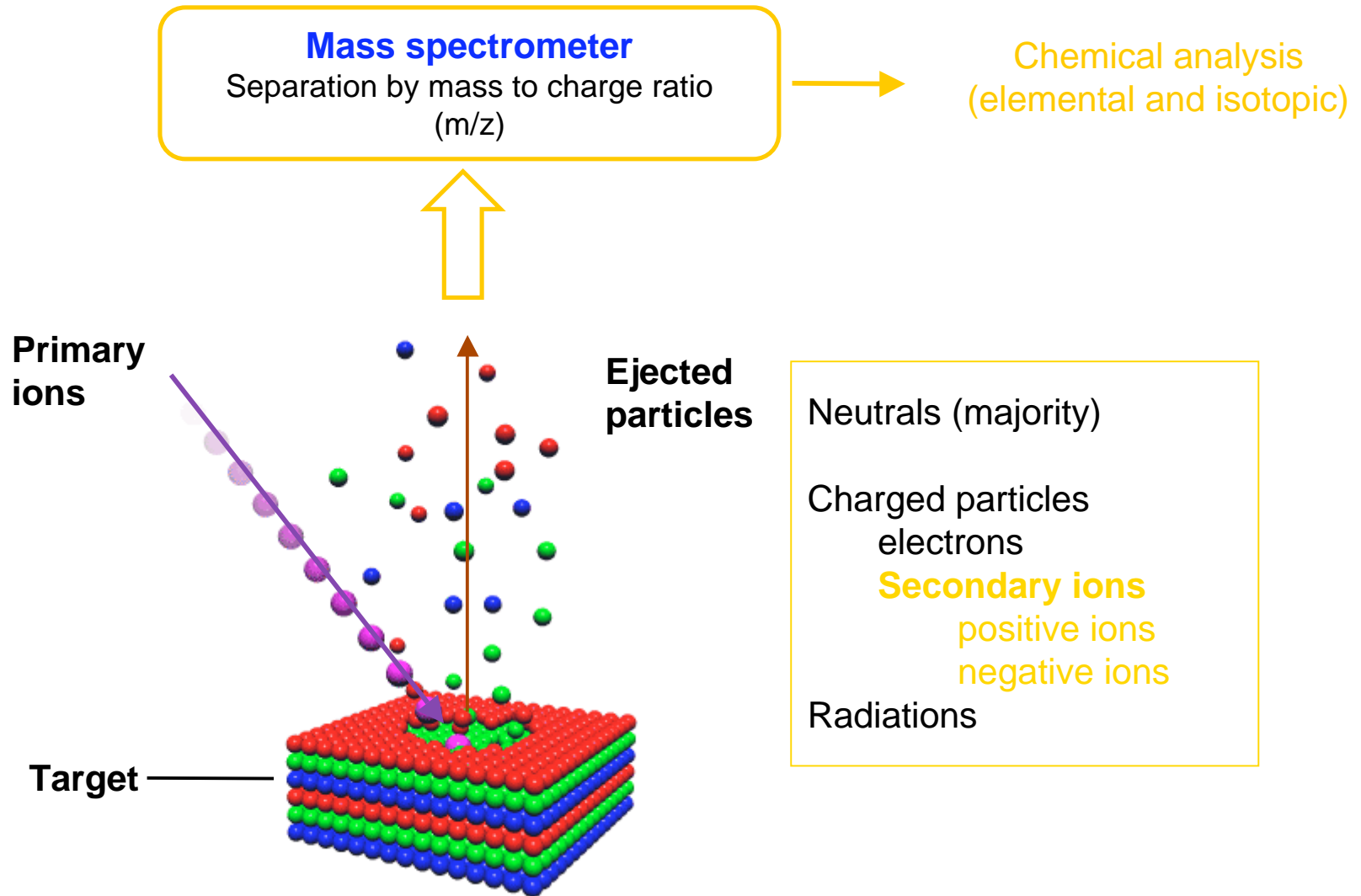


# Outline

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  - 3D analysis
  - Sensitivity
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  - Biomed
  - Nanomaterials
5. Future developments



# Secondary Ion Mass Spectrometry



André Guinier est né à Nancy où son père Philibert Guinier, membre de l'Académie des Sciences dans la section d'économie rurale, était directeur de l'École Forestière. Il entre à l'École Normale Supérieure en 1930 et prépare une thèse en cristallographie. Ses premiers travaux sont consacrés à la conception et à la réalisation d'une chambre de diffraction des rayons X qui permet d'étudier la diffusion des rayons X au voisinage immédiat du faisceau incident. C'est en étudiant les défauts cristallins que Guinier découvre (en même temps que Preston) ce que l'on a appelé les "zones de Guinier-Preston", zones de concentration de l'un des types d'atomes composant un alliage (le premier exemple fut Al-Cu). Ces "zones G-P" ont un grand intérêt en métallurgie. Après sa thèse soutenue en 1939, il propose le sujet de thèse de Raimond Castaing qui donnera lieu à la Microsonde de Castaing.



Raimond Castaing  
(1921 – 1998)

**Electron microprobe**



Alfred Benninghoven  
Université de Münster

**Static SIMS**



Georges Slodzian  
Université Paris-Sud Orsay

**Dynamic SIMS**



# Direct image ion microscope\_

relation de Lagrange-Helmholtz,  $\sqrt{V_0}h_0\alpha = \sqrt{V_1}h_1\alpha_1$  où  $\alpha$  et  $\alpha_1$  sont les ouvertures du côté objet et du côté image, complète cet ensemble de formules bien connus en optique (21).

Le dispositif de post-accelération constitue la première lentille de notre système téléobjectif, il donne de l'image virtuelle  $I_0'$  filtrée par le prisme une image réelle  $I_1$  située près du foyer image  $F_1$ . Par contre, l'image du cross-over  $C'$  est virtuelle et située en  $C_1$ .

b) Lentille de projection. — L'image  $I_1$  a un grandissement trop faible pour être utilisée directement dans

le convertisseur. Il faut associer au système de post-accelération une lentille supplémentaire qui projette l'image  $I_1$  sur la cathode du convertisseur. Par ailleurs cette lentille donne du cross-over  $C_1$  une image réelle  $C_1$ . Si, au niveau de  $C_1'$ , on place l'écran fluorescent destiné à recevoir l'image électronique, on pourra donner au trou pratiqué dans l'écran pour laisser passer le faisceau d'ions, les dimensions du cross-over  $C_1$ : la surface utile de l'écran ne sera donc partiellement pas réduite par la présence du trou.

La lentille de projection est simplement constituée par une lentille électrostatique unipotentielle dont les caractéristiques

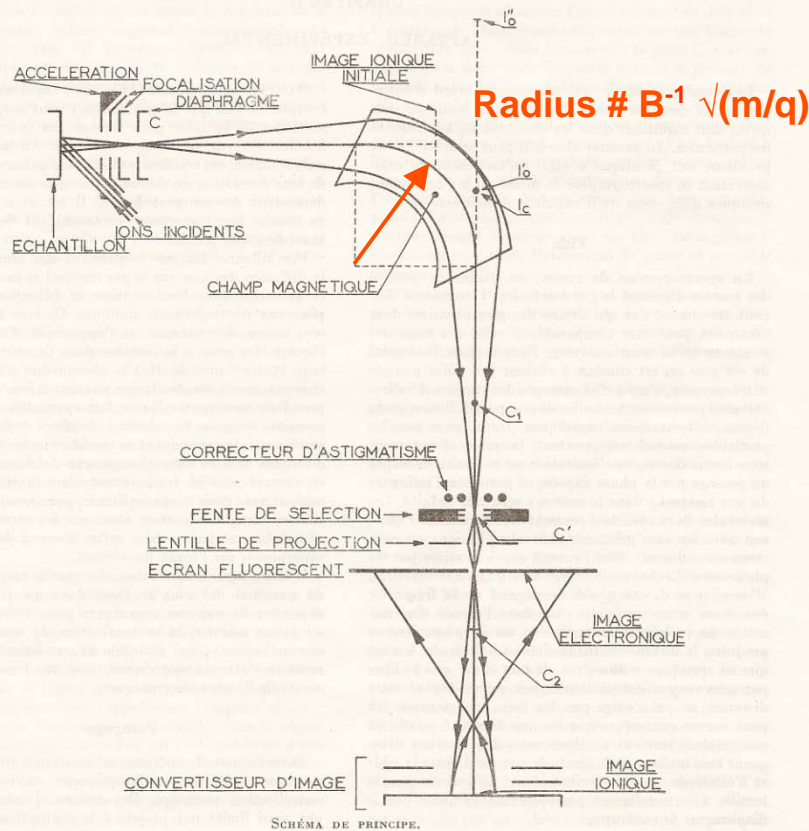
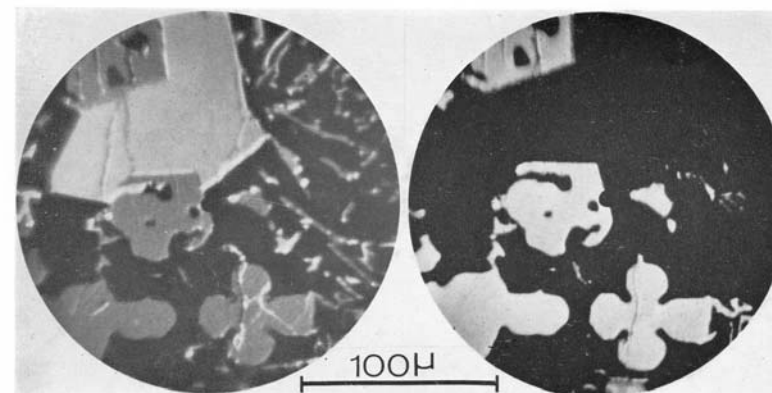


PLANCHE IV



Si<sup>+</sup>

Mg<sup>+</sup>



Al<sup>+</sup>

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**Extremely Low Impact Energy SIMS:** The **IMS Wf** achieves **sub-nm** depth resolution with new EXLIE configuration. [Learn more >>](#)

**Come and meet us at:** EMPG XIII, Toulouse, France, April 12-14 [Full show schedule >>](#)



Claude Allègre,  
prix Crawford (= prix Nobel de Géologie)



INSTITUT DE FRANCE  
Académie des sciences

membre

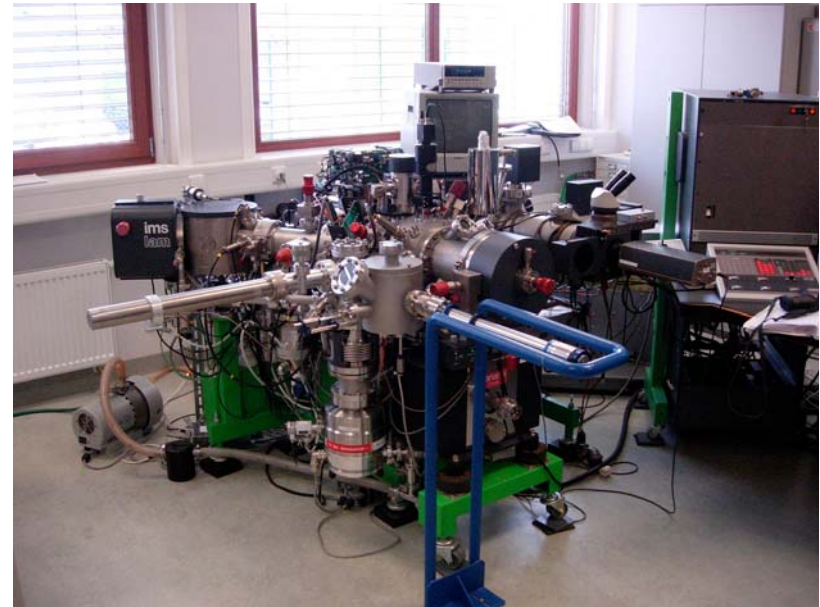
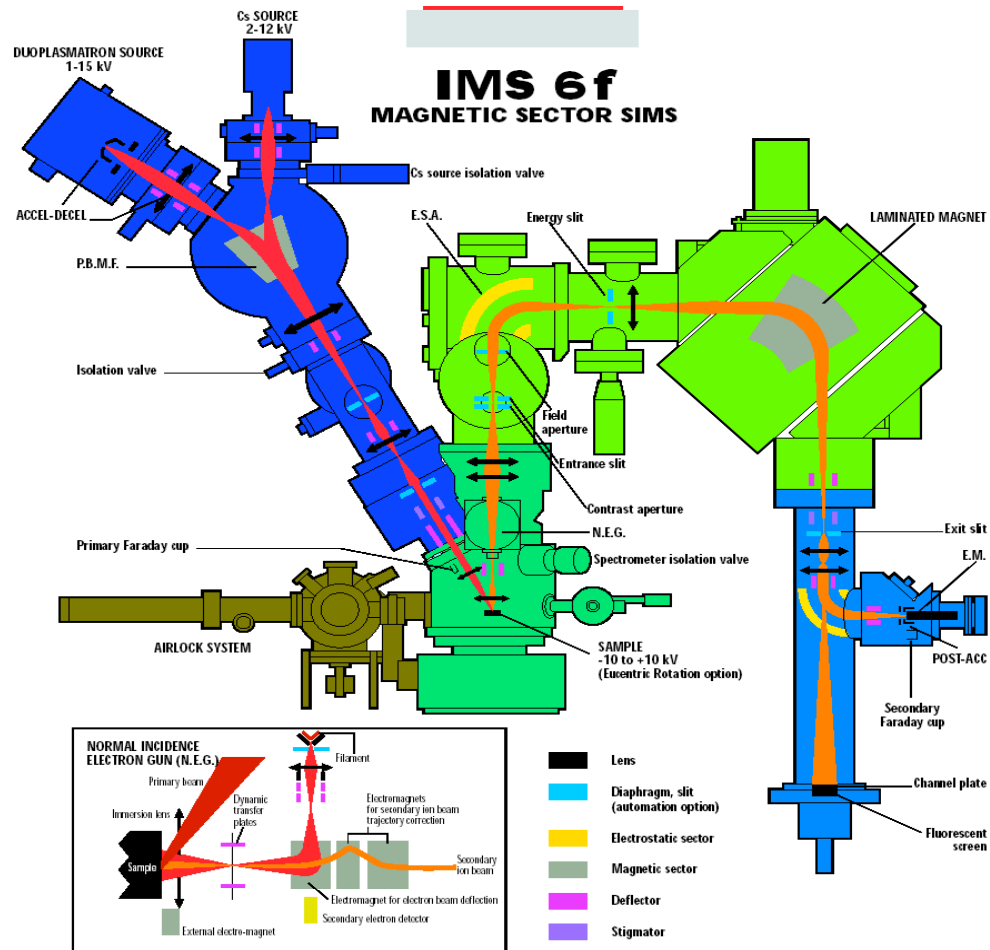


Georges Slodzian

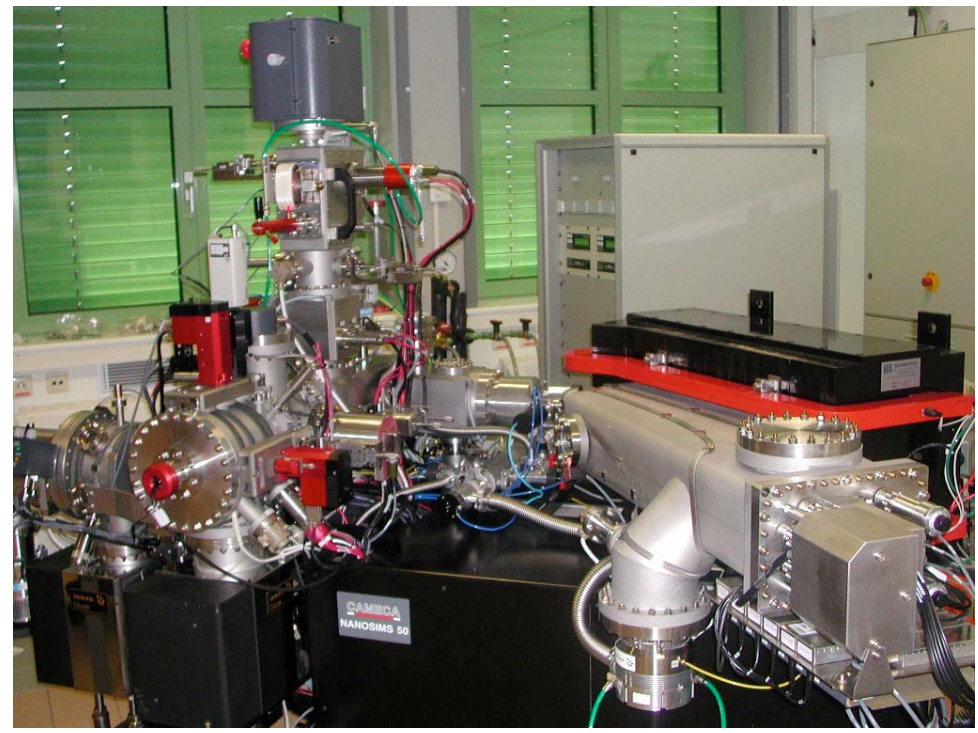
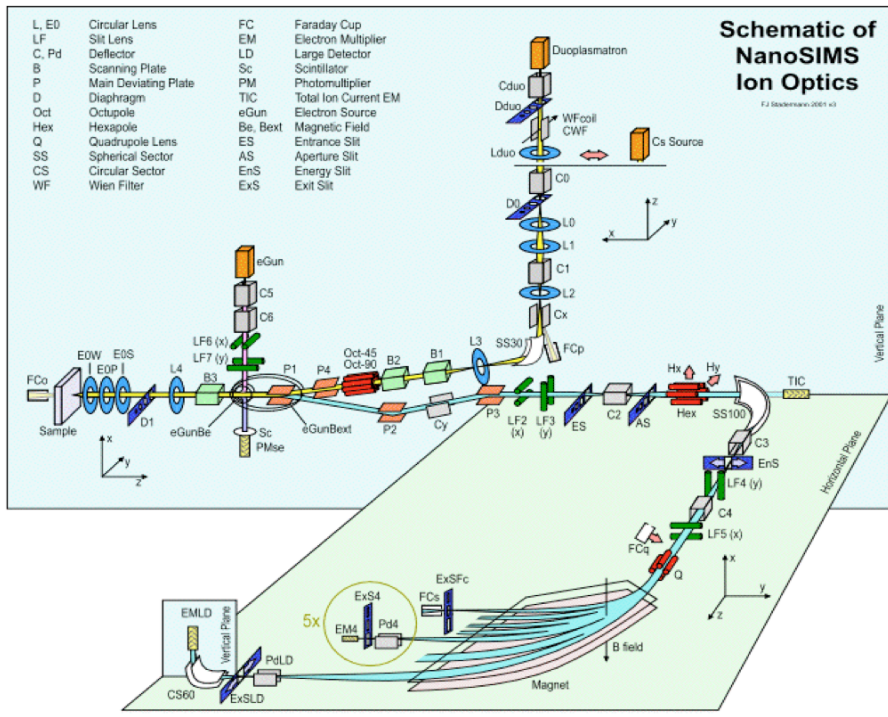


INSTITUT DE FRANCE  
Académie des sciences

correspondant



**IMS 1280**

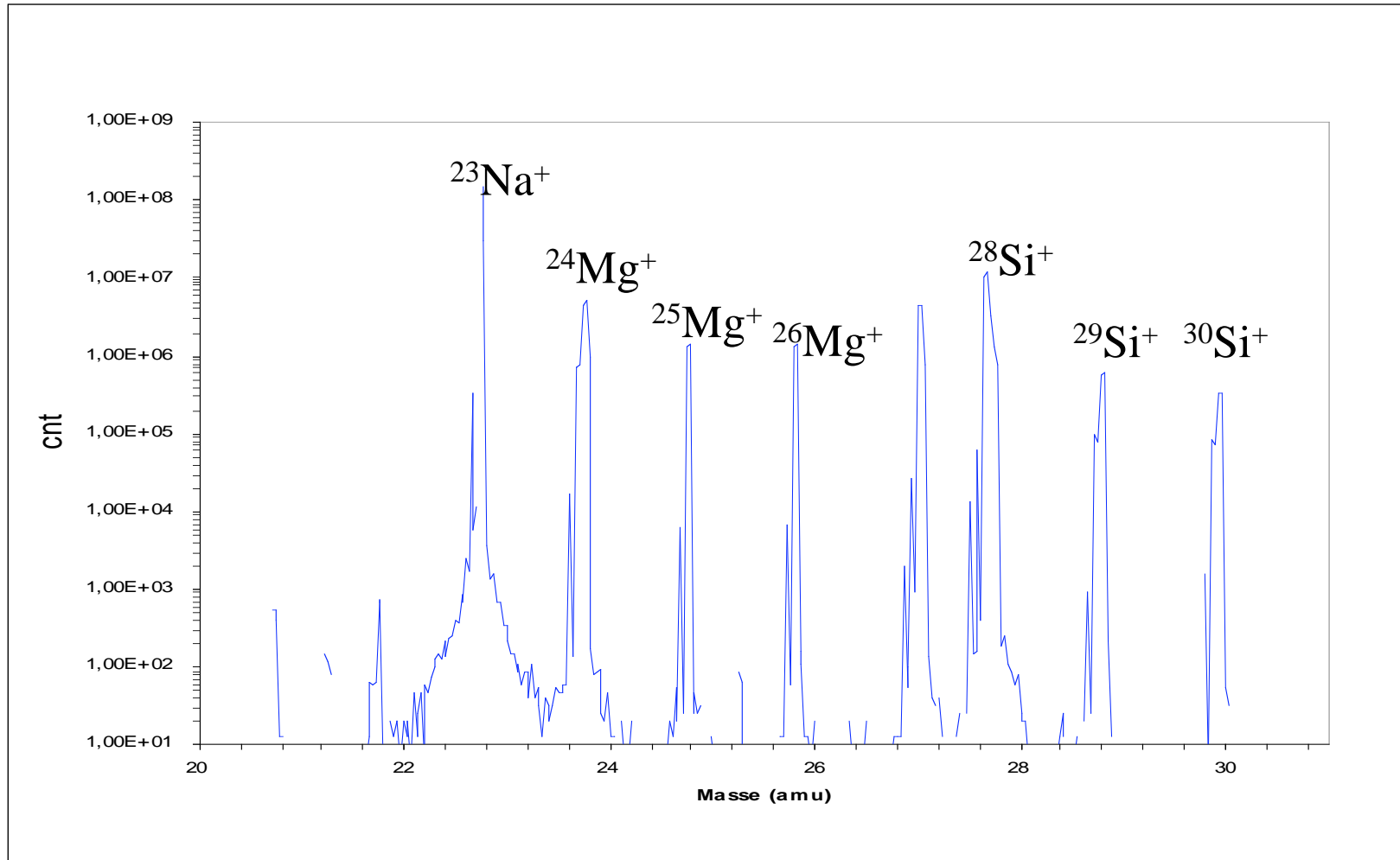


# Outline

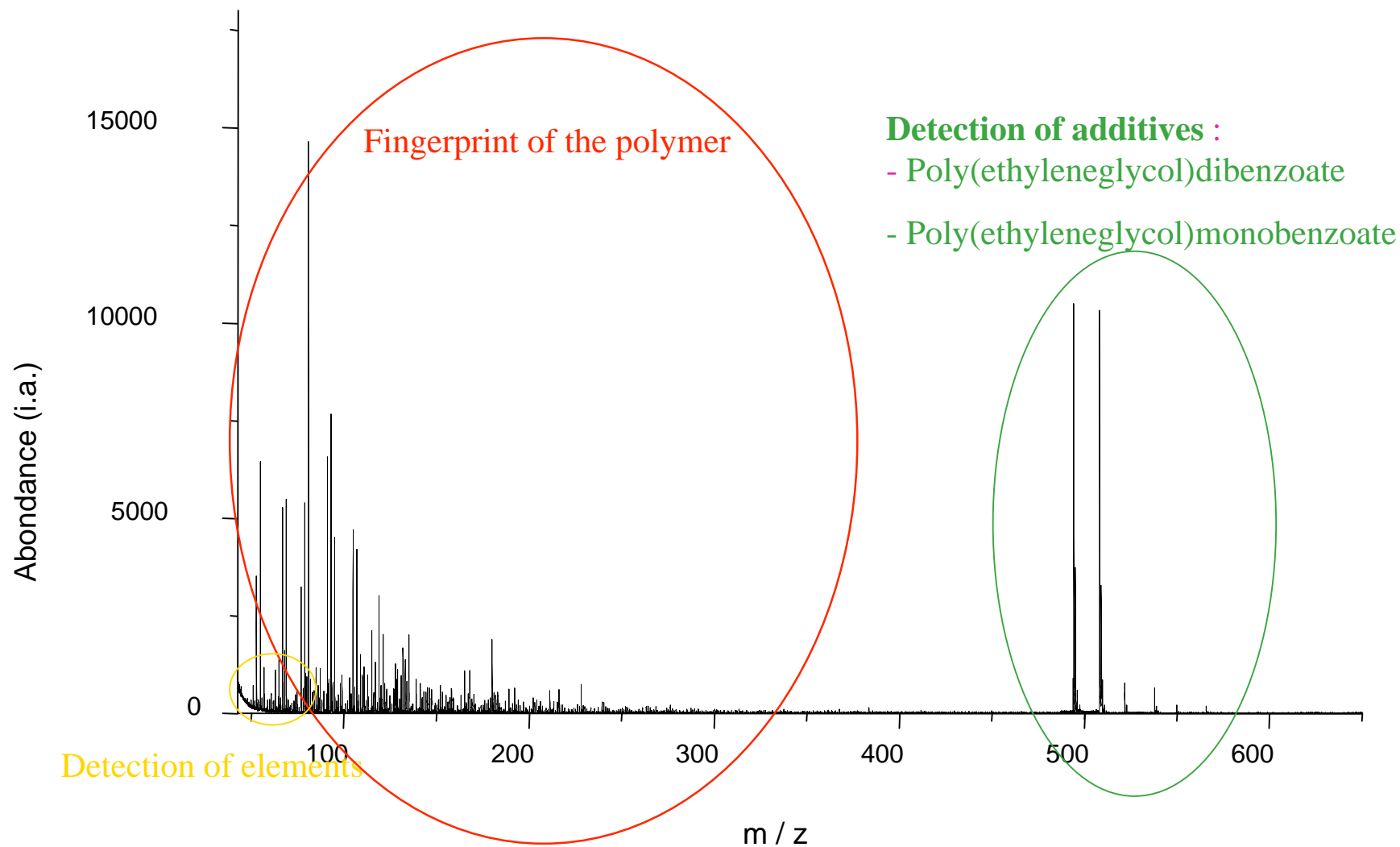
1. Ion/matter interaction : impinging and outgoing particles
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# Mass Spectrometry



# Mass Spectrometry



# Mass Spectrometry

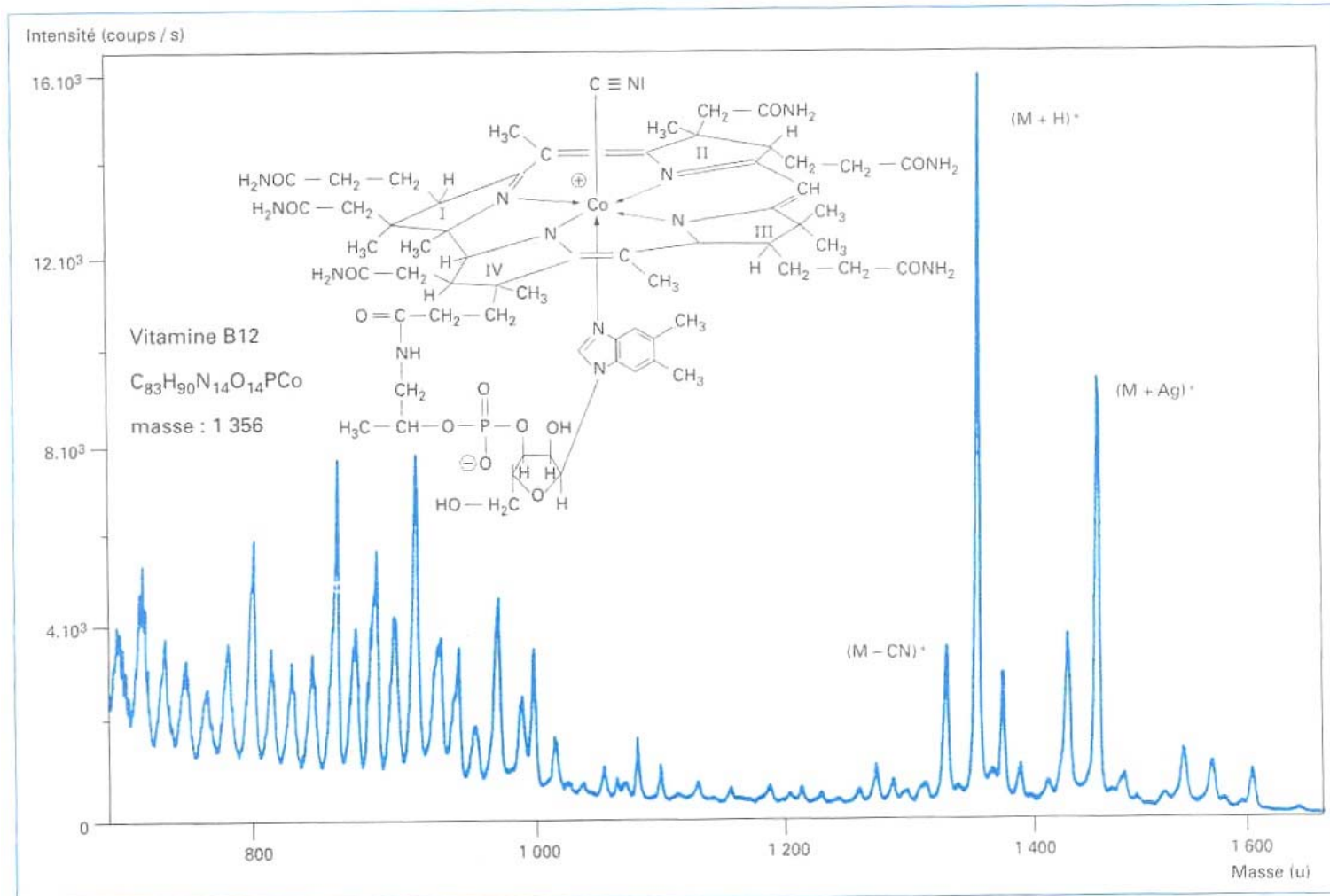
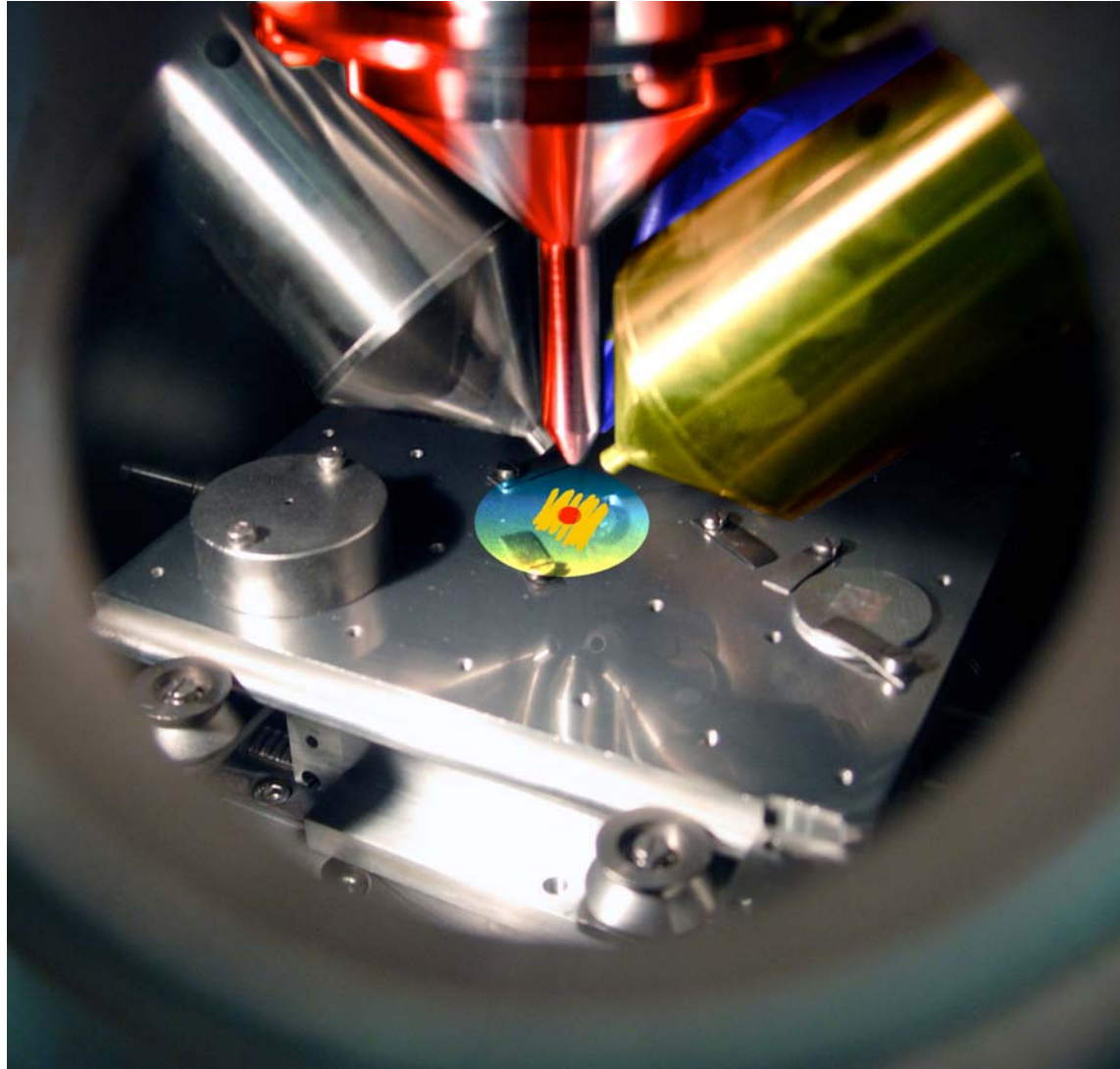


Figure 2 - Spectre de masse par SIMS à temps de vol d'un dépôt de vitamine B12 (masse moléculaire 1 356) sur une plaque d'argent [2]

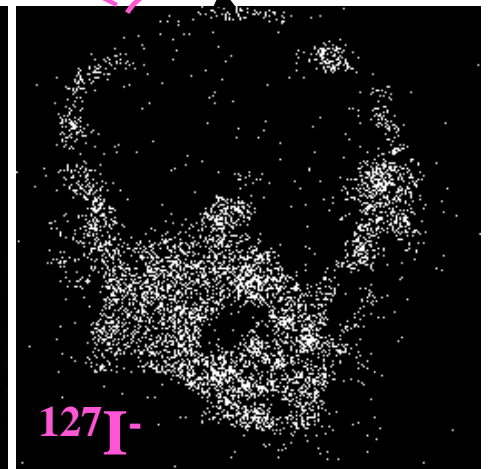
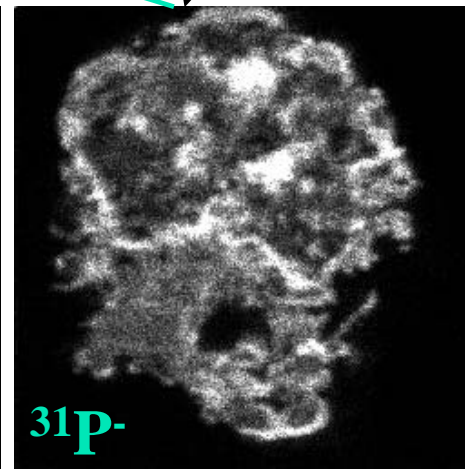
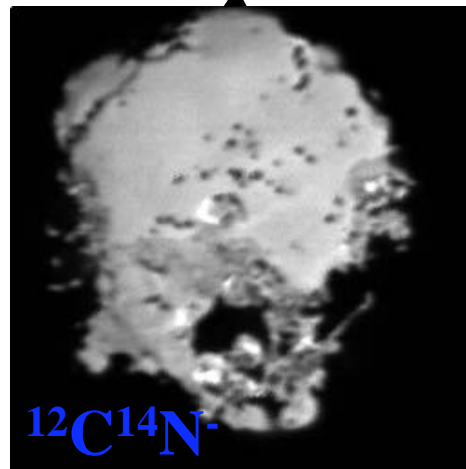
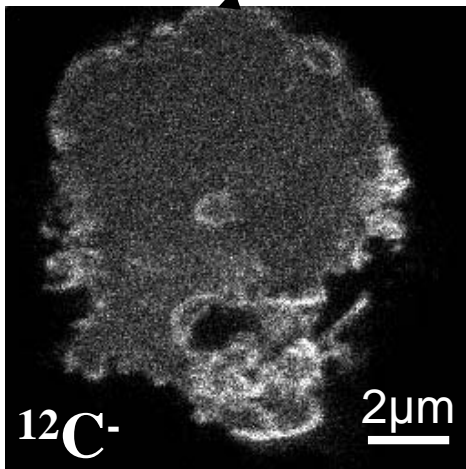
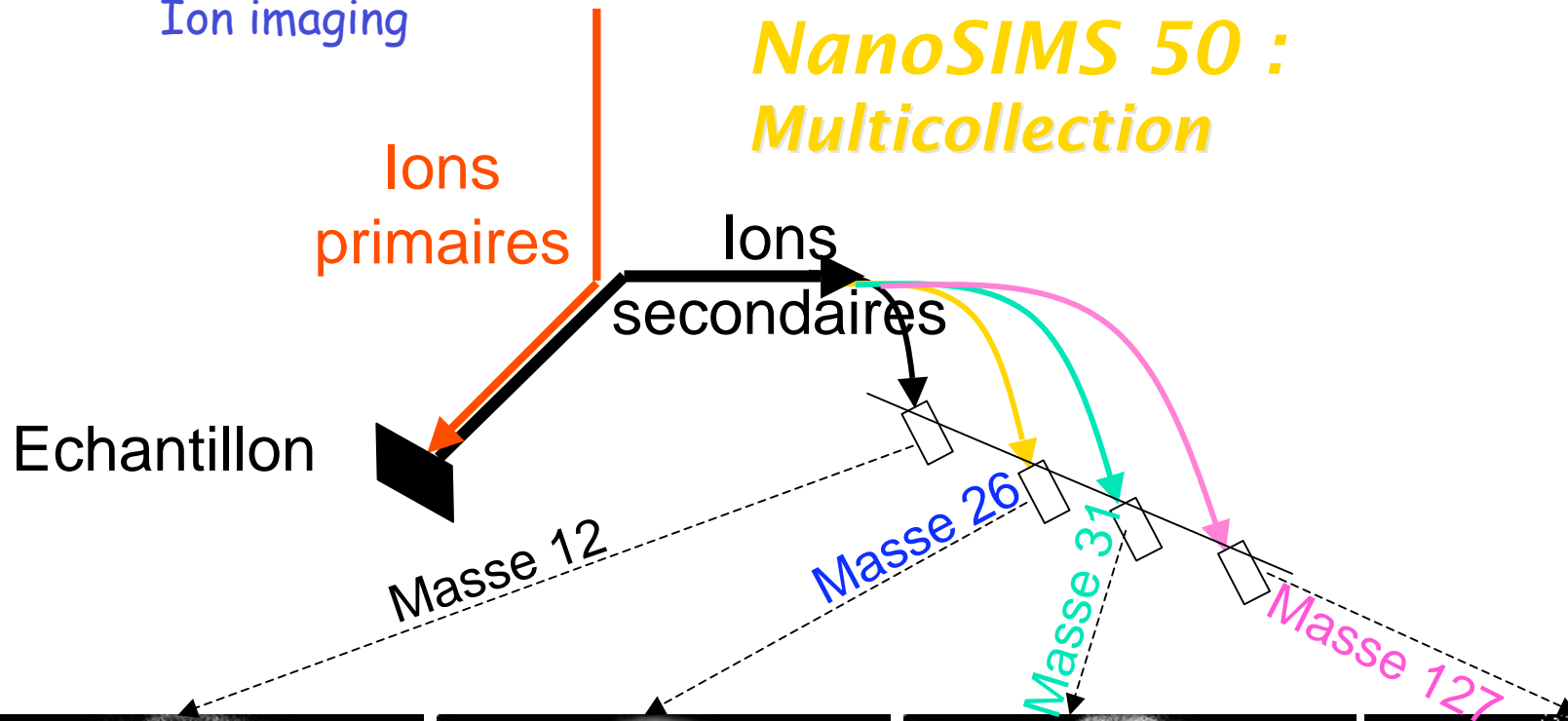


## Ion imaging



Ion imaging

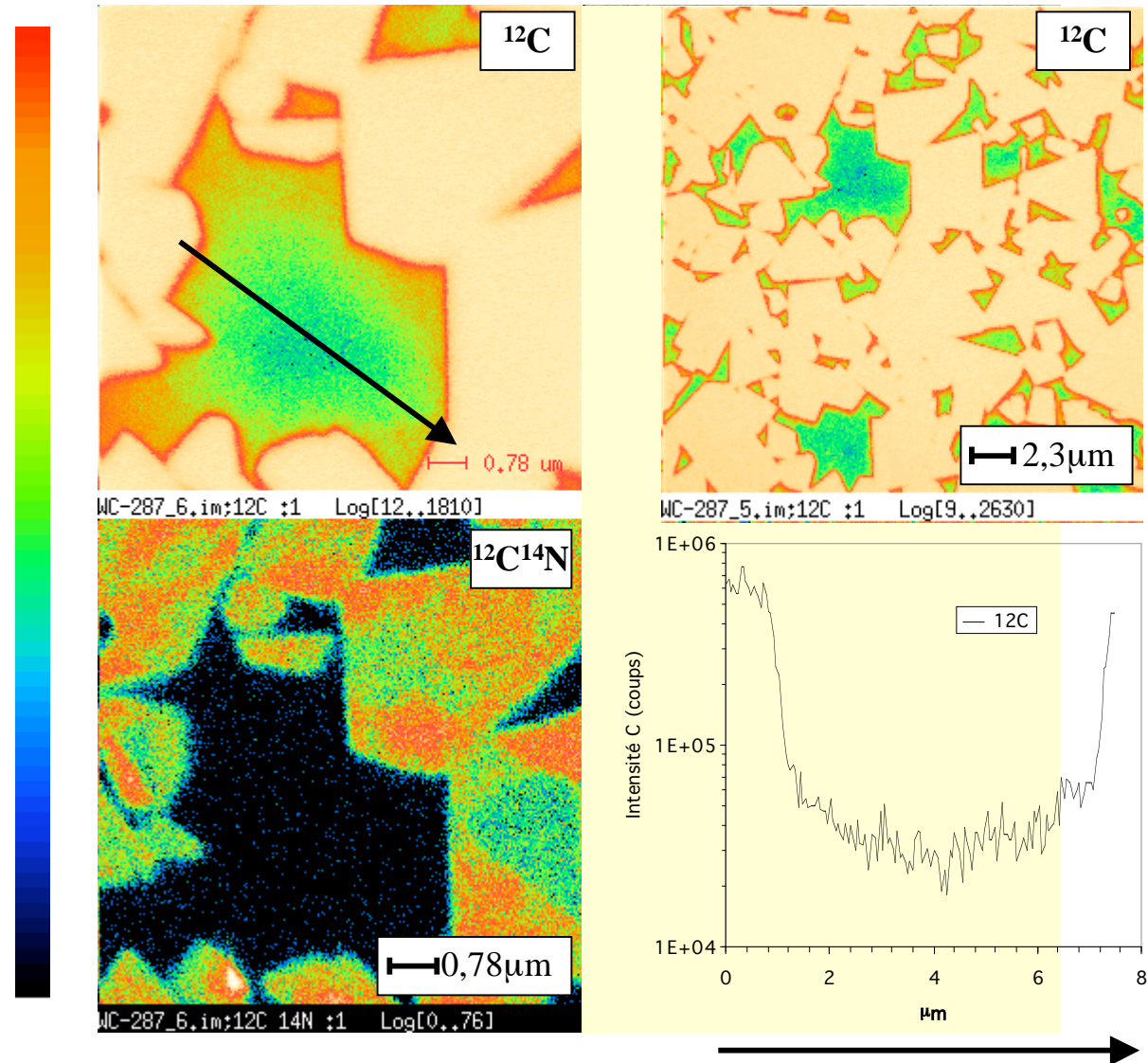
# NanoSIMS 50 : Multicollection



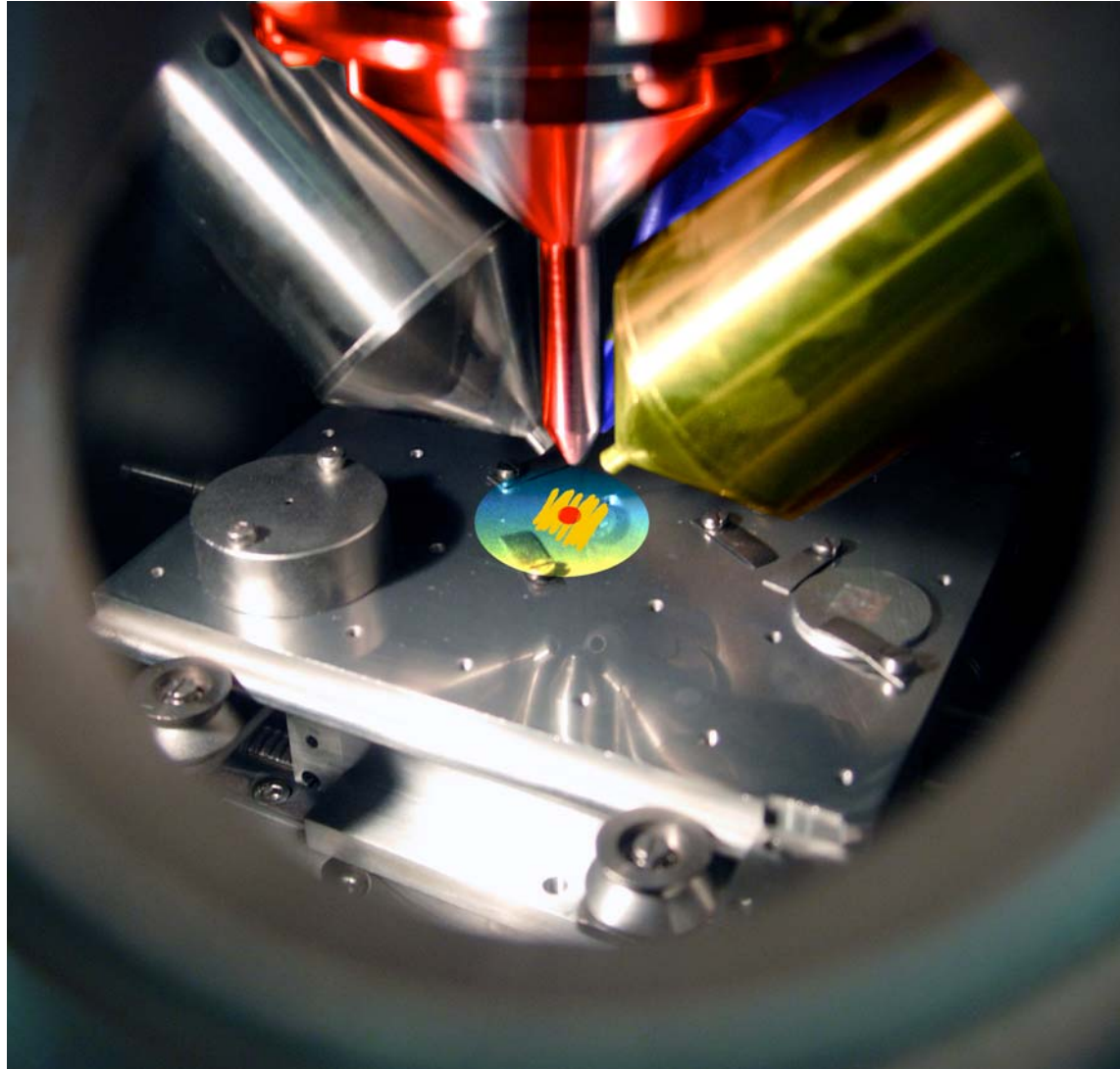
## Ion imaging

### Carbure de tungstène

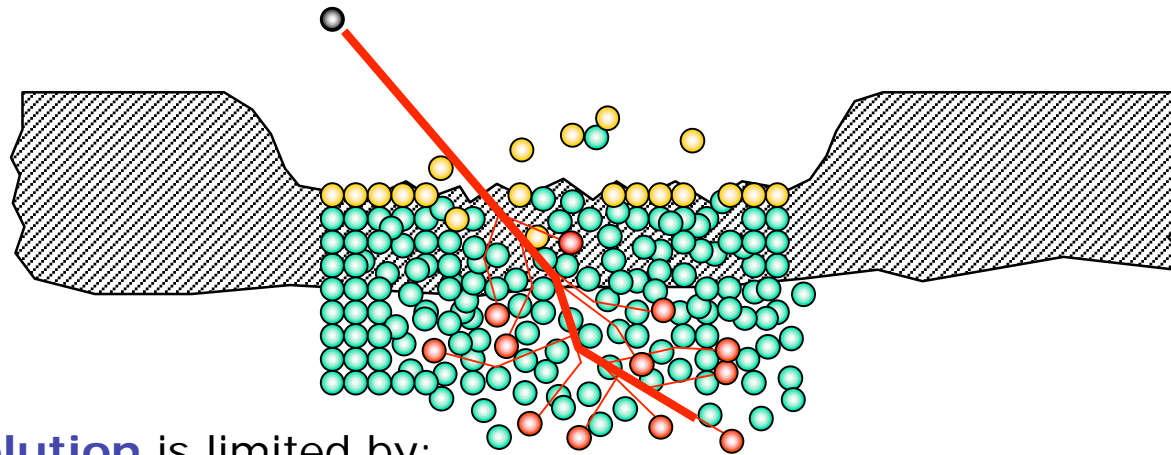
- Vérification de l'homogénéité du liant
- Diffusion dans le liant



## Depth profiling



## Depth profiling

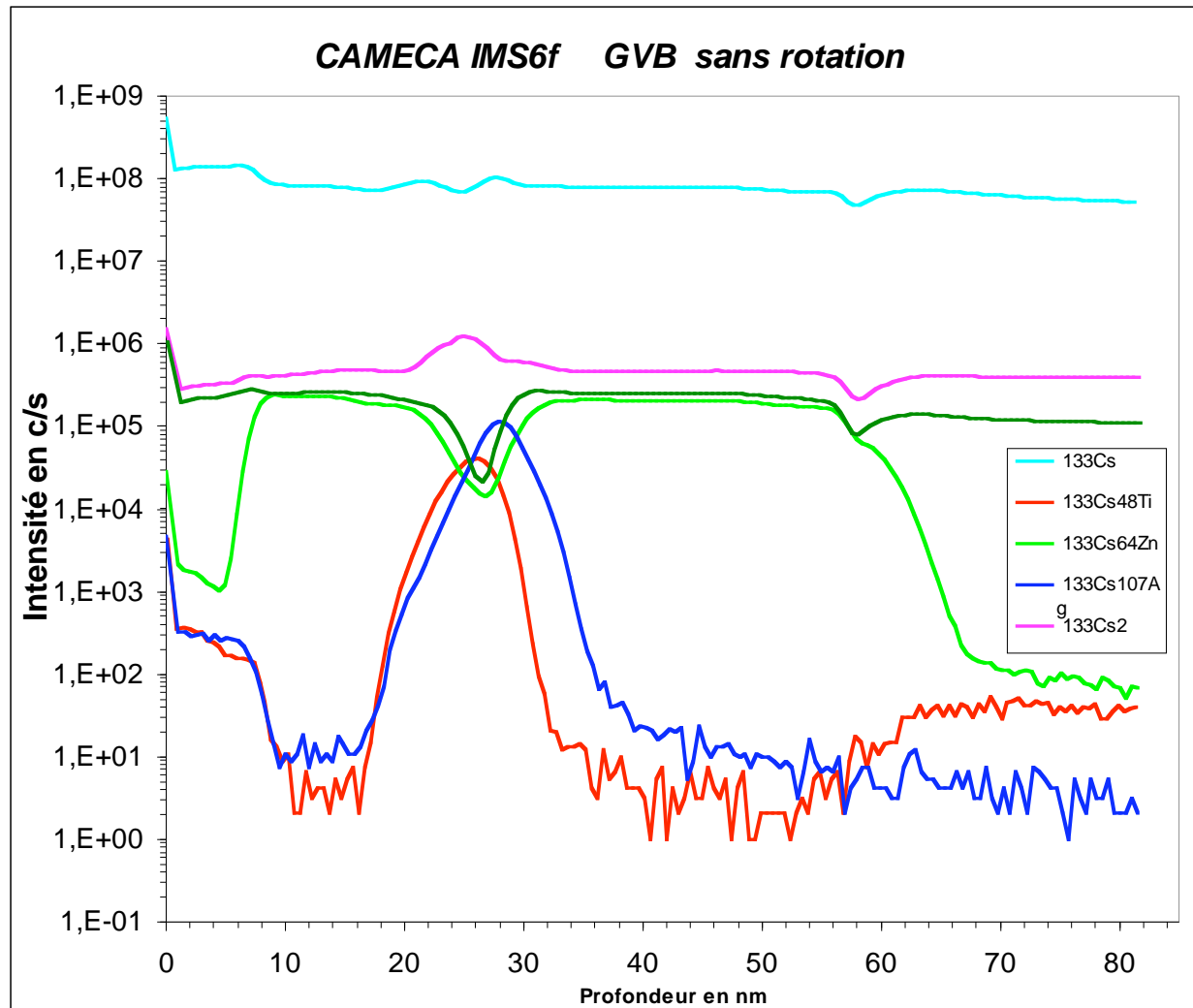


The **depth resolution** is limited by:

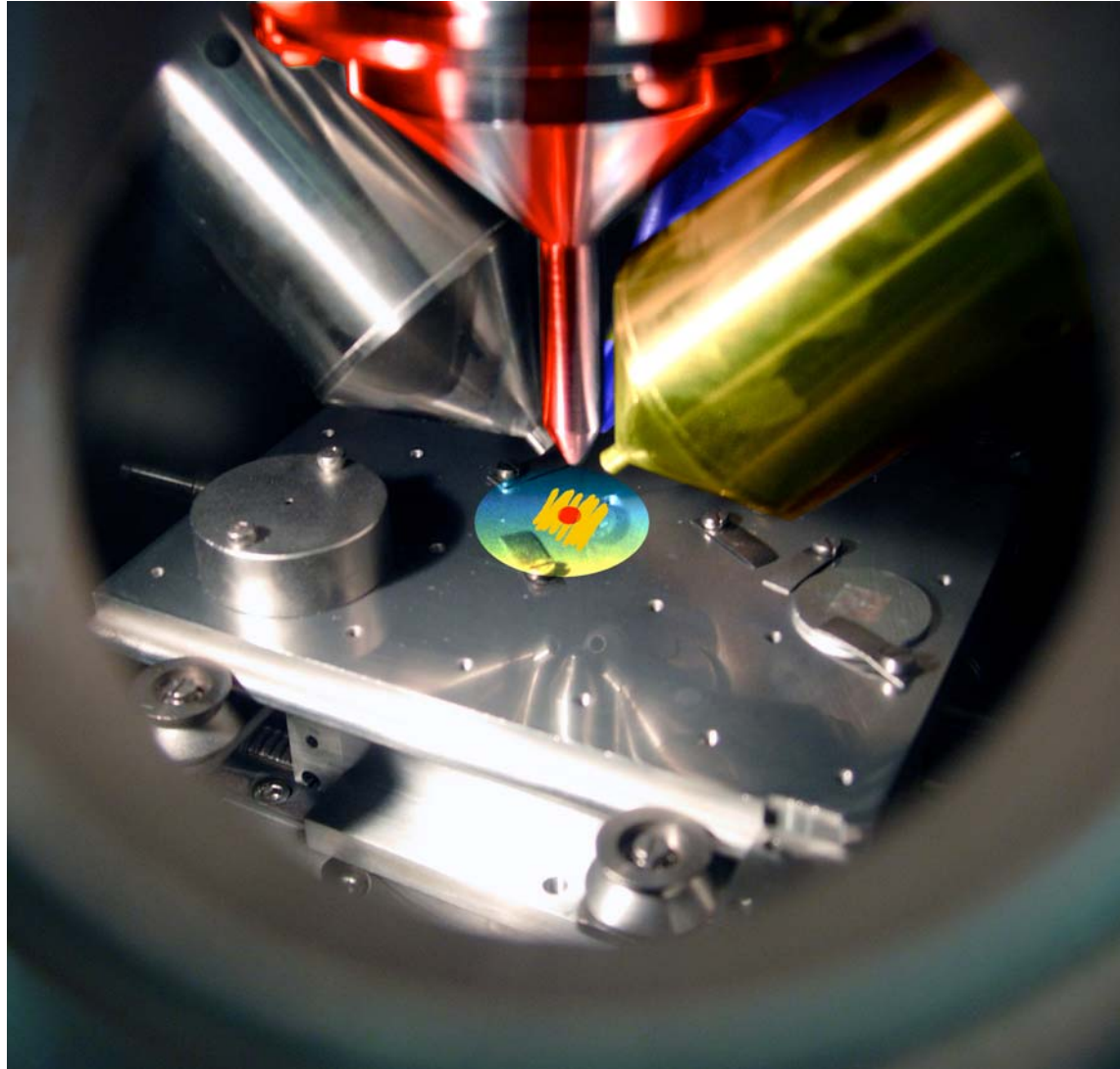
- **collision cascades** (target atoms mixing)
- **roughening effects** (non-flat bottom crater)
- **crater edge effects** (crater walls)

High *depth* resolution requires **low impact energy** (250eV to 1keV) and **convenient** primary beam **incidence angle**

## Depth profiling

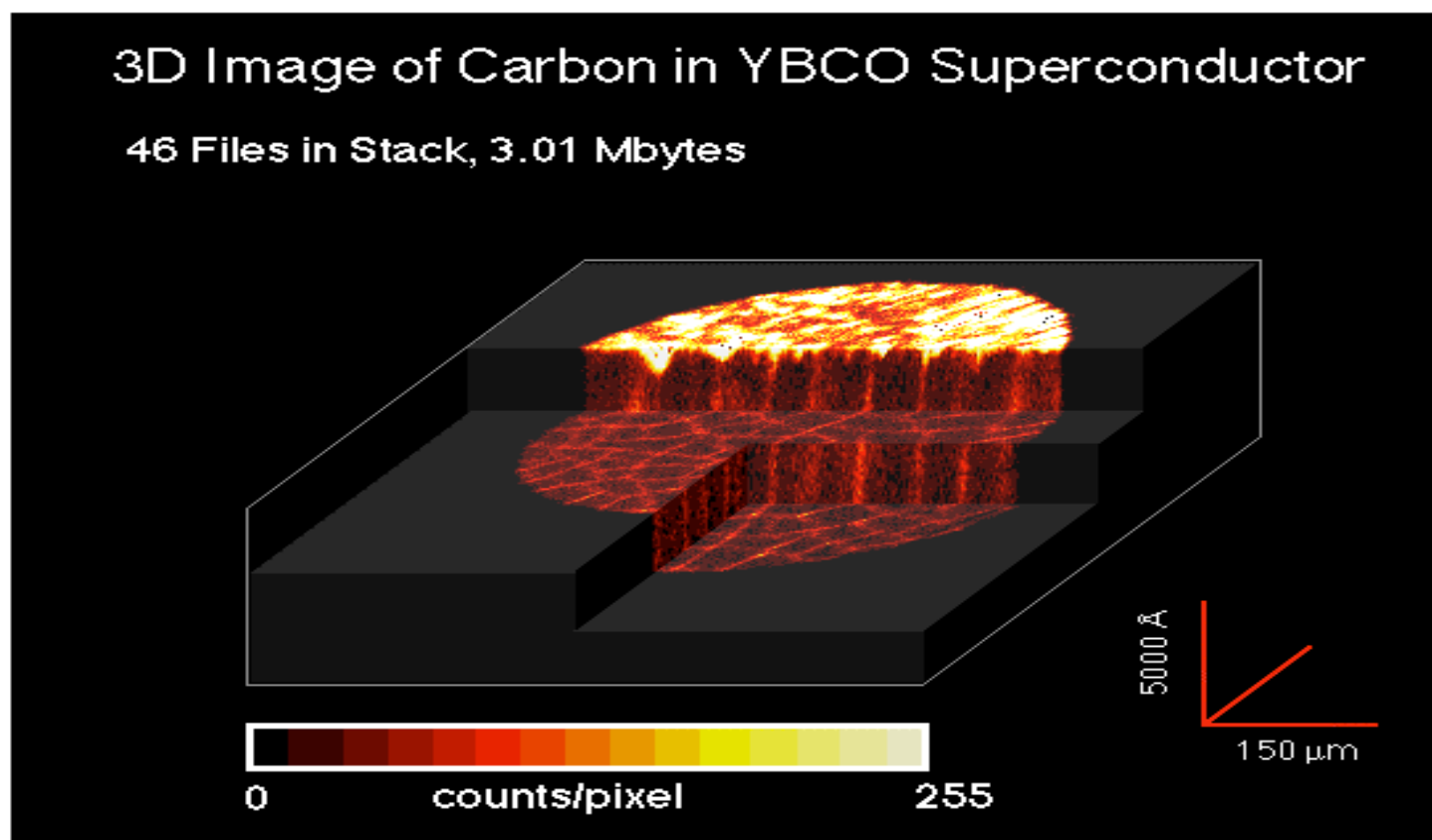


## 3D analysis



3) Imaging + sputtering = 3D

## Carbon in a Thin-Film Superconductor RAE (IMS 3f)





## Outline

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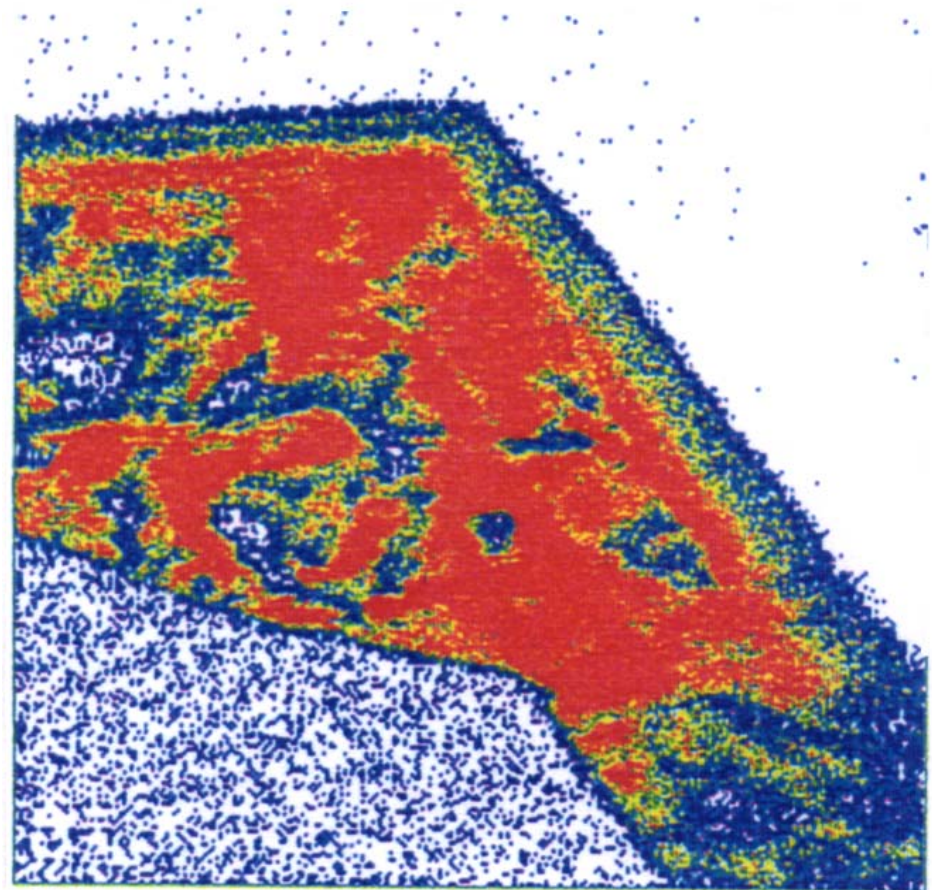


# Trace element mapping

Au<sup>-</sup> ion image

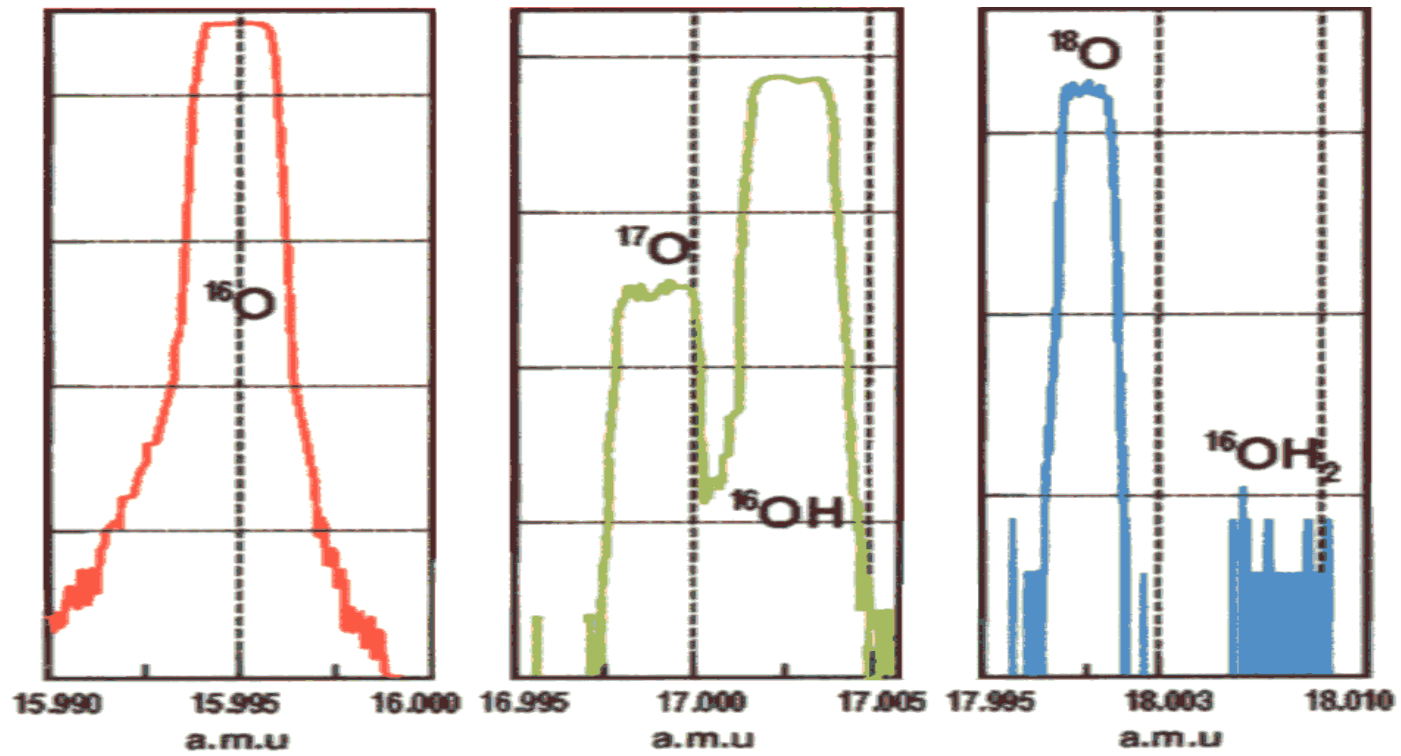
GOLD ANALYSIS IN ARSENOPYRITE

Arsenopyrite: FeAsS



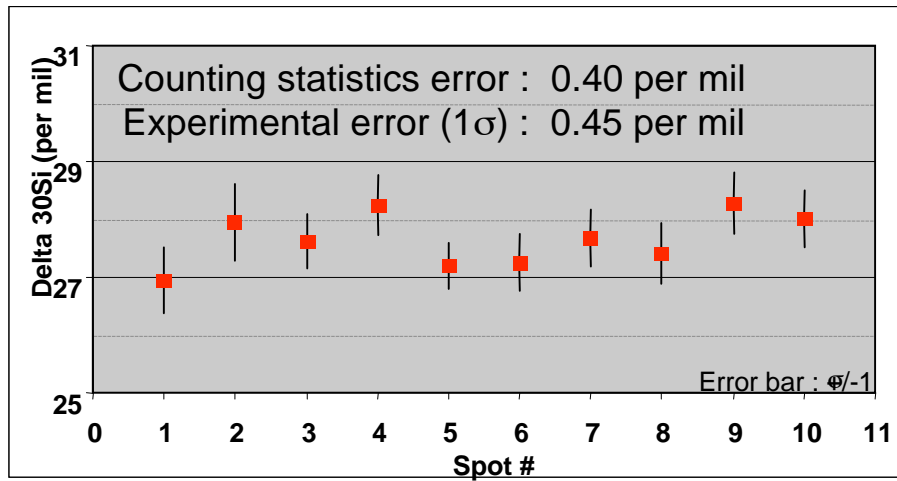
Field of view 100 x 100  $\mu\text{m}^2$

# Geochronology

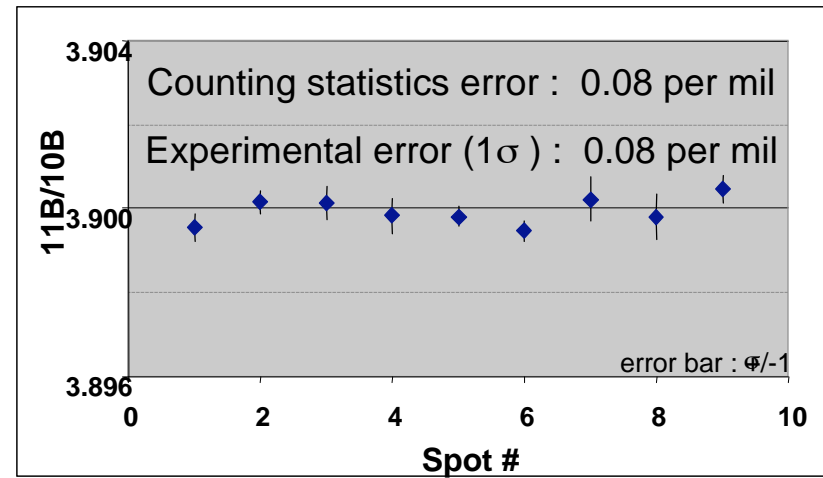


# Geochronology

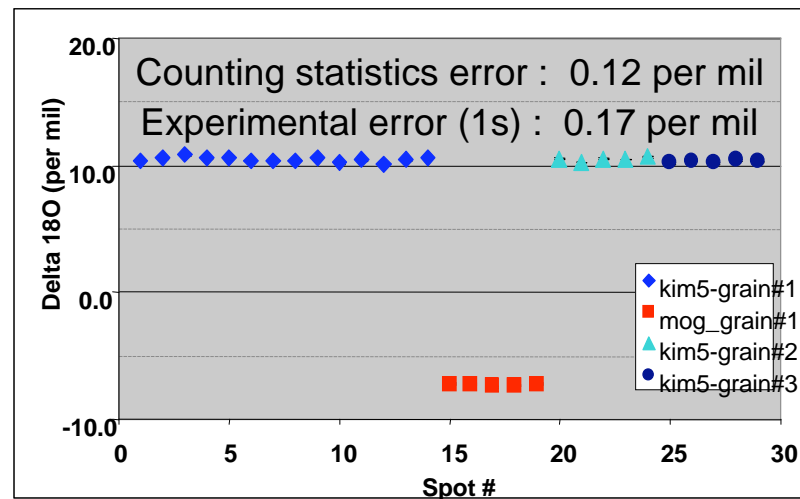
## SILICON ISOTOPES IN GLASS



## BORON ISOTOPES IN TOURMALINE



## OXYGEN ISOTOPES IN ZIRCON



# Geochronology: Zircon radiodating

Zircon is one of the most useful geochronometers.



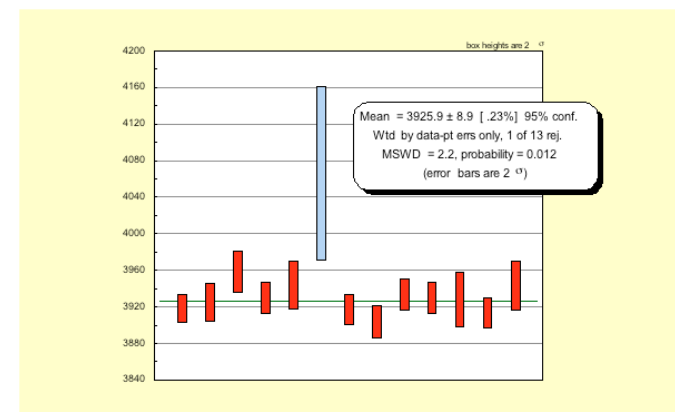
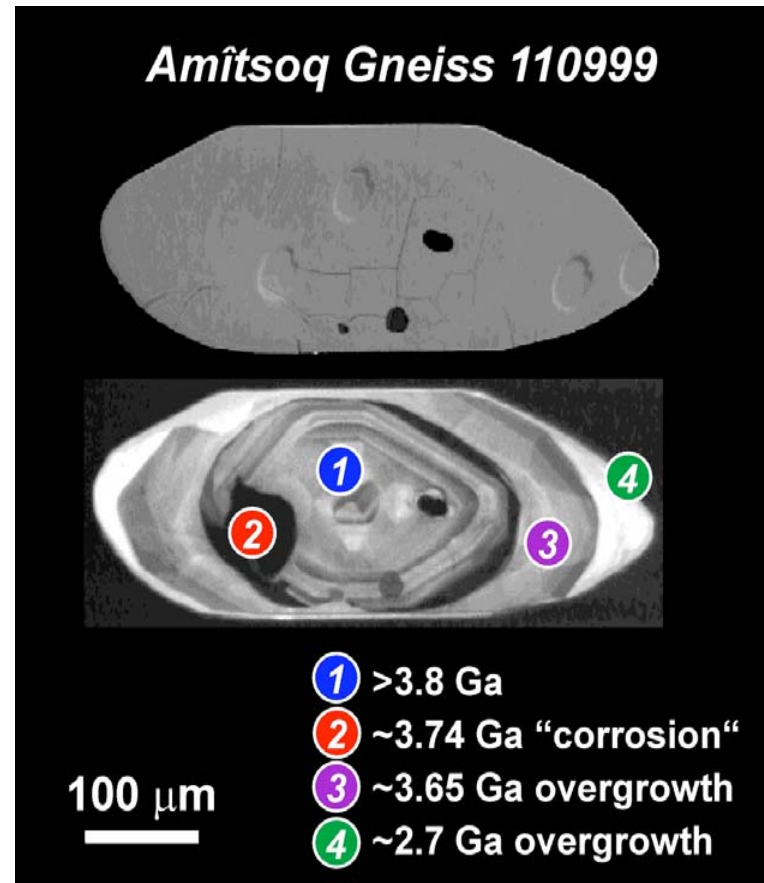
- ✓ remarkably resistant material
- ✓ two clocks:

$^{235}U \rightarrow ^{207}Pb$  ( $\lambda \sim 0.7$  billion years)

$^{238}U \rightarrow ^{206}Pb$  ( $\lambda \sim 4.4$  billion years)

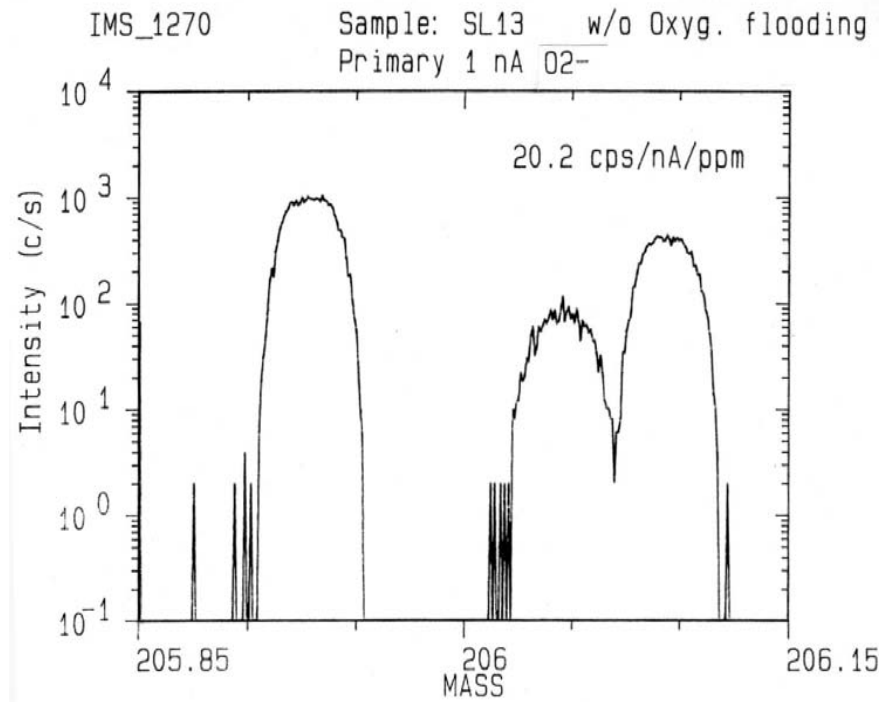
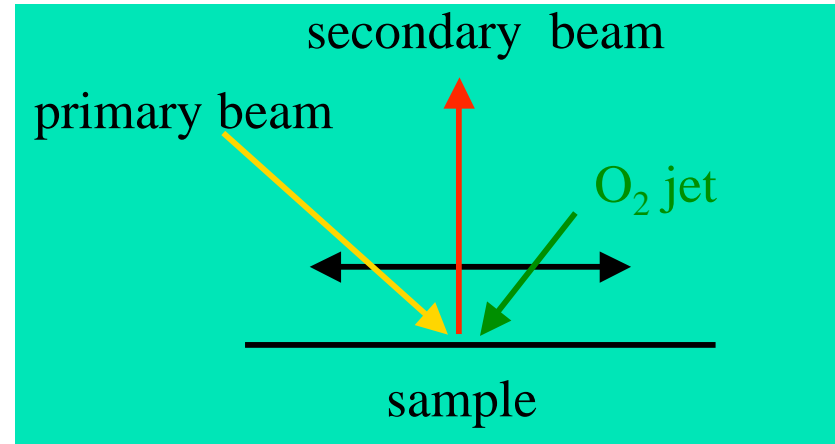
Oldest zircon:  $\sim 4.40$  billion years (Australia)

Age of the Earth:  $\sim 4.55$  billion years

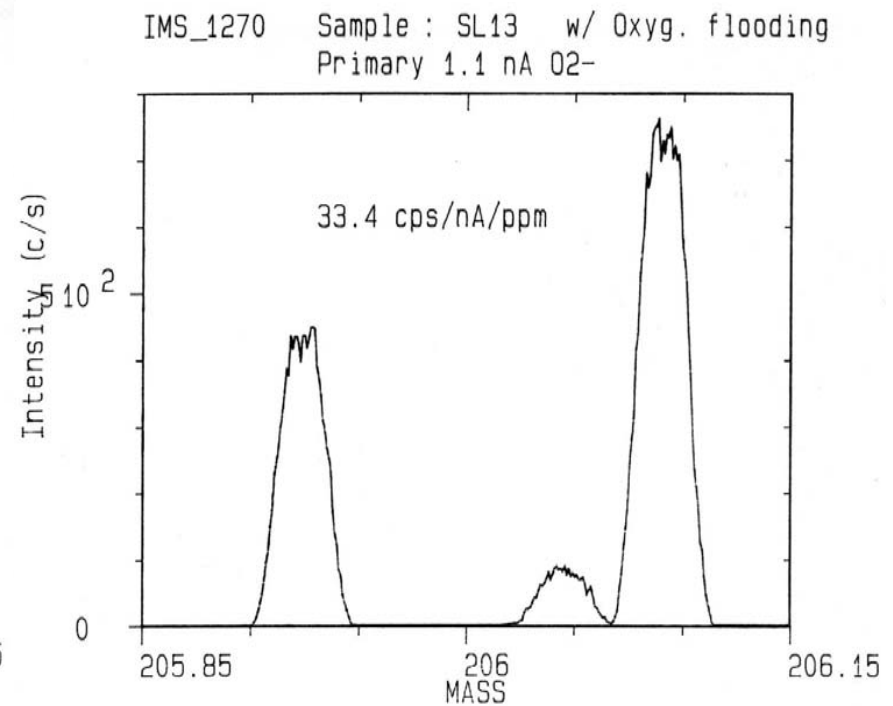


Courtesy of NORSIMS

# Geochronology



O<sub>2</sub><sup>-</sup> primary ions , w/o  
oxygen flooding



O<sub>2</sub><sup>-</sup> primary ions , with  
oxygen flooding

# Outline

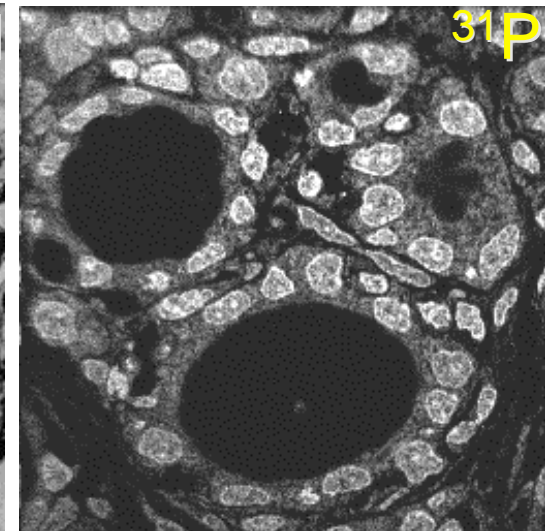
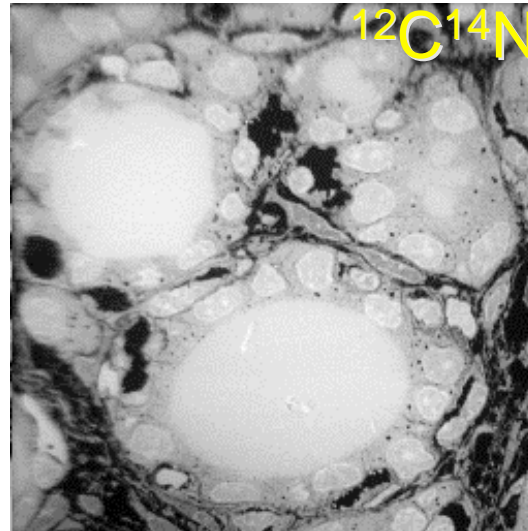
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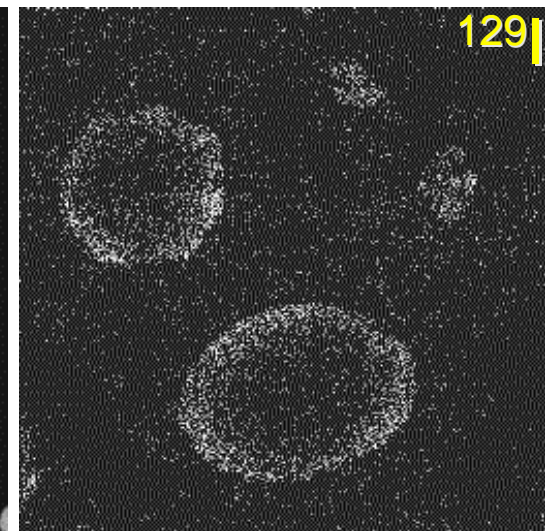
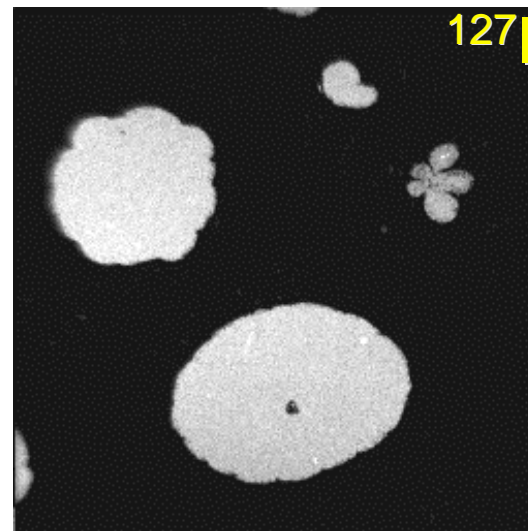
## Bio Med

### Radiotoxicology / Nuclear medicine:

Imaging  $^{127}\text{I}$ /  $^{129}\text{I}$   
distribution in thyroid

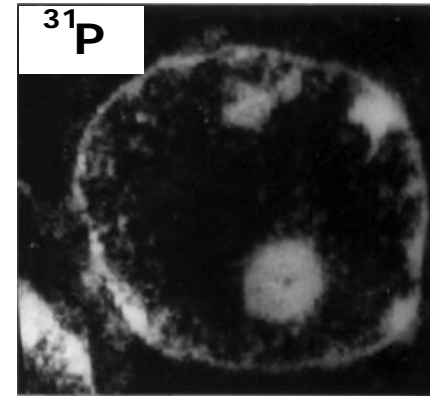
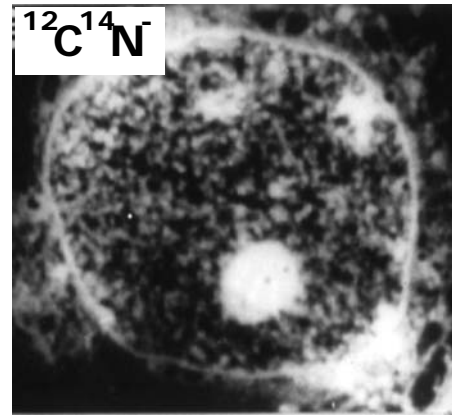
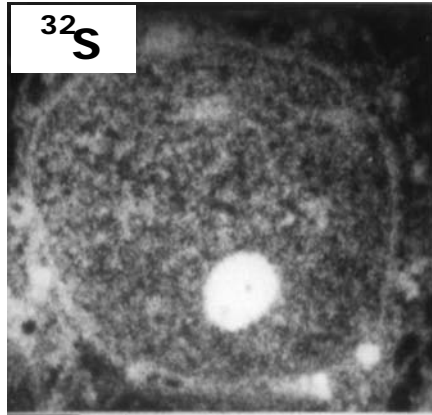


Raster  $60 \times 60 \mu\text{m}^2$

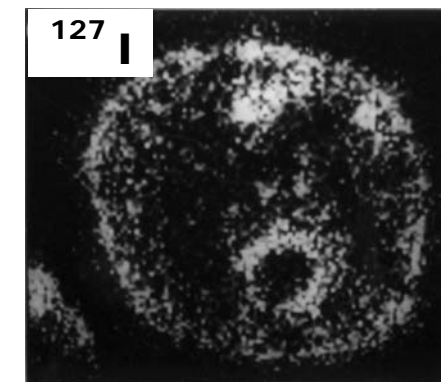
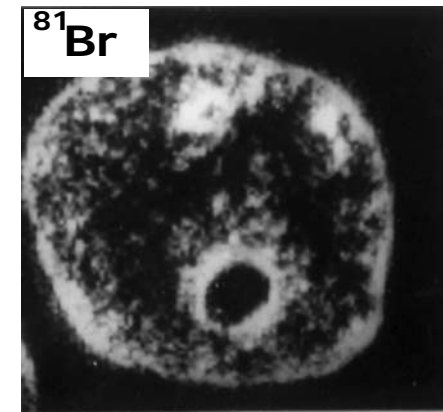
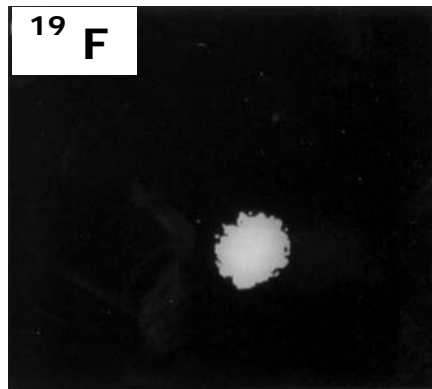




MCF-7 mammary carcinoma cell:  
use of halogenous markers



Field of view:  
10μm x 10μm



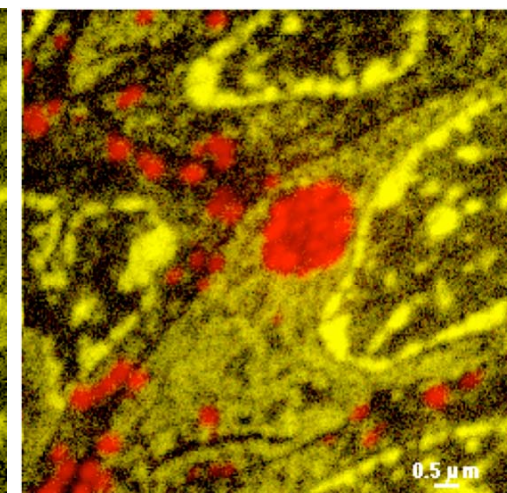
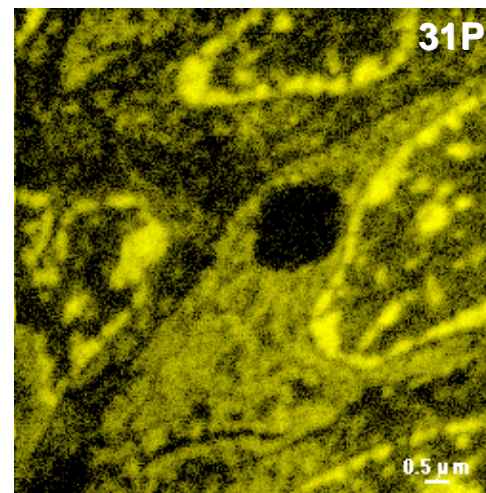
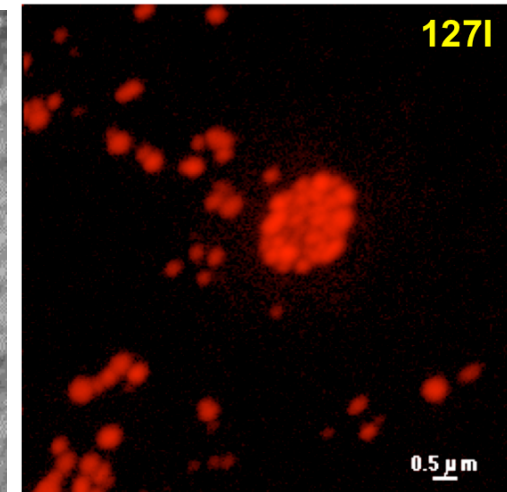
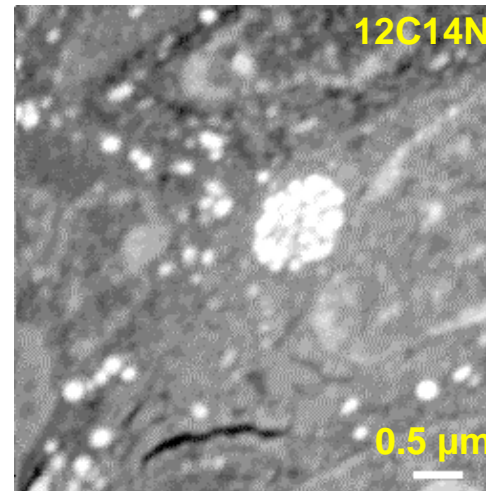
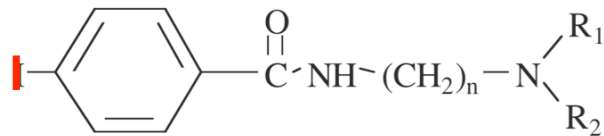
Incorporation of BrdU (bromodeoxyuridine), IdU (iododeoxyuridine) and 5FU (5-fluorouracile) compounds in the same cell.

The last four images are collected simultaneously from same sputtered volume (multi-collection).

## Pharmaco-toxicology: Targeting melanin cells

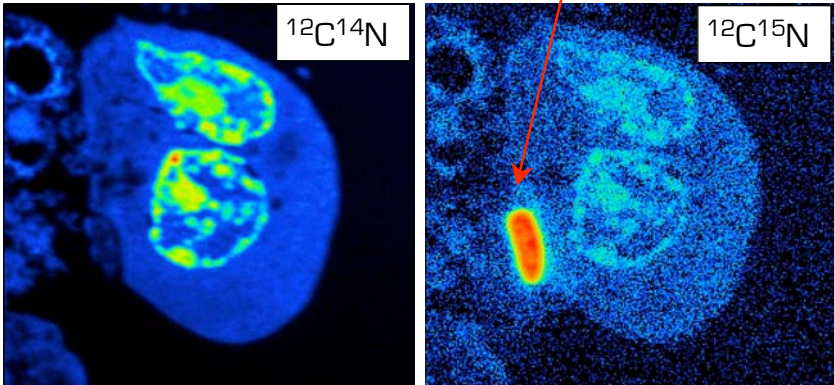
- CN :proteins
- P :DNA
- morphology

### General Structure of BZA



**E.coli labelled with  $^{15}\text{N}$   
at time  $t = t_1$**

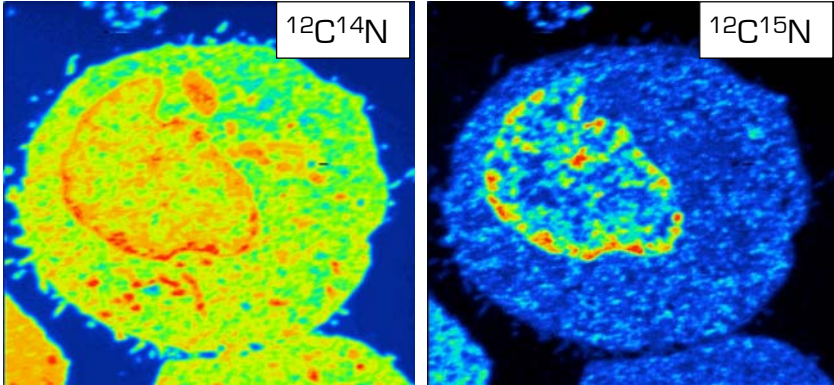
Natural abundance  
 $^{14}\text{N}$  99,7%  
 $^{15}\text{N}$  0,3%



**Analyzed area : (12 x 12)  $\mu\text{m}^2$**

**E.coli labelled with  $^{15}\text{N}$   
at time  $t = t_2 > t_1$**

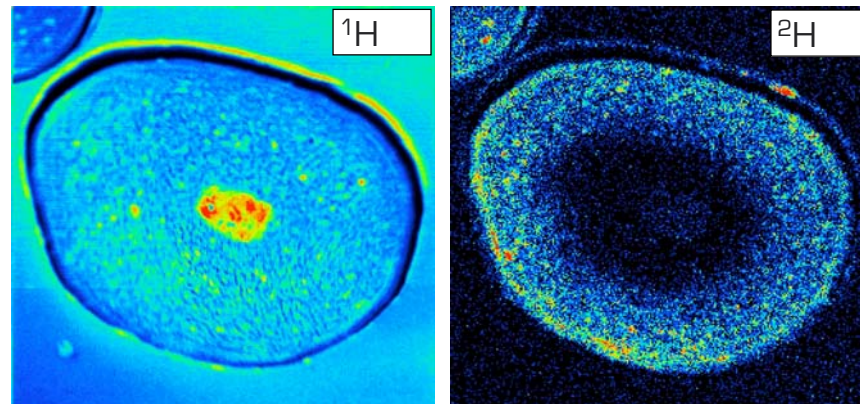
Bacteria destroyed by immune  
system



# Bio Med

Biology, Cosmetic

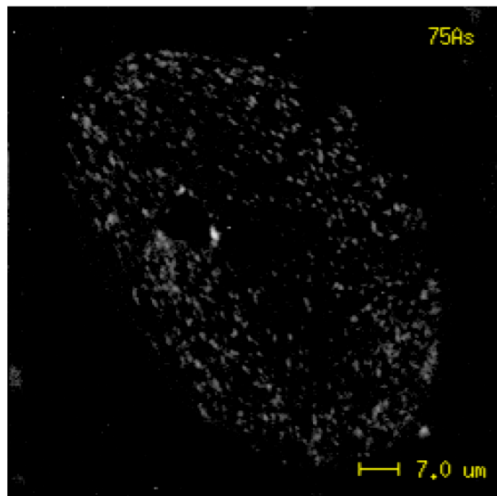
Molecule  $C_xD_y$



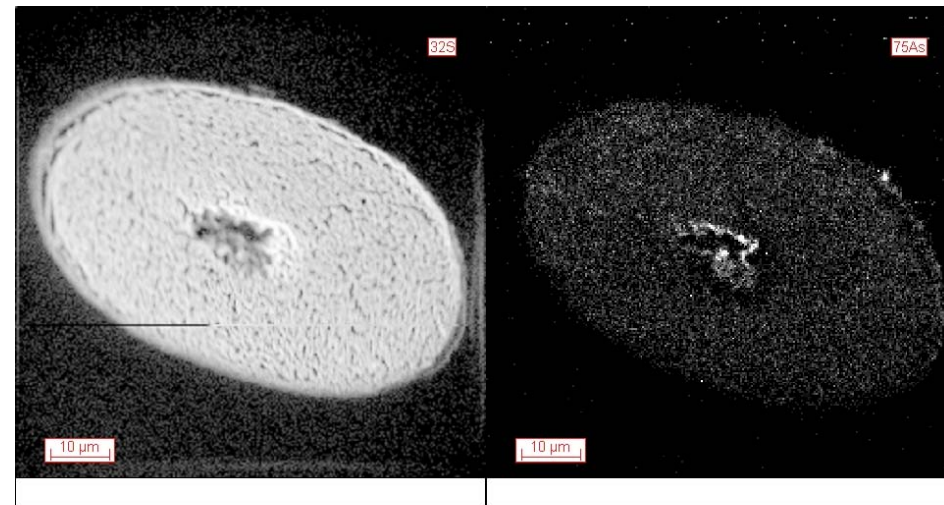
**Incorporation of an isotopically (D) labelled  
active molecule in human hair  
Analyzed area : (80 x 80)  $\mu\text{m}^2$**

Courtesy of L'Oreal

# Hairs from St H el ene .....



Reference Hair

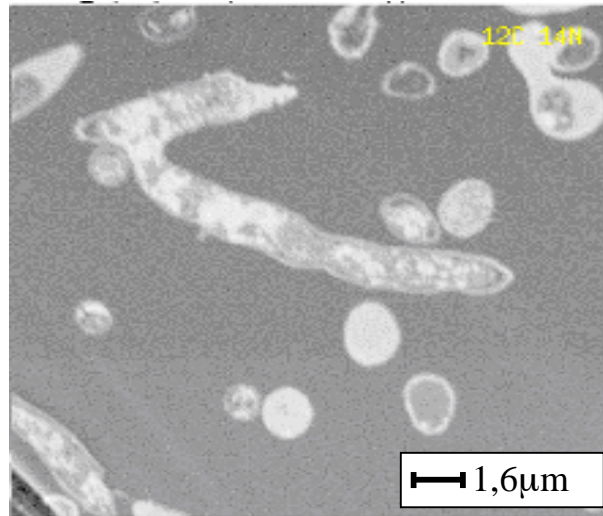


Hairs from St H el ene

# $^{15}\text{N}$ : stable isotope tracer used in vegetal cells

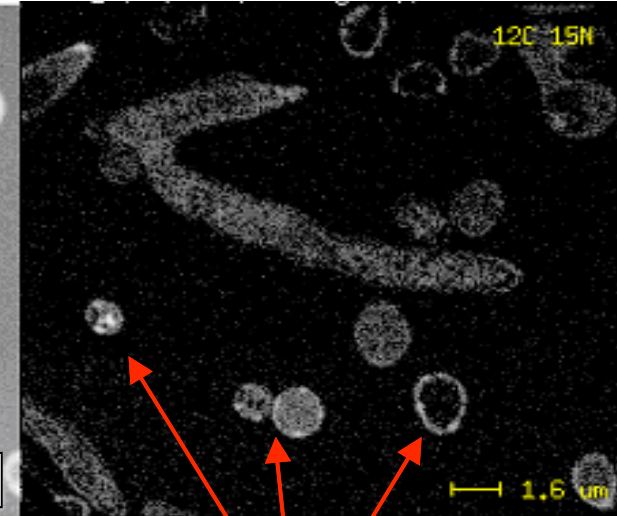
(20x20)  $\mu\text{m}^2$

$^{14}\text{N}$



1,6  $\mu\text{m}$

$^{15}\text{N}$



1,6  $\mu\text{m}$

High levels  $^{15}\text{N}$

Mushroom cells cultured in  $^{15}\text{N}$  enriched media, 15 min  
↳ Identification of specific sites for N fixation

$^{15}\text{N} / ^{14}\text{N}$

# Outline

1. Ion/matter interaction : impinging and outgoing particles
2. Instrumentation
3. General capabilities
  - Elemental range
  - Ion imaging
  - Depth profiling
  - 3D analysis
4. Applications
  - Geochronology
  - Biomed
  - Nanomaterials
5. Future developments



# Nanomaterials

## R&D in Semi conductors

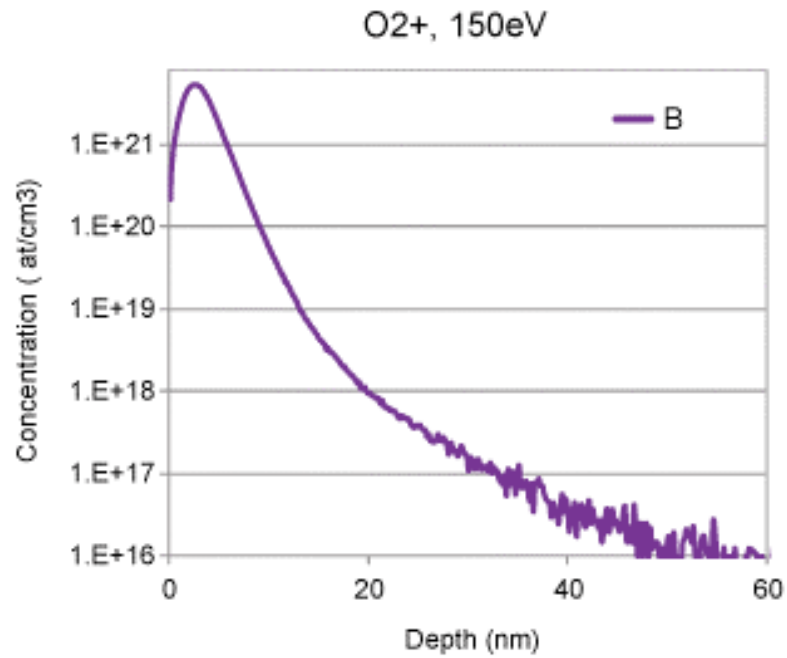
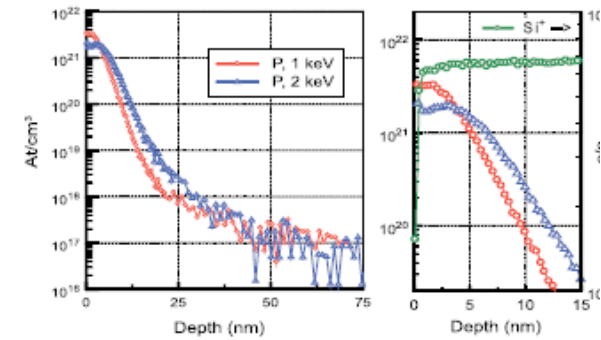
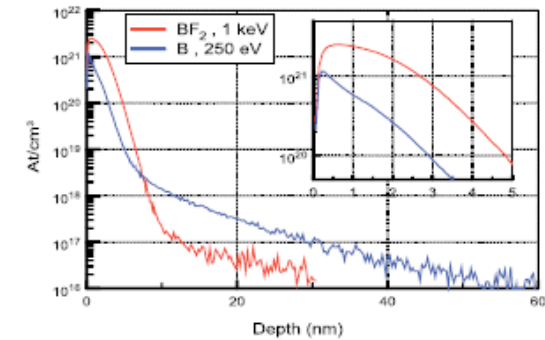


Figure 3:  
2.2keV boron implant  
in silicon analyzed with  
150eV O2+ primary  
beam

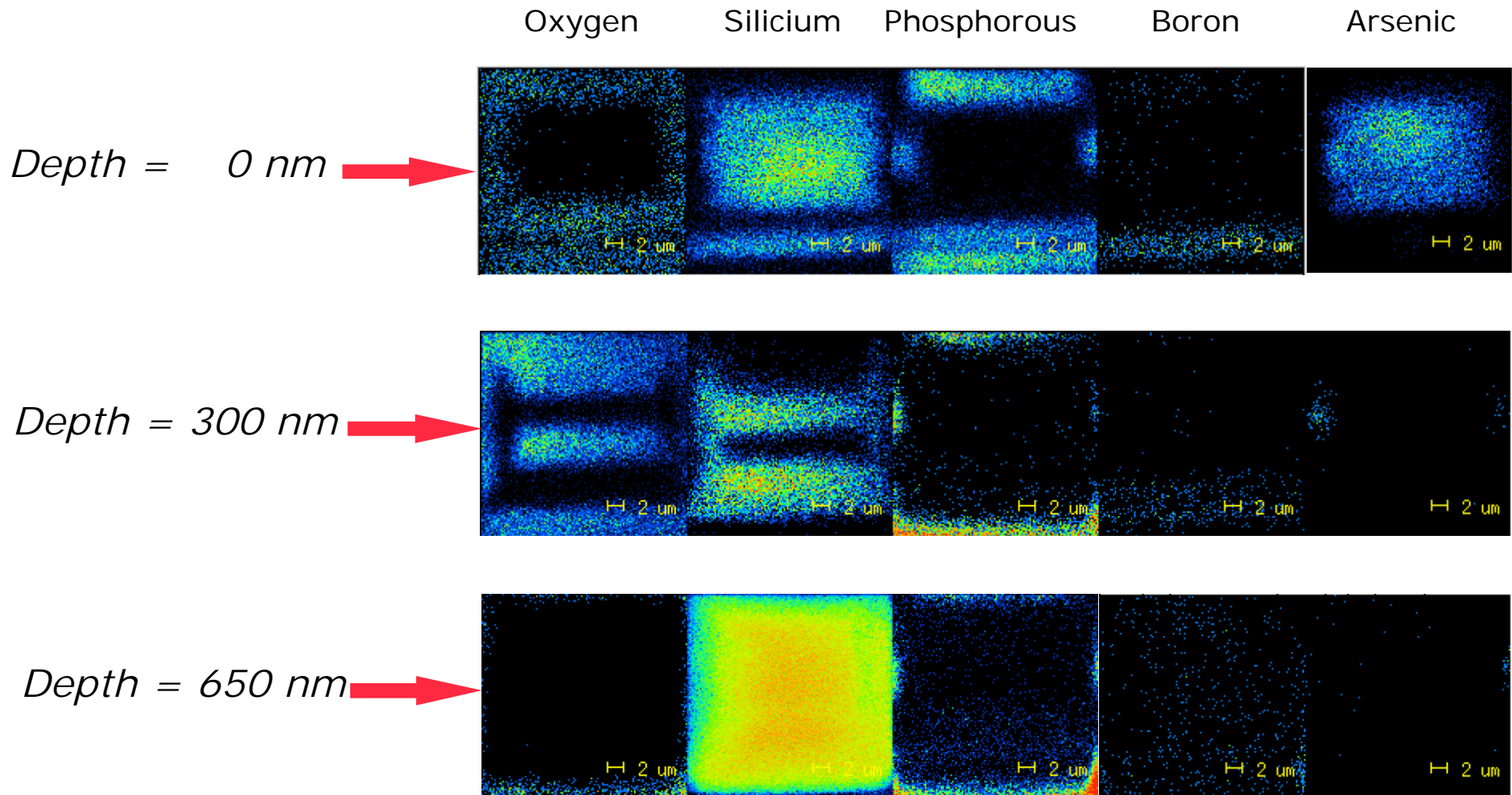




# Nanomaterials

Image depth profile in N-MOS gate:

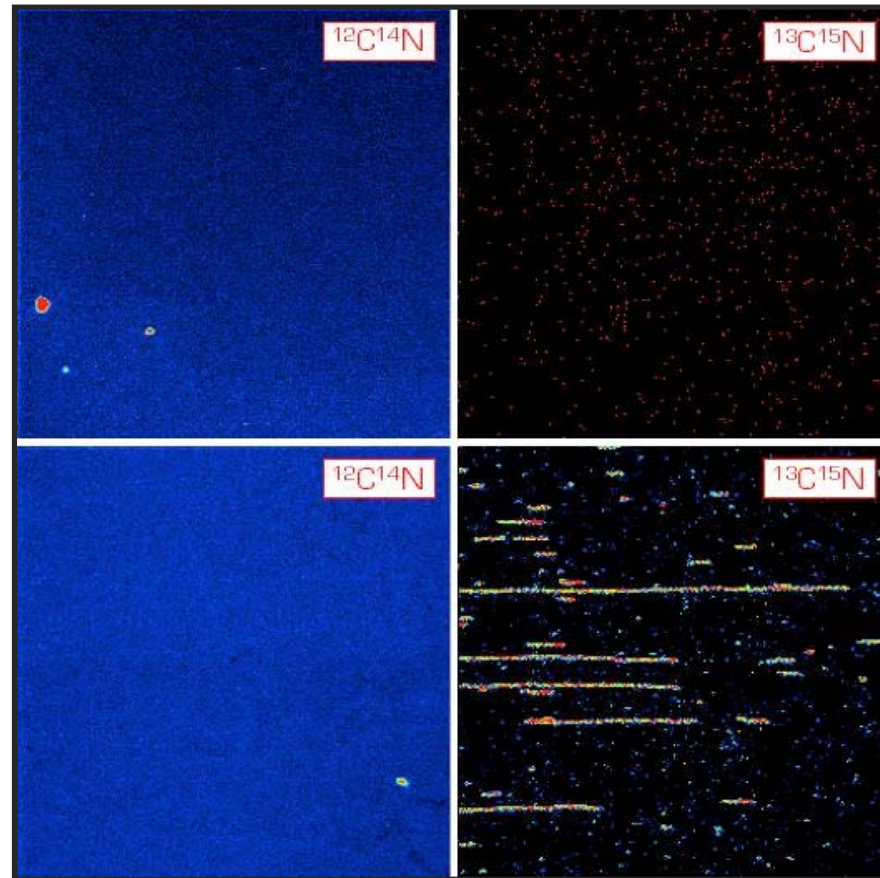
3) Imaging + sputtering = 3D



# Outline

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High resolution NanoSIMS 50 images of  $^{12}\text{C}^{14}\text{N}$  and  $^{13}\text{C}^{15}\text{N}$  of double-labelled *Bacillus subtilis* DNA combed on wafers without Cs deposition (top) and with prior Cs deposition (bottom).  
Field of view :  $(15 \times 15) \mu\text{m}^2$





## Centre de Recherche Public – Gabriel Lippmann

Belvaux, LUXEMBOURG

4 departments: EVA / IST / **SAM** / REA