Imagerie élémentaire par LIBS pour la caractérisation des cristaux

V. Motto-Ros[1,2]

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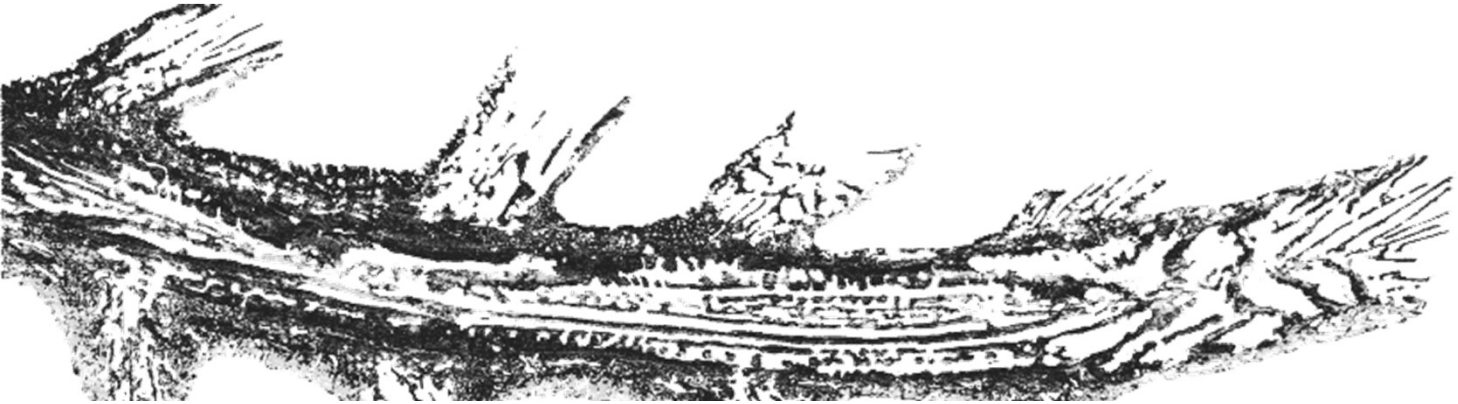
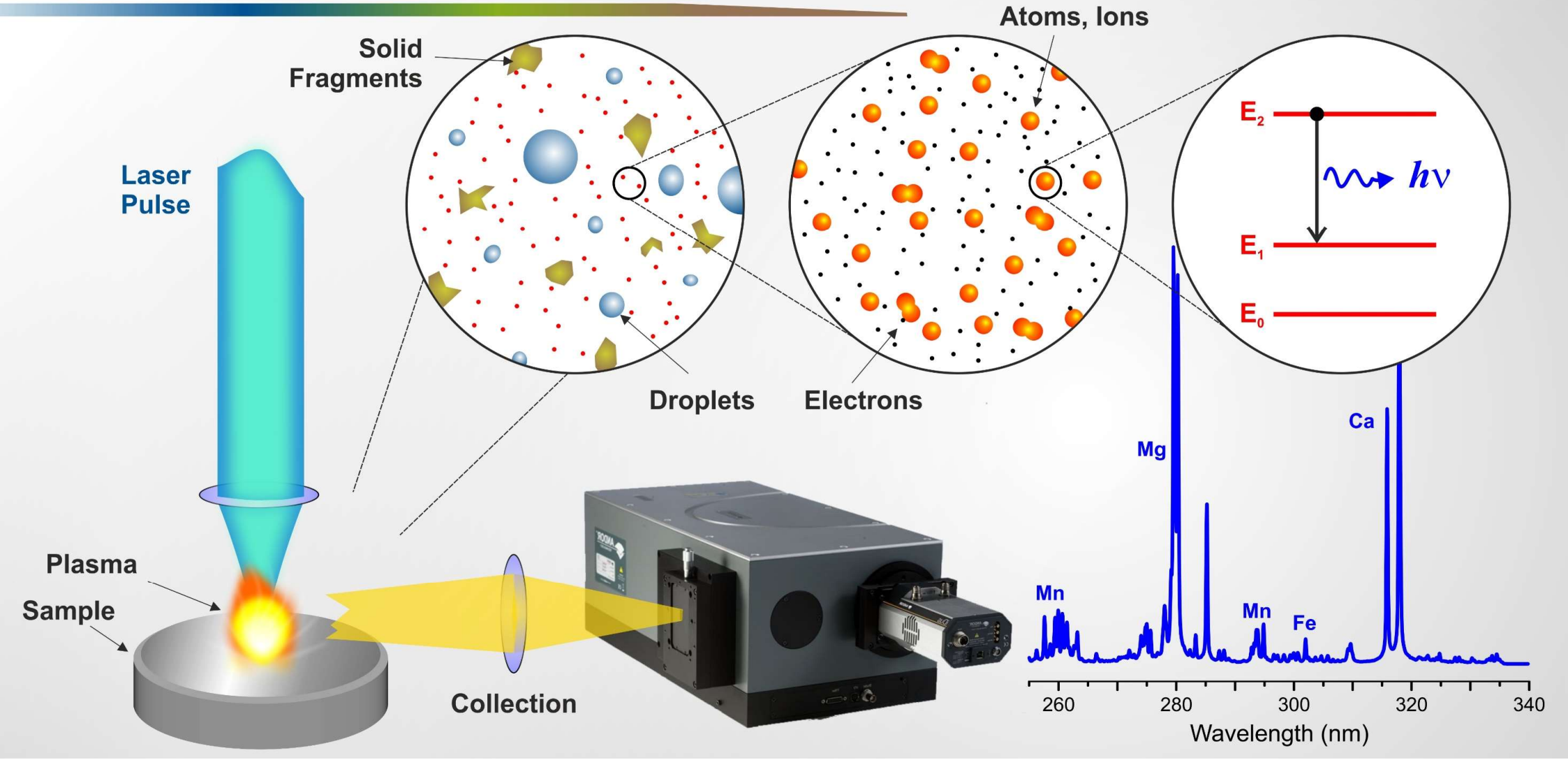
[1]*Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS, 69622 Villeurbanne, France*
[2]*Ablatom SAS, 10 Rue Ada Byron,* 69622 Villeurbanne, France



Journées thématiques
Défauts dans les cristaux
2 & 3 septembre 2021

Laser-Induced Breakdown Spectroscopy (LIBS)

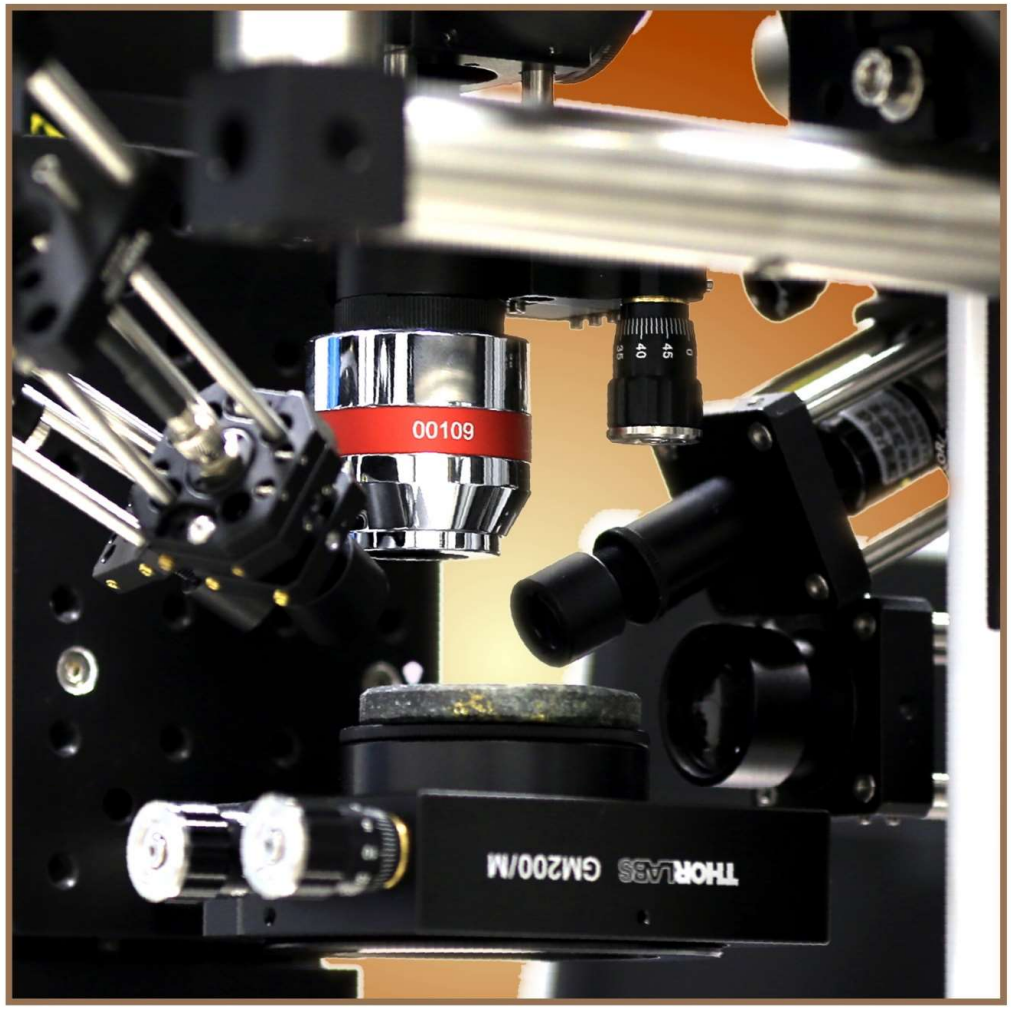
Principe




Une technique attractive pour l'analyse *in situ*
Mars 2021 (NASA)

Plan

Imagerie élémentaire par LIBS

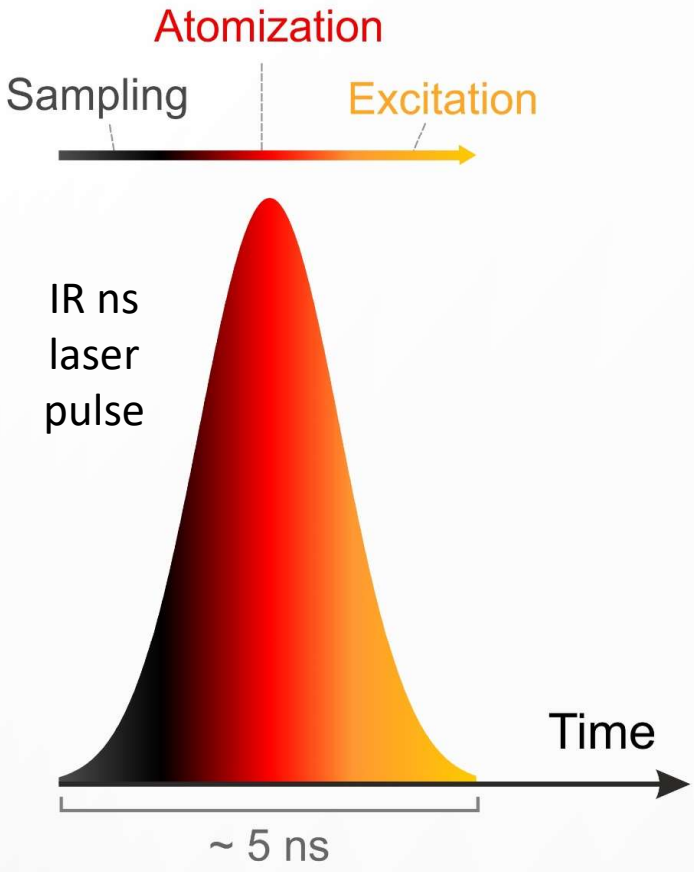


Bases
Chronologie
Principe & Instrumentation
Passage en revue
Quelques exemples
Perspectives

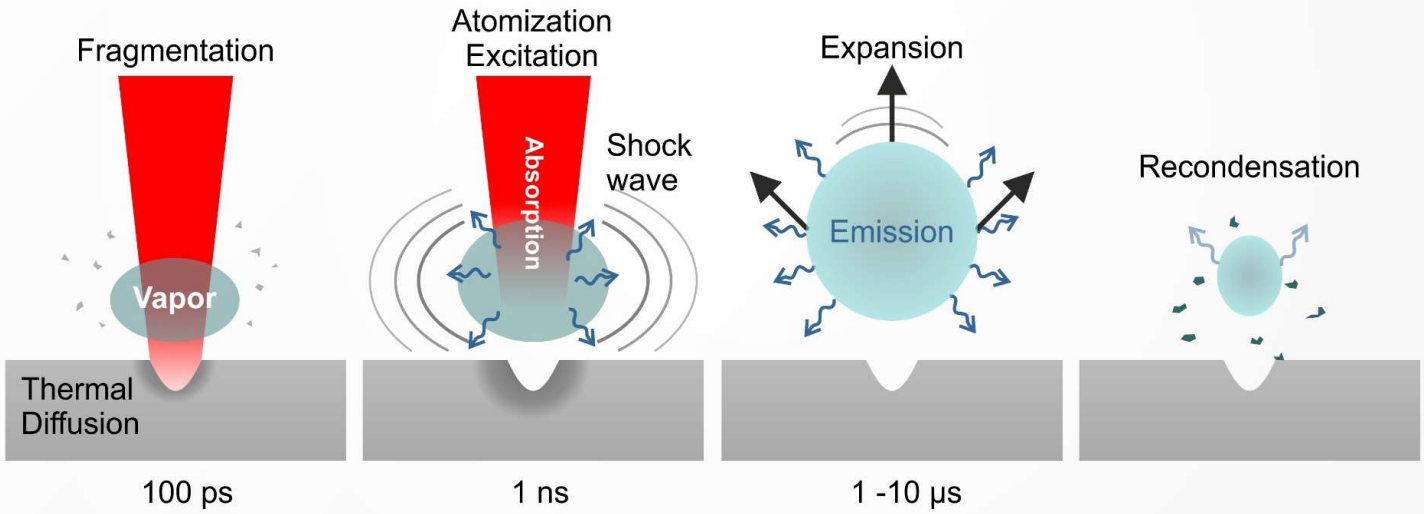
Plasma induit par laser

Description rapide

3 effets en 1!



Mécanismes



Plasma induit par laser

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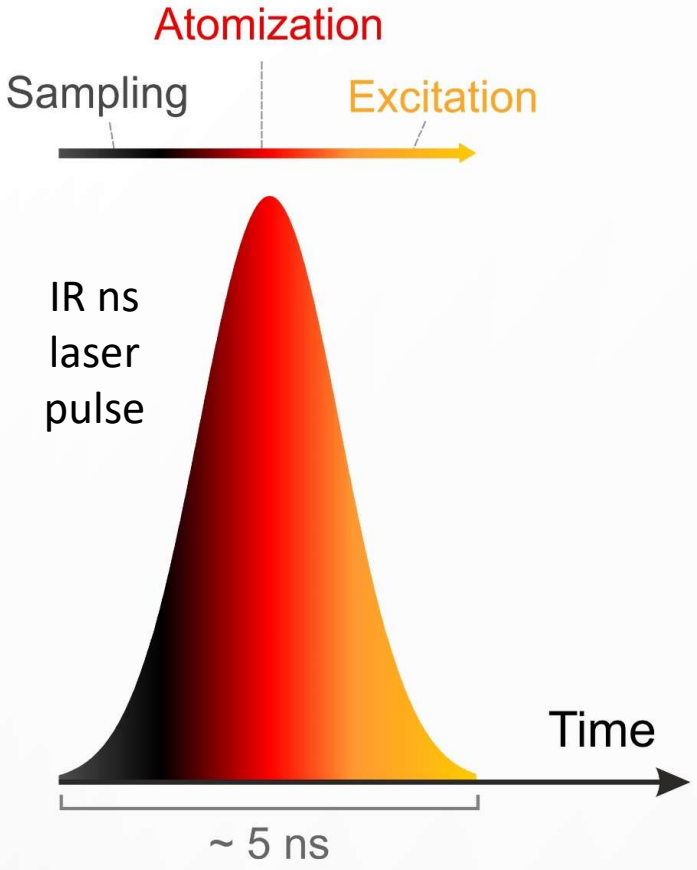
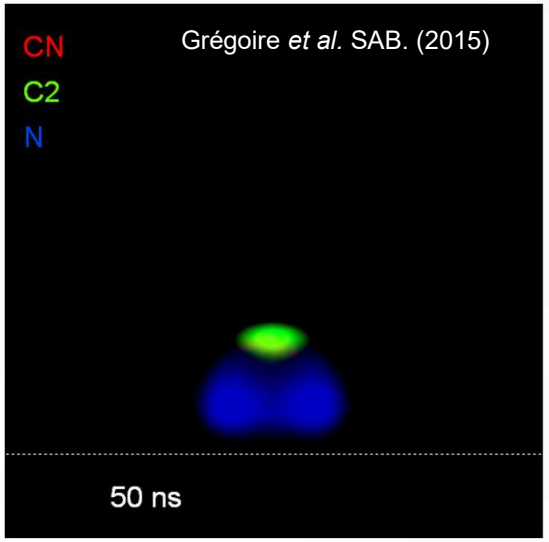
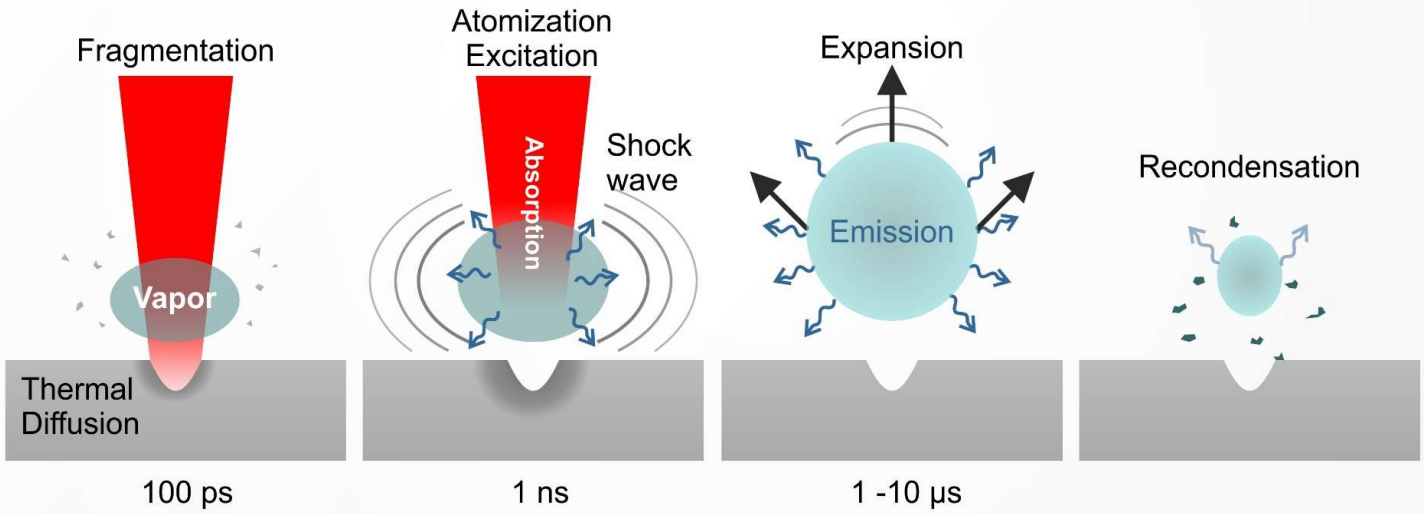


Mécanismes





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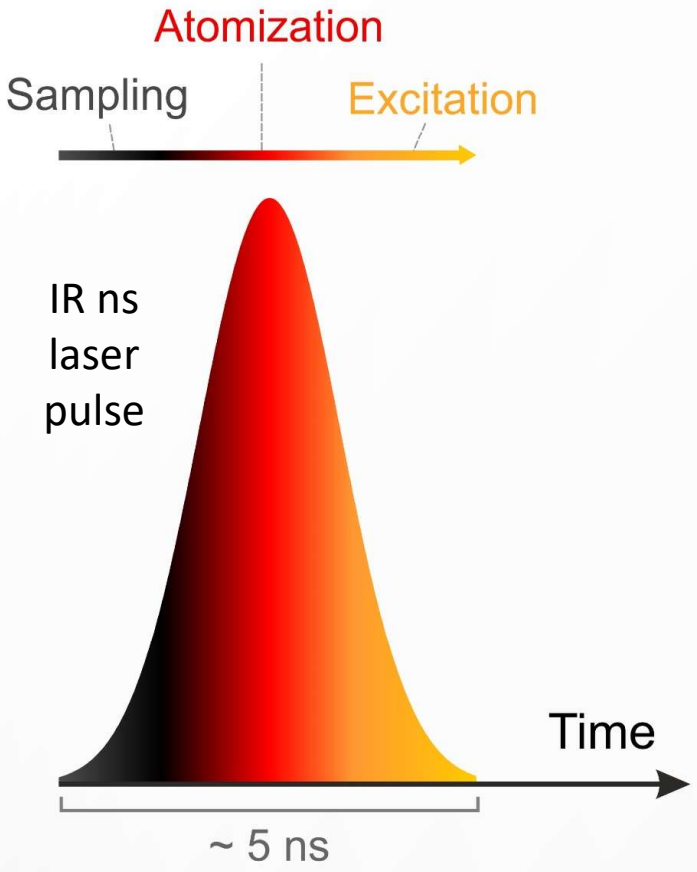
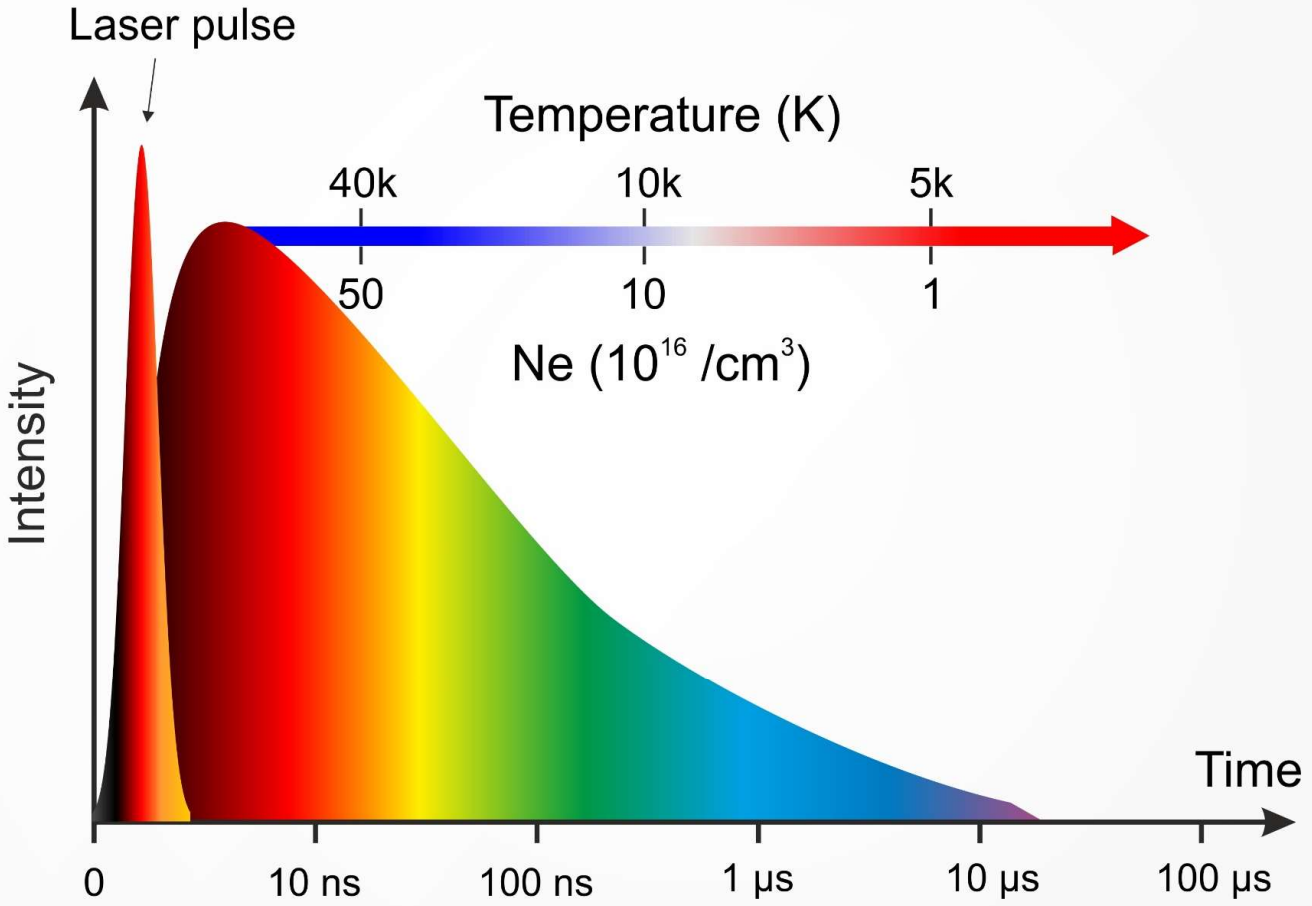


Evolution temporelle



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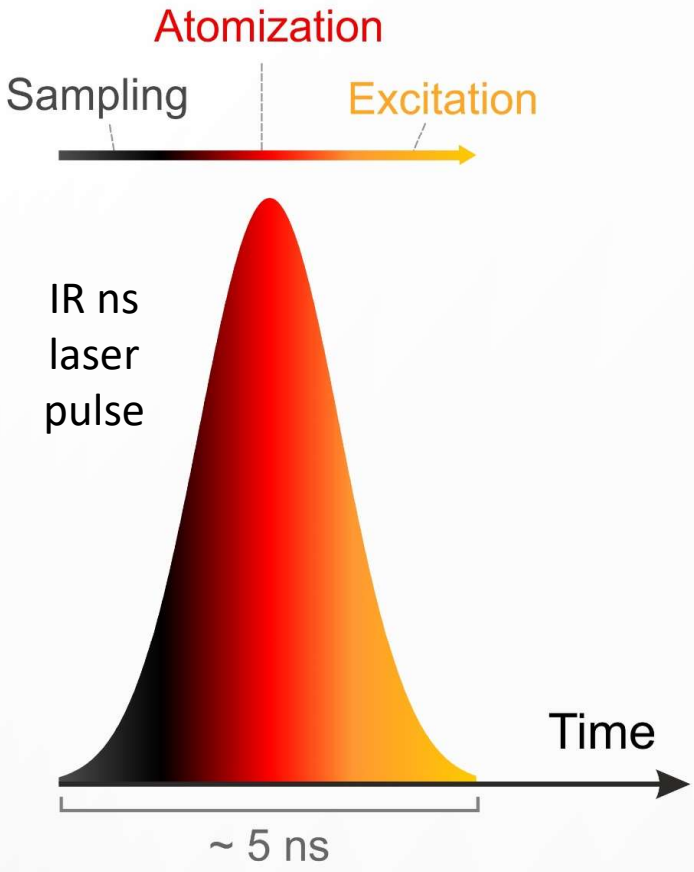
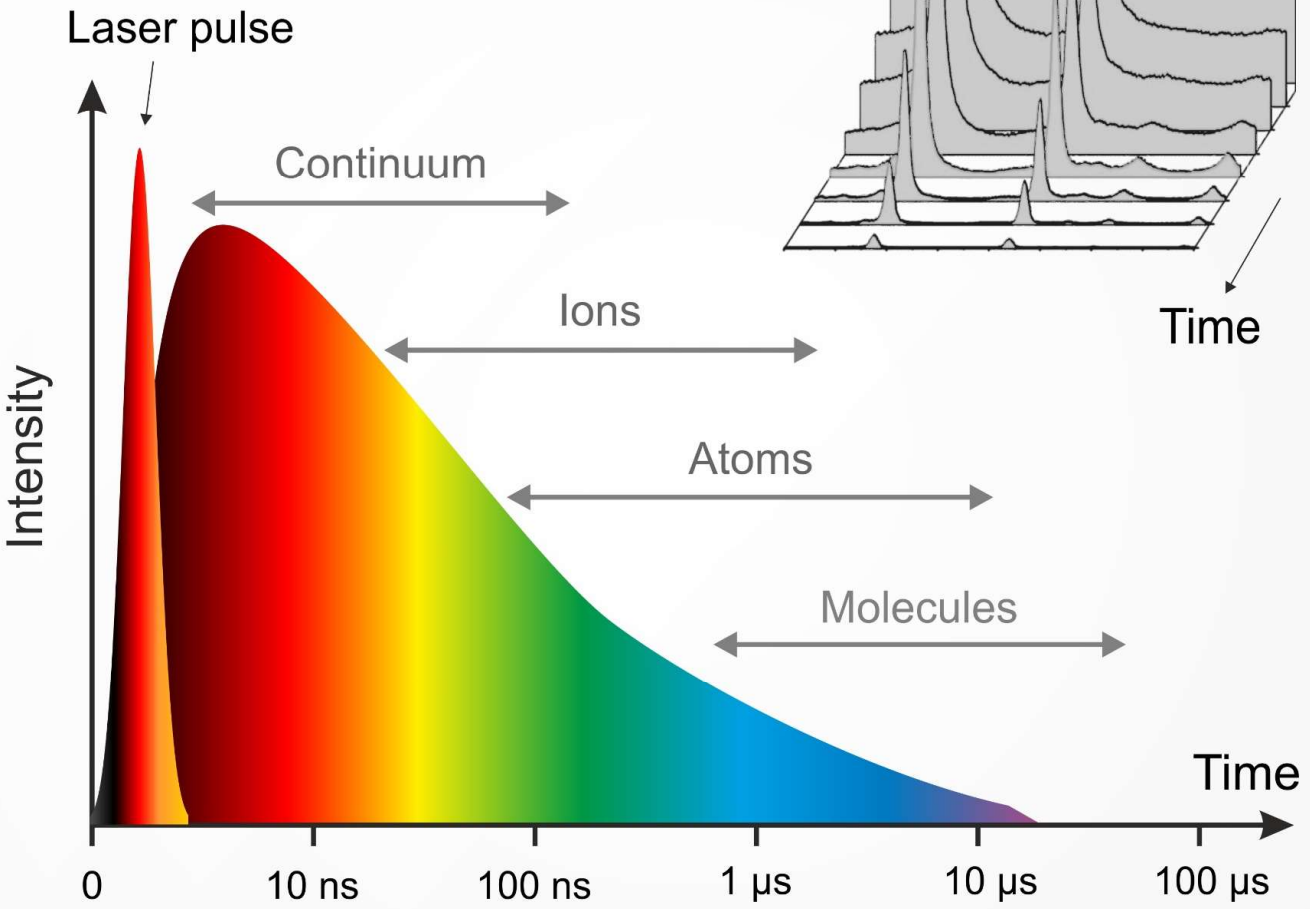


Evolution temporelle



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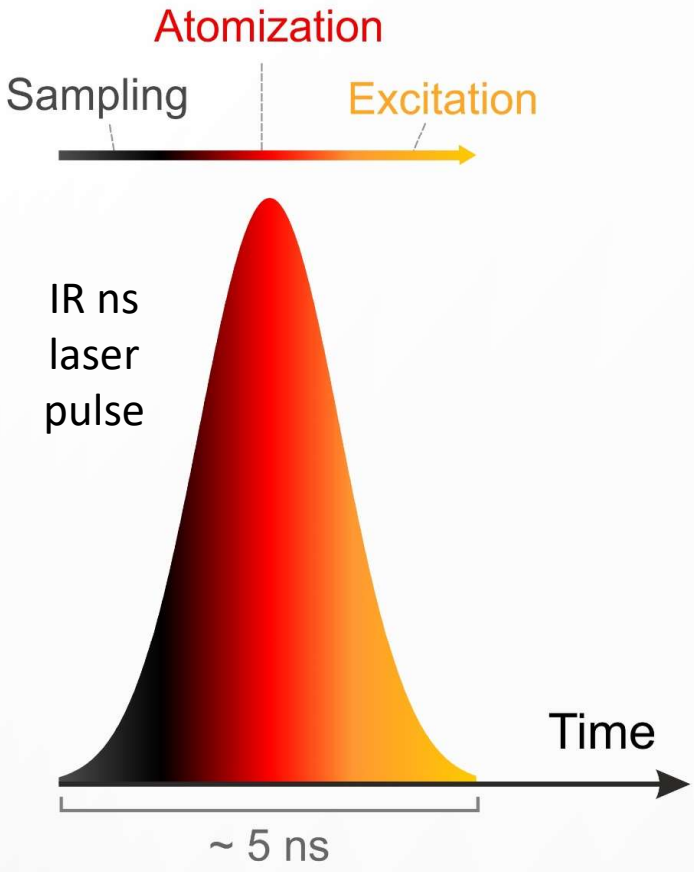

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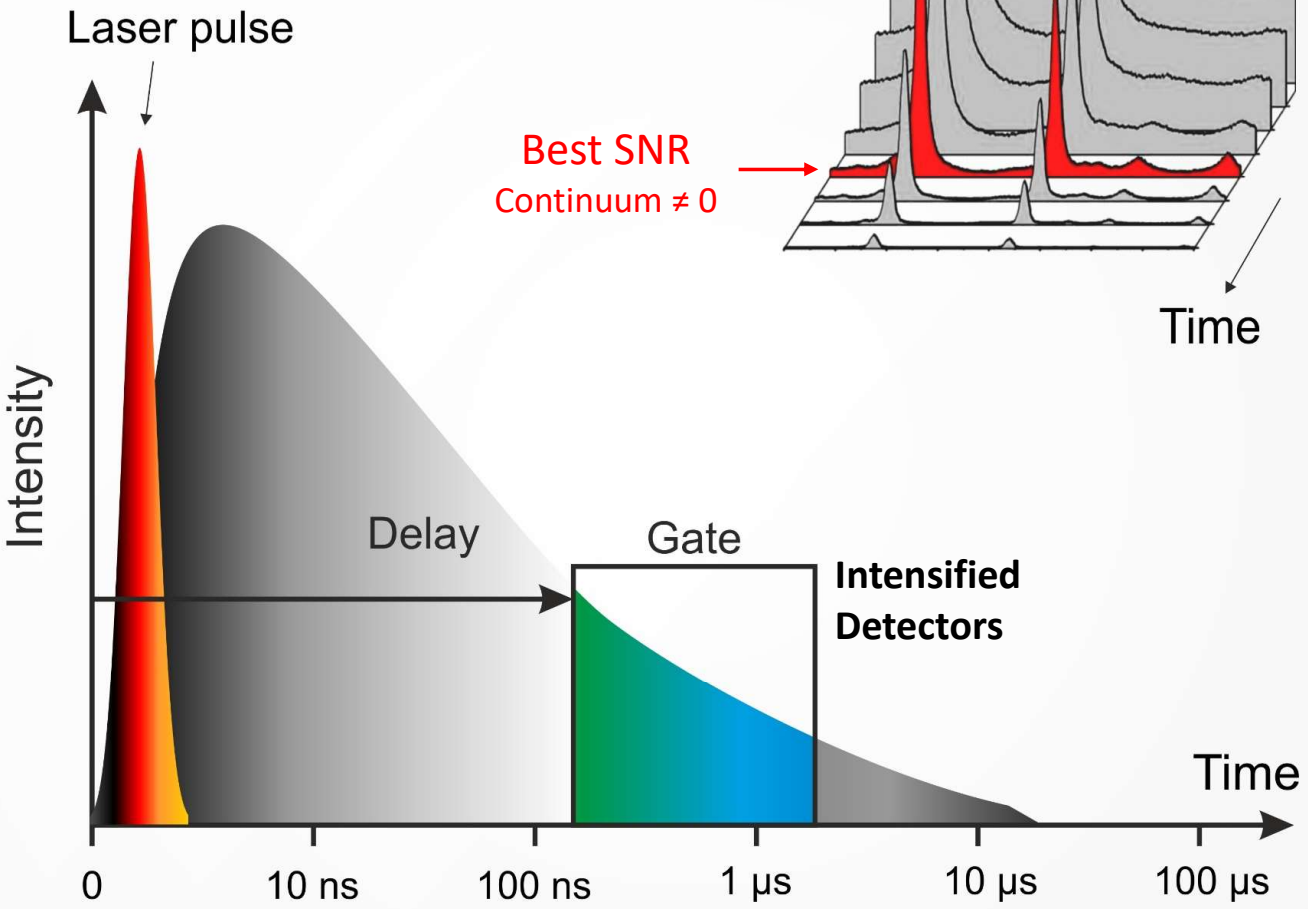
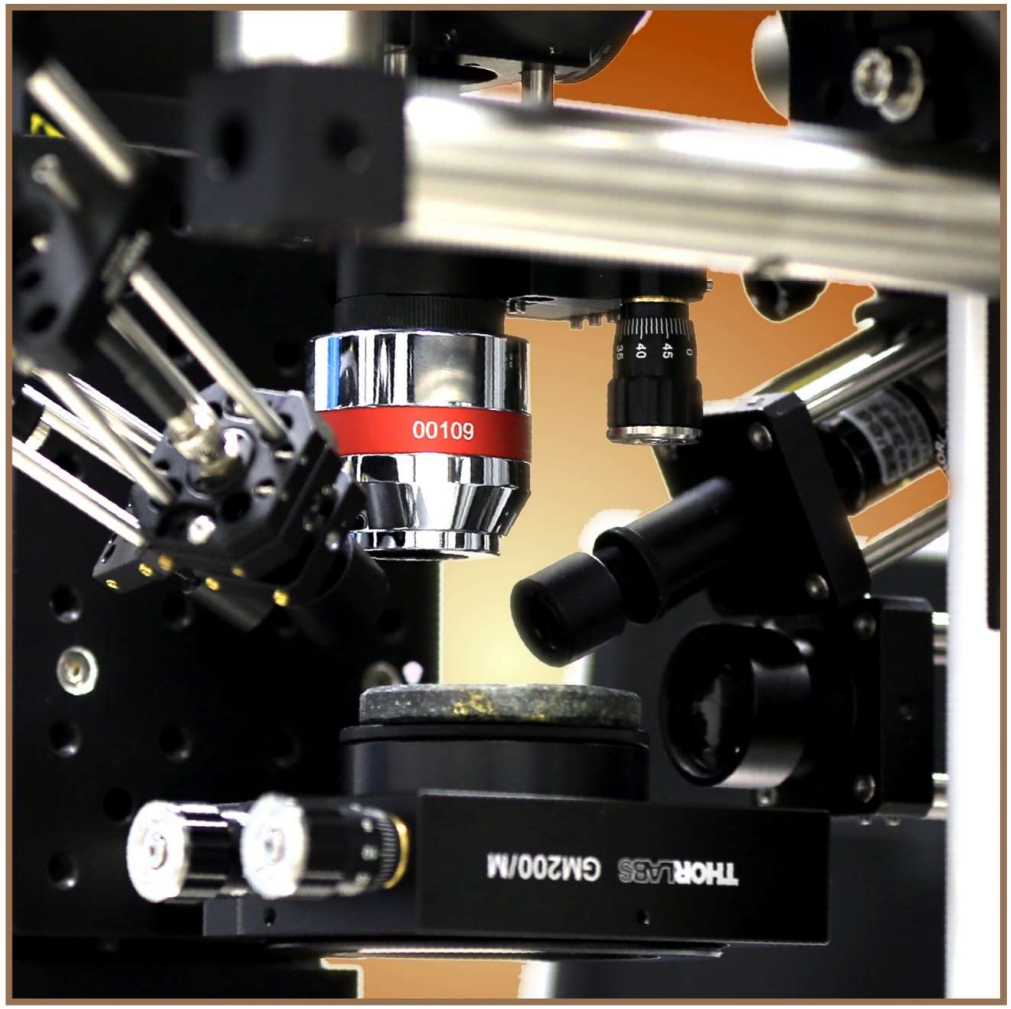


Plan

Imagerie élémentaire par LIBS



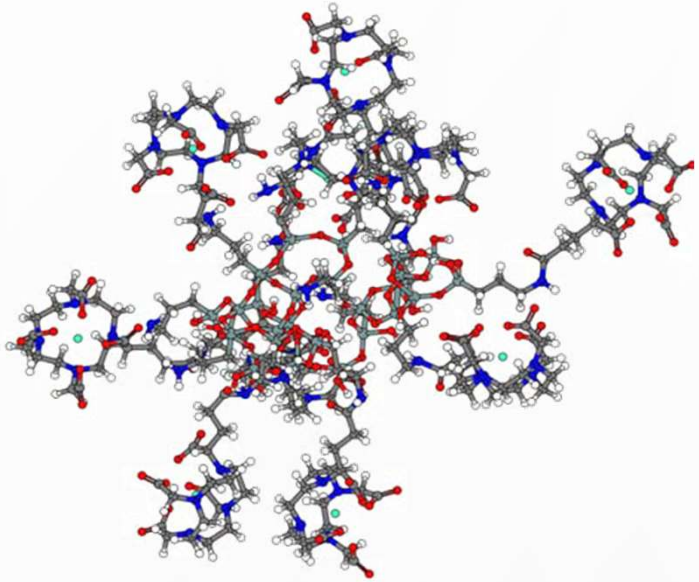
Imagerie élémentaire à l'ILM

À l'origine du projet

Toxicologie des AGuiX? (équipe Fennec)

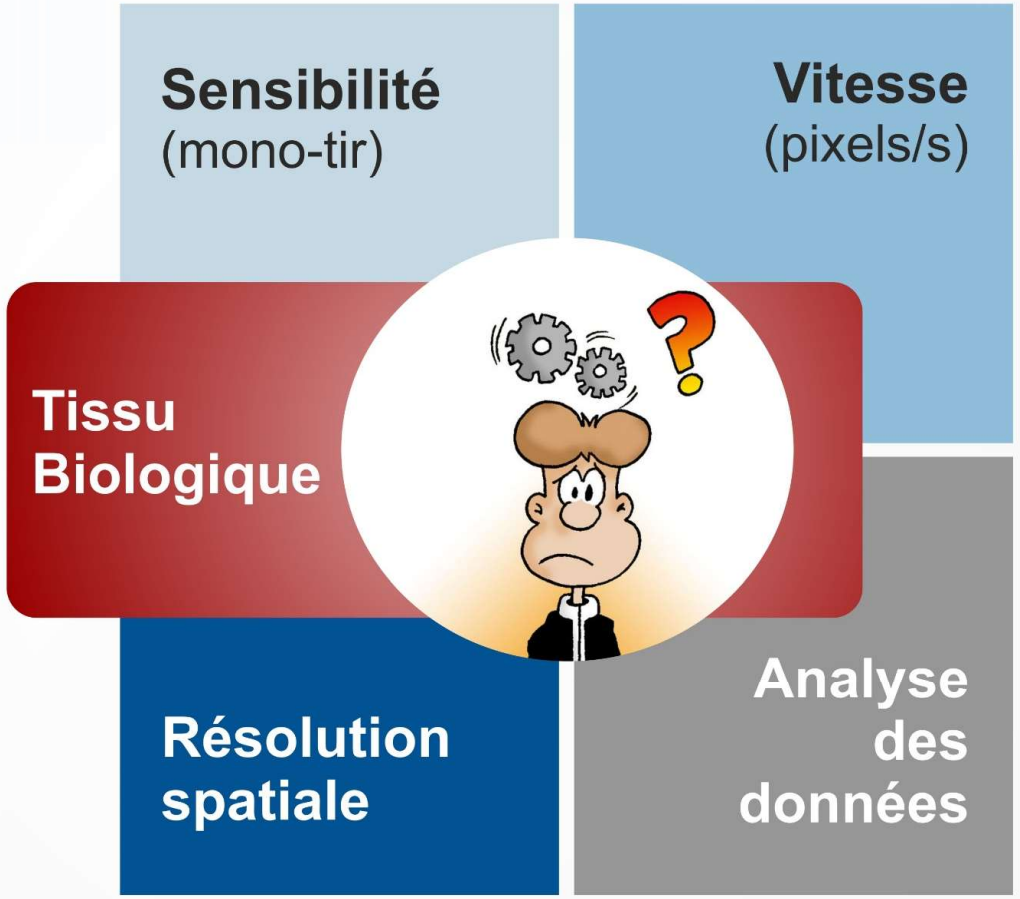
Elimination rénale?

AGuIX **Si/Gd-Based NPs < 5 nm**



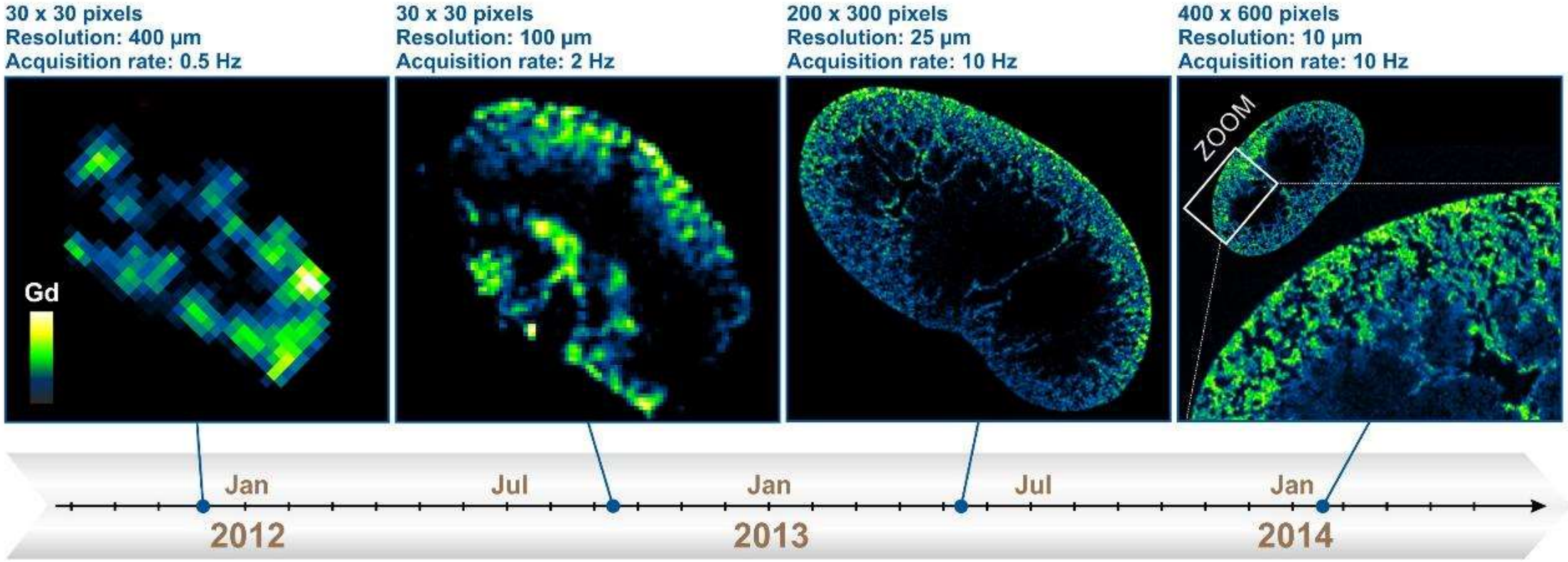
Lux, F. *et al.* Angew. Chem. Int. Ed. Engl. 50, (2011).

Vous avez dit défi?



Brève chronologie

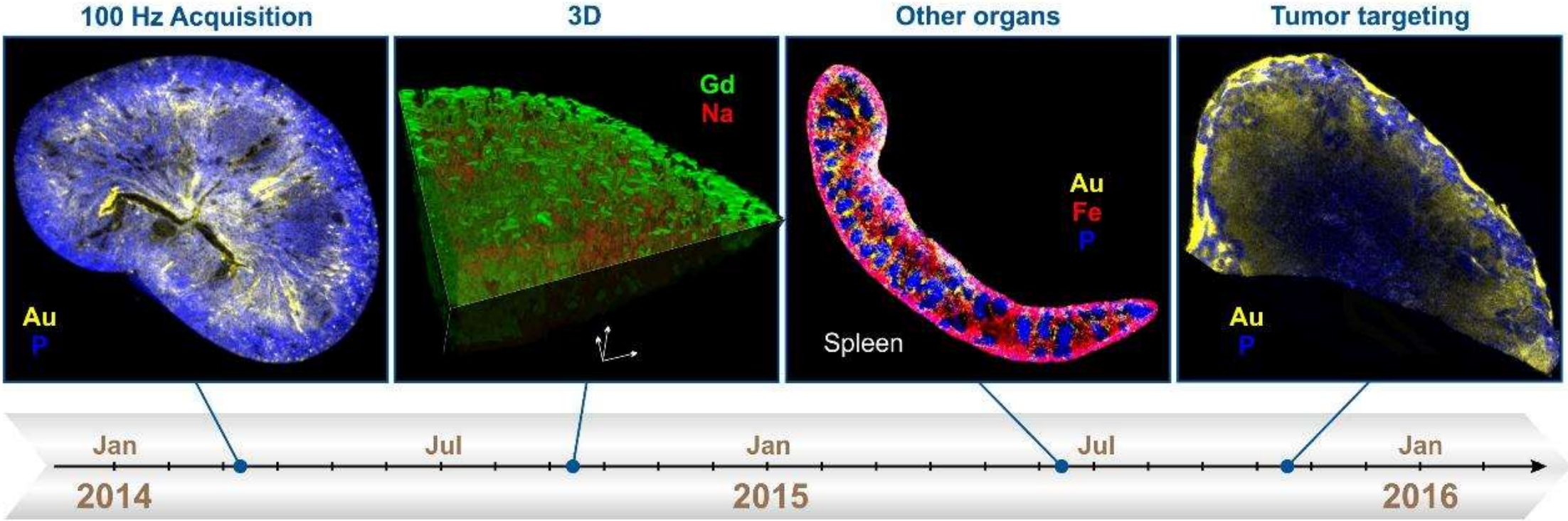
Imagerie LIBS à l'ILM (2012-2014)



Motto-Ros et al., SAB (2013)
Motto-Ros et al., APL (2013)
L. Sancey *et al.*, Sci. Rep. **4** (2014)
L. Sancey, *et al.*, J. Vis. Exp. (2014)

Brève chronologie

Imagerie LIBS à l'ILM (2014-2016)



A. Detappe *et al.* J. Cont. Rel. (2016)
Y. Gimmenez *et al.* Sci. Rep. (2016)
S. Kunjachan *et al.*, Nano letters **15** (2015)
L. Sancey *et al.*, ACS Nano **9** (2015)
A. Moussaron *et al.*, Small **9** (2015)

Brève chronologie

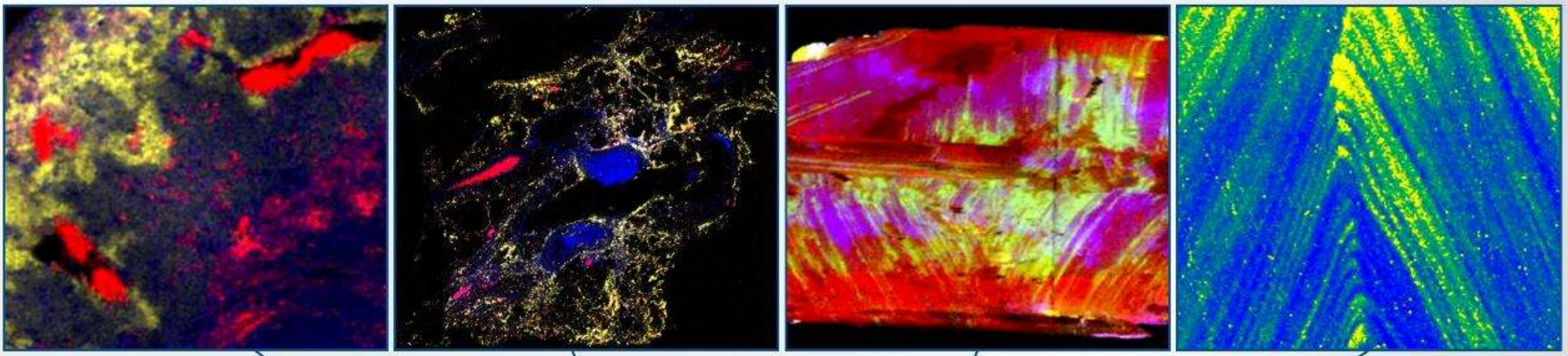
Imagerie LIBS à l'ILM (2016-2021)

iLM Institut Lumière Matière

cetim Grand Est

OPTOLYSE

Biologie | **Médecine** | **Géologie** | **Industrie**



Détection et Validation d'applications

F. Trichard *et al.* JAAS (2017)
J. Caceres *et al.* Sci. Rep. (2017)
F. Trichard *et al.* Spectrochim. Act. B (2017)
S. Moncayo *et al.* Spectrochim. Act. B (2017)
L. Bassel *et al.*, Environ. Sci. Pollut. Res. (2016)
G. Alombert-Goget *et al.*, Optical Materials (2016)

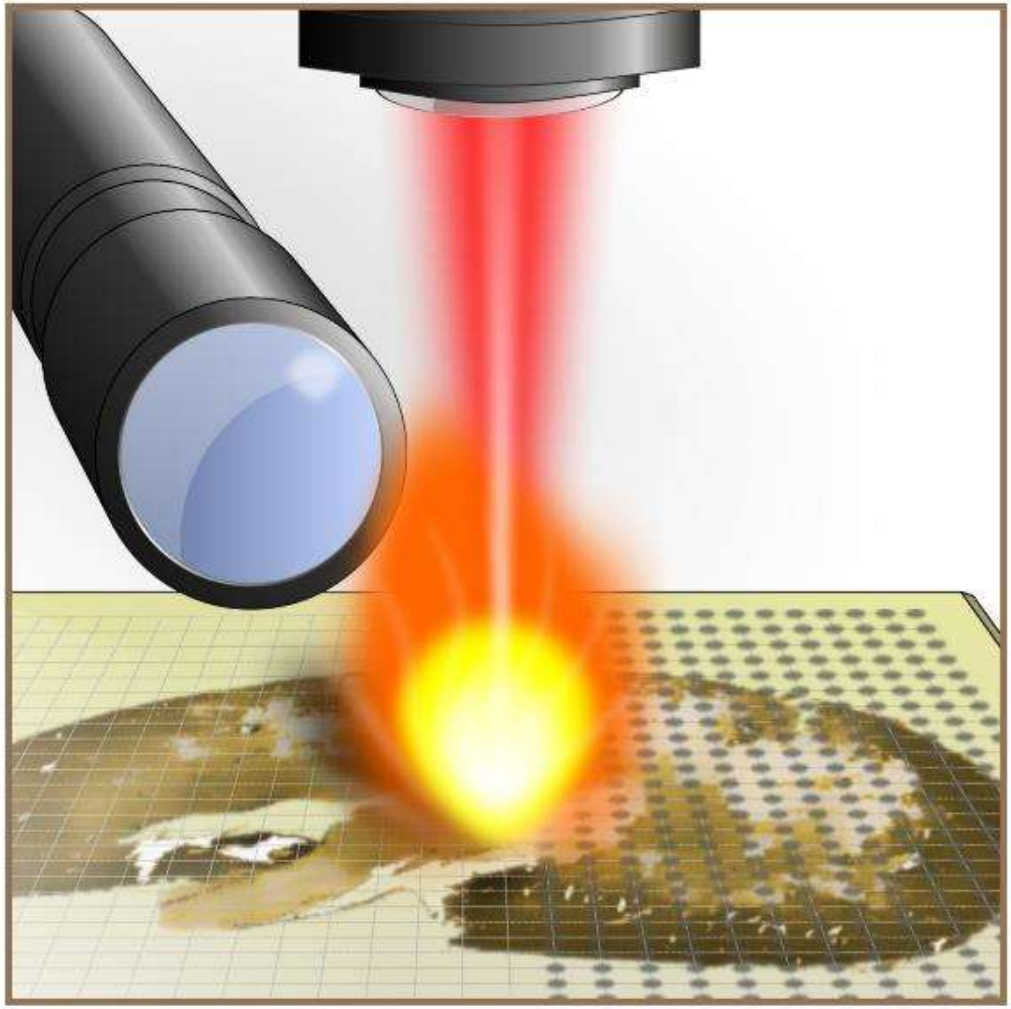
ABLATOM

Spin-off de l'Université de Lyon

www.ablatom.com

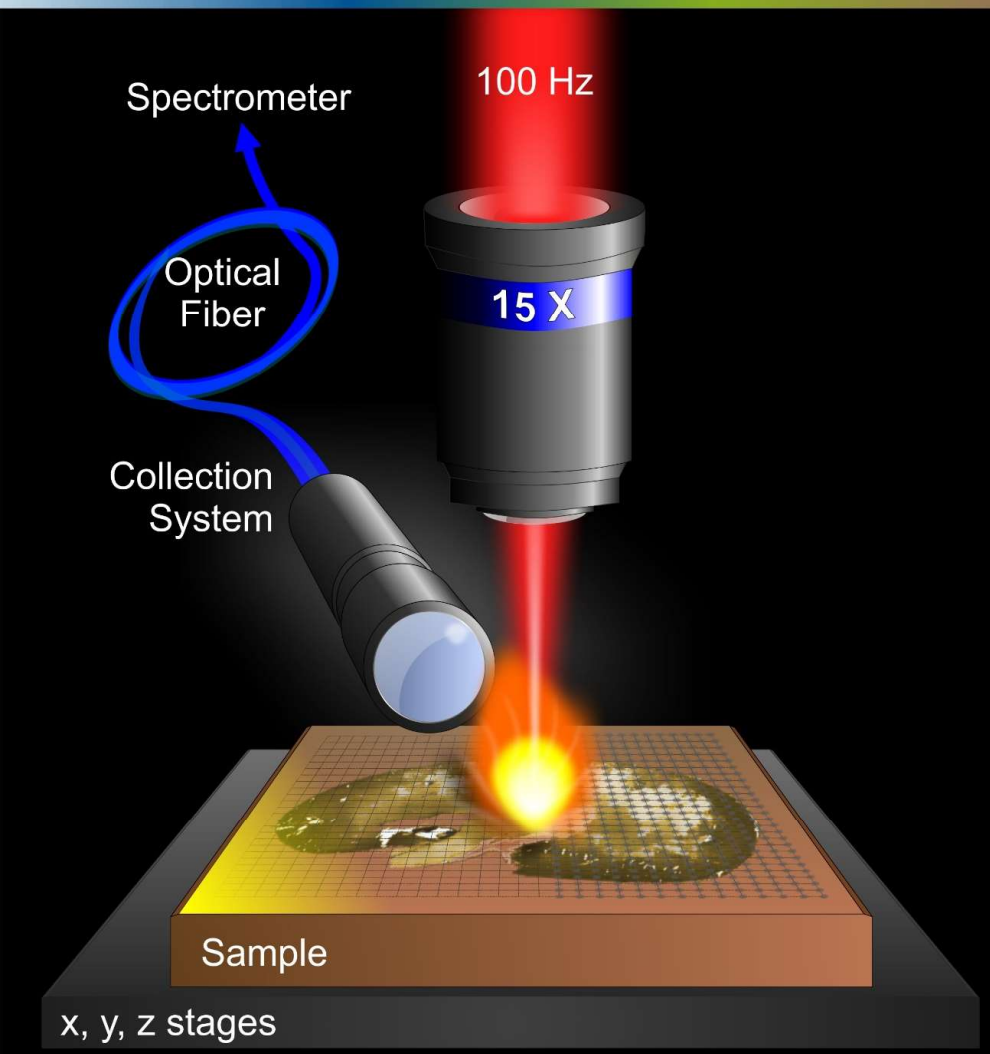
Plan

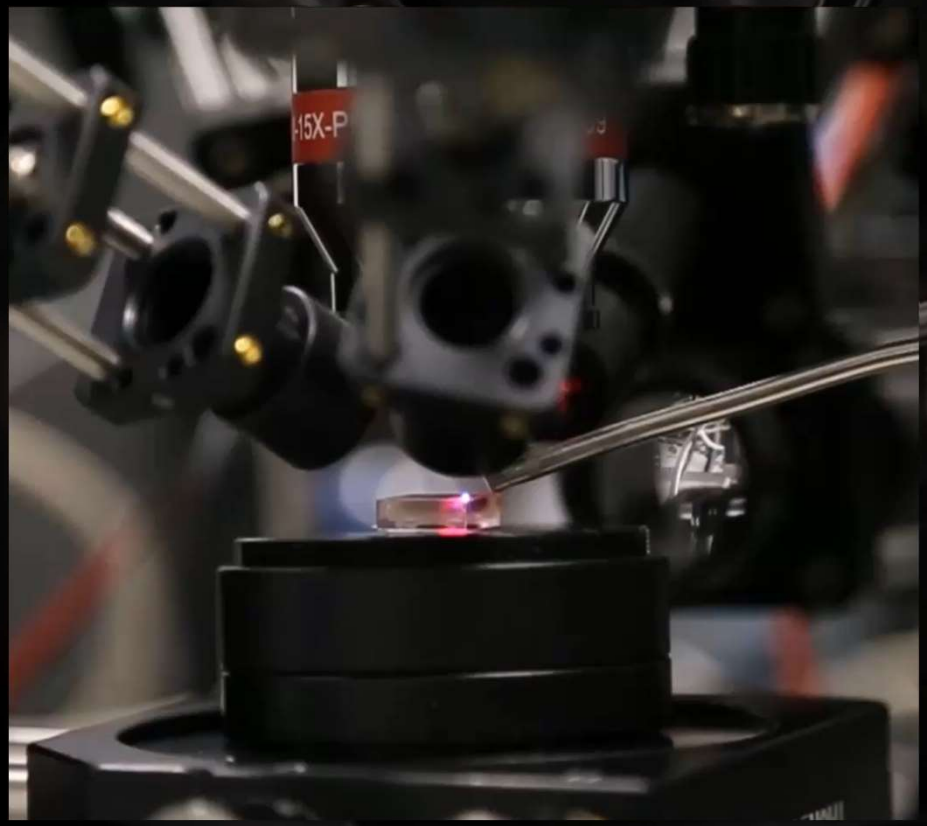
Imagerie élémentaire par LIBS



Imagerie élémentaire par LIBS

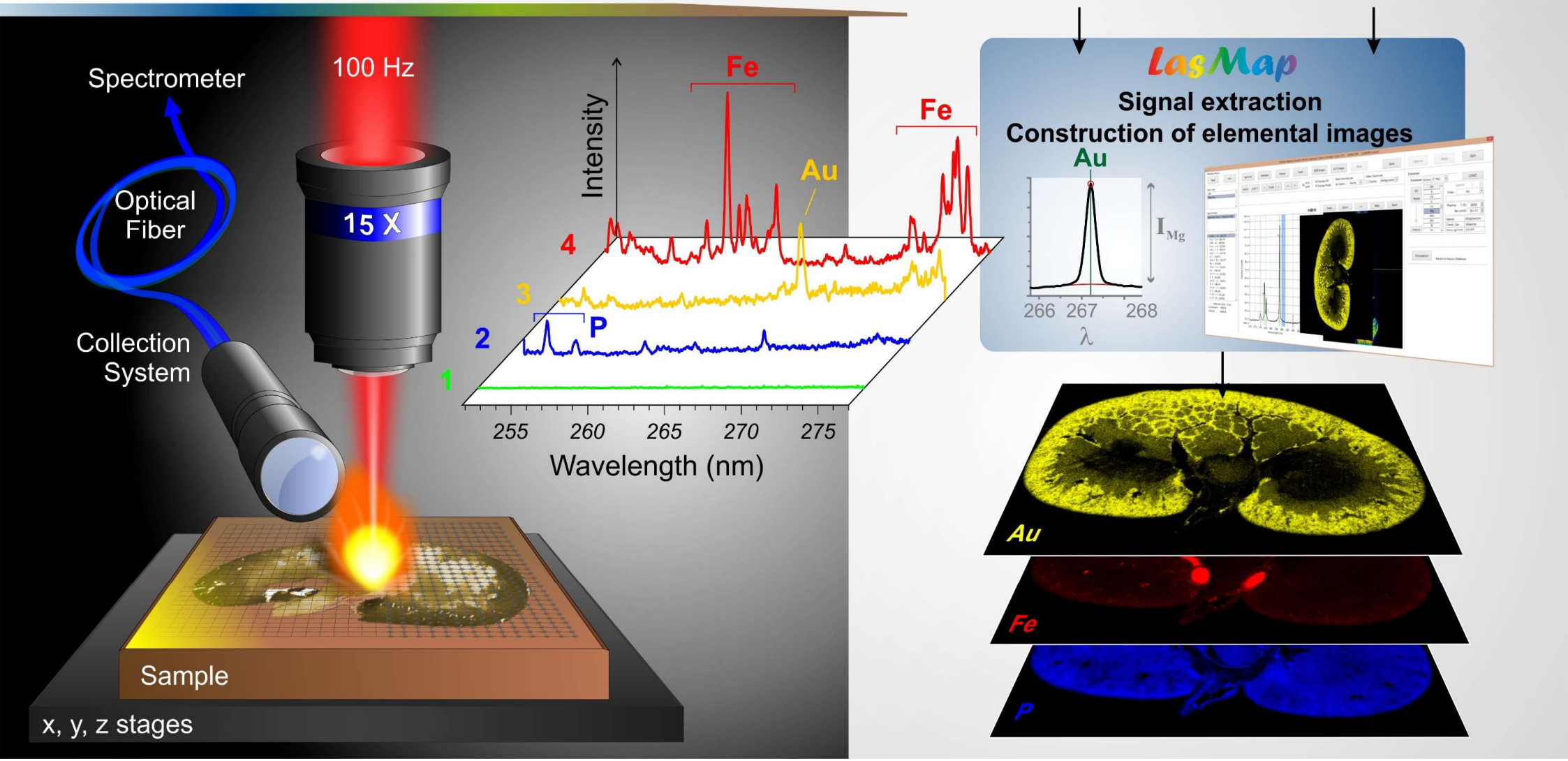
Principe

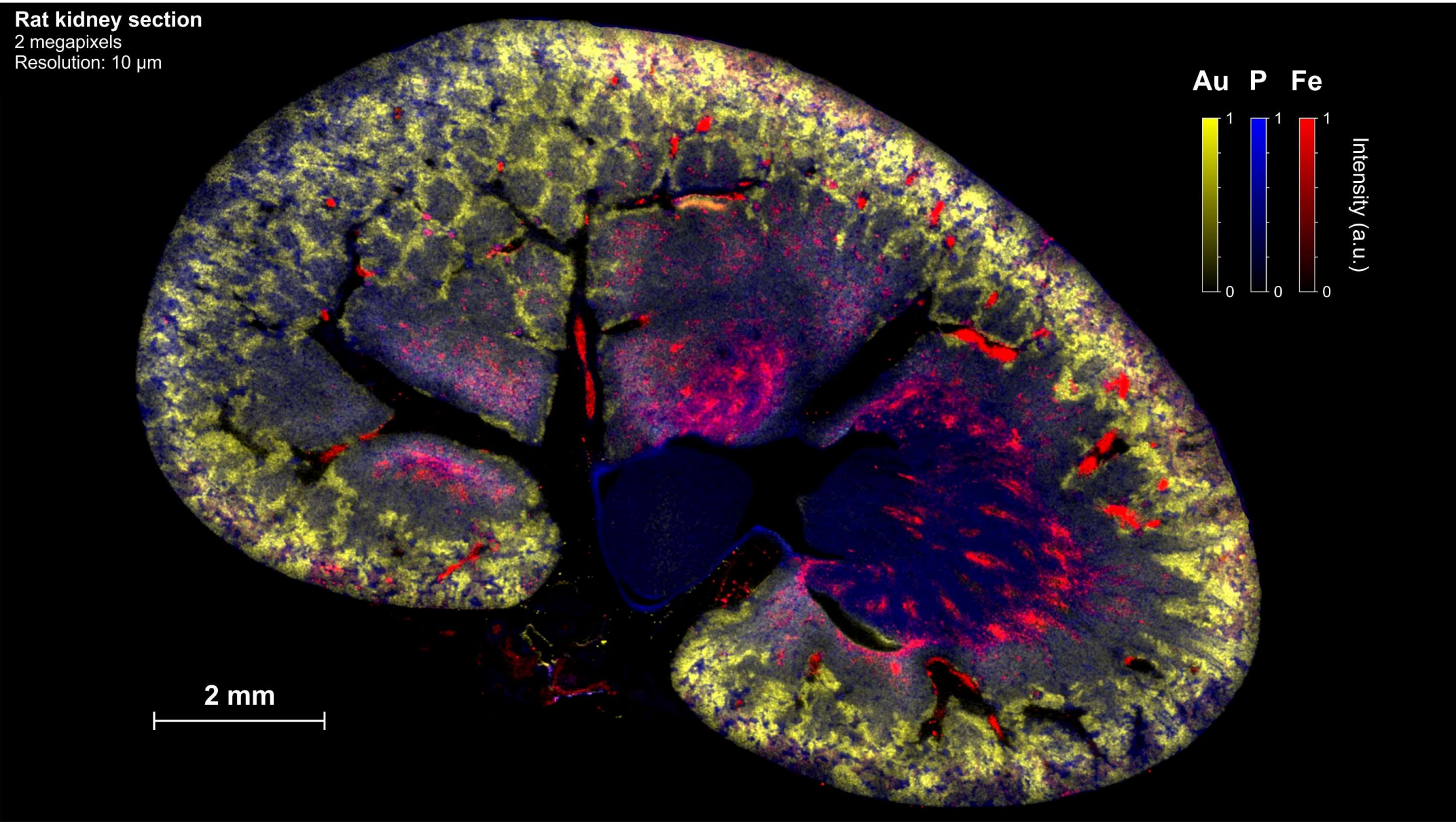


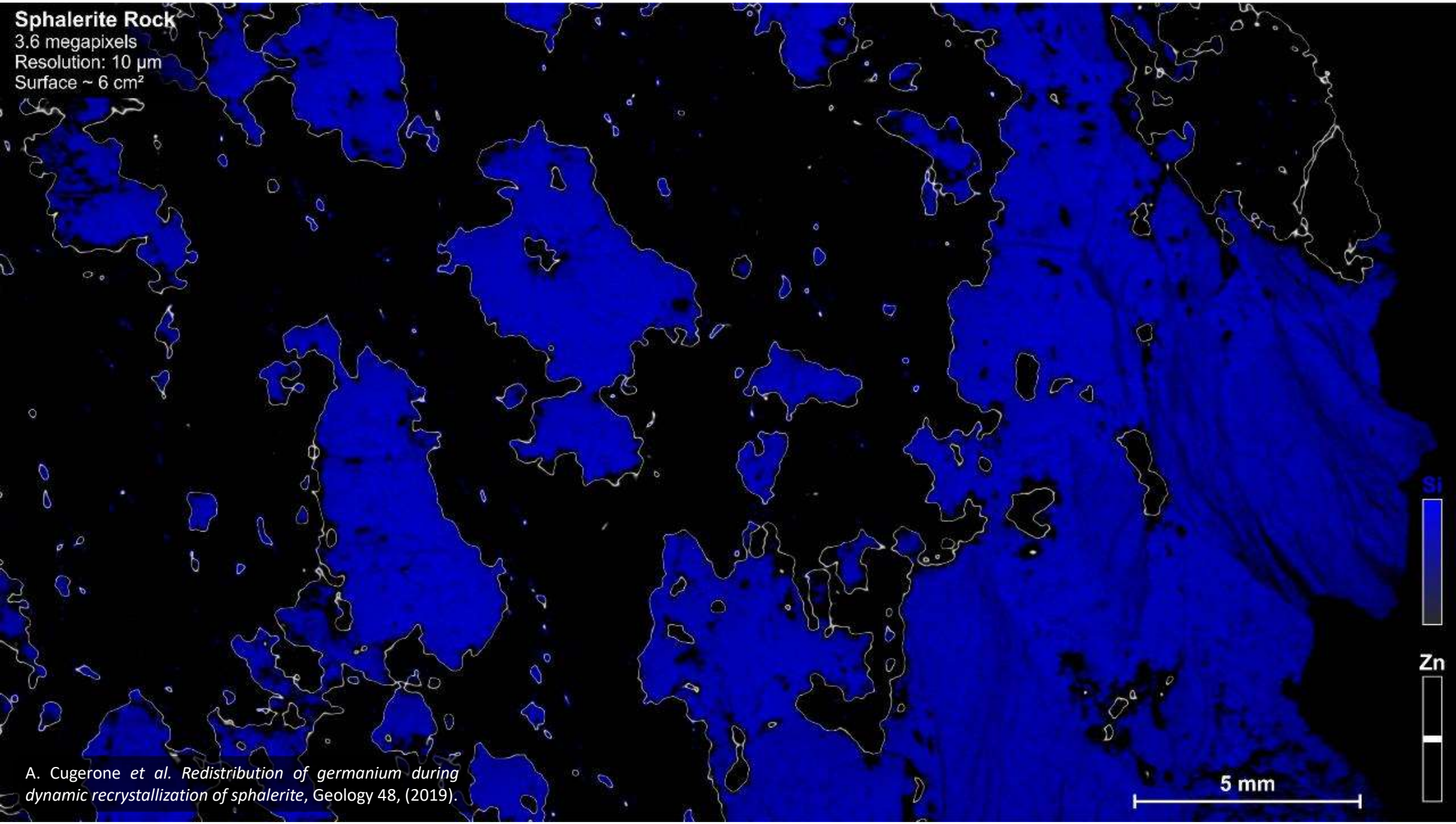


Imagerie élémentaire par LIBS

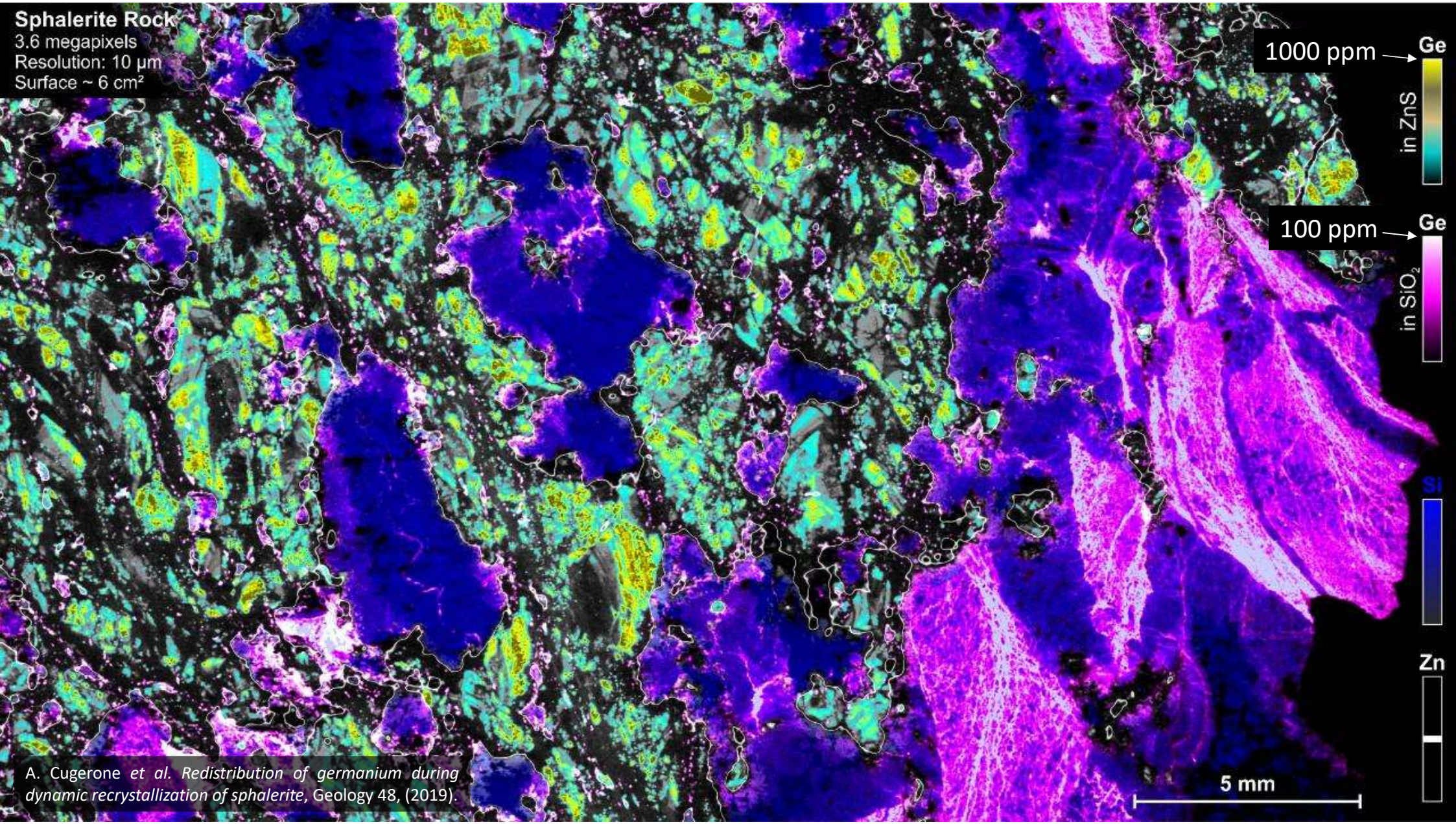
Principe




Rat kidney section
2 megapixels
Resolution: 10 µm
Au
P
Fe
1
0
1
0
1
0
Intensity (a.u.)
2 mm

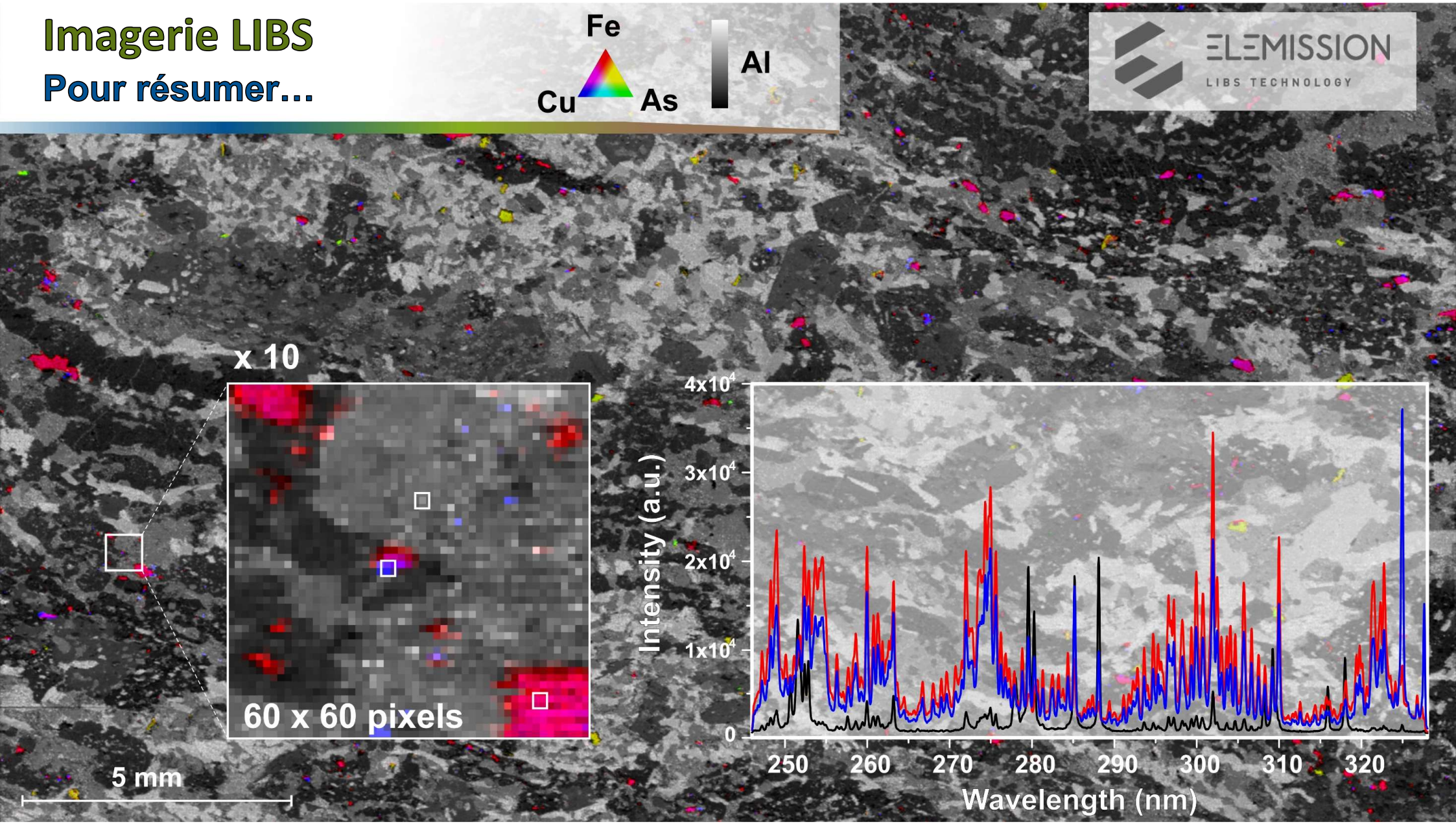


A. Cugerone *et al. Redistribution of germanium during dynamic recrystallization of sphalerite*, Geology 48, (2019).


Sphalerite Rock
3.6 megapixels
Resolution: 10 µm
Surface ~ 6 cm²
1000 ppm
Ge
in ZnS
100 ppm
Ge
in SiO2
Si
Zn
5 mm
A. Cugerone et al. Redistribution of germanium during dynamic recrystallization of sphalerite, Geology 48, (2019).

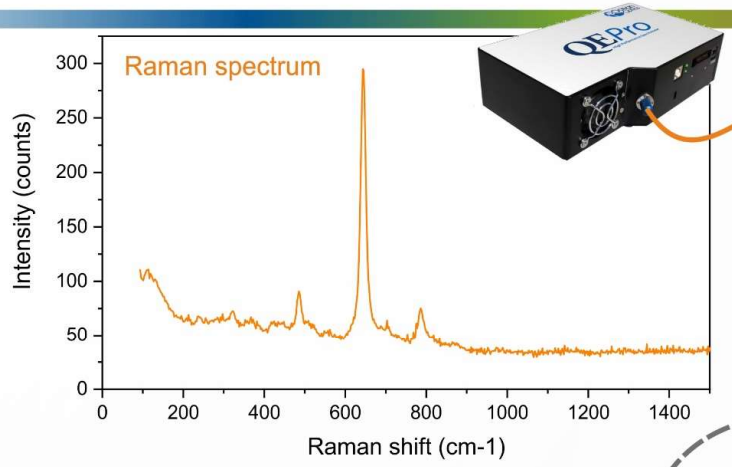
Imagerie LIBS

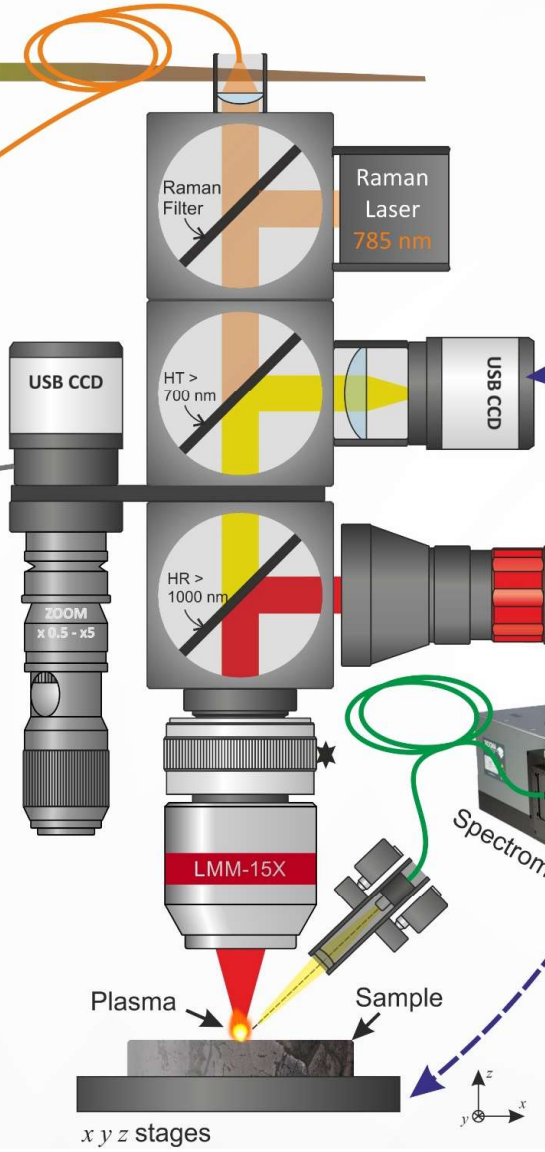
Pour résumer…

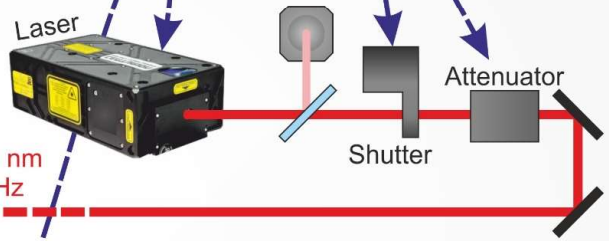


Instrumentation

Microscope “maison”







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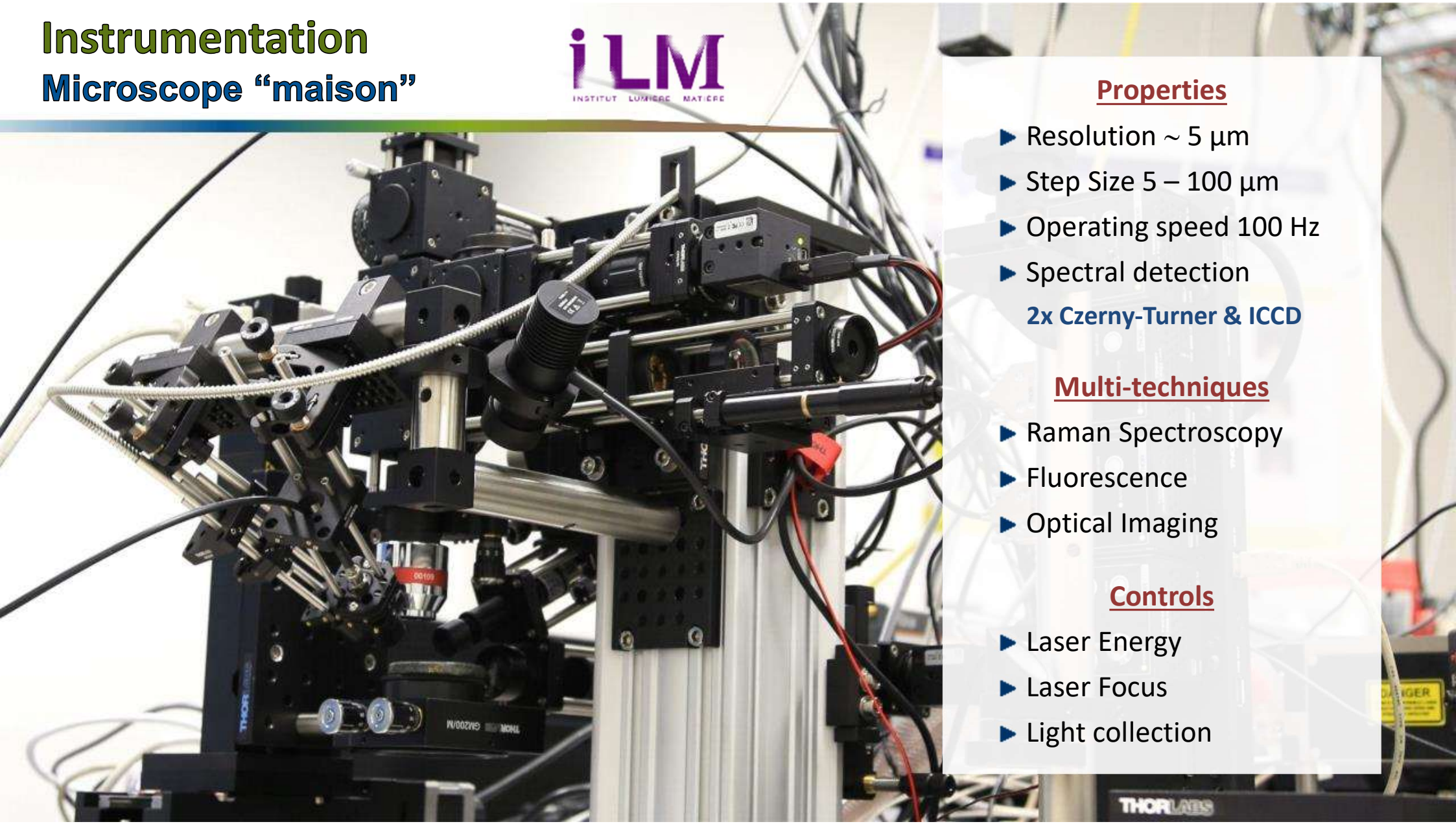


Properties

- Resolution ~ 5 µm
- Step Size 5 – 100 µm
- Operating speed 100 Hz
- Spectral detection

  2x Czerny-Turner & ICCD

Multi-techniques

- Raman Spectroscopy
- Fluorescence
- Optical Imaging

Controls

- Laser Energy
- Laser Focus
- Light collection

Equipements à l'ILM

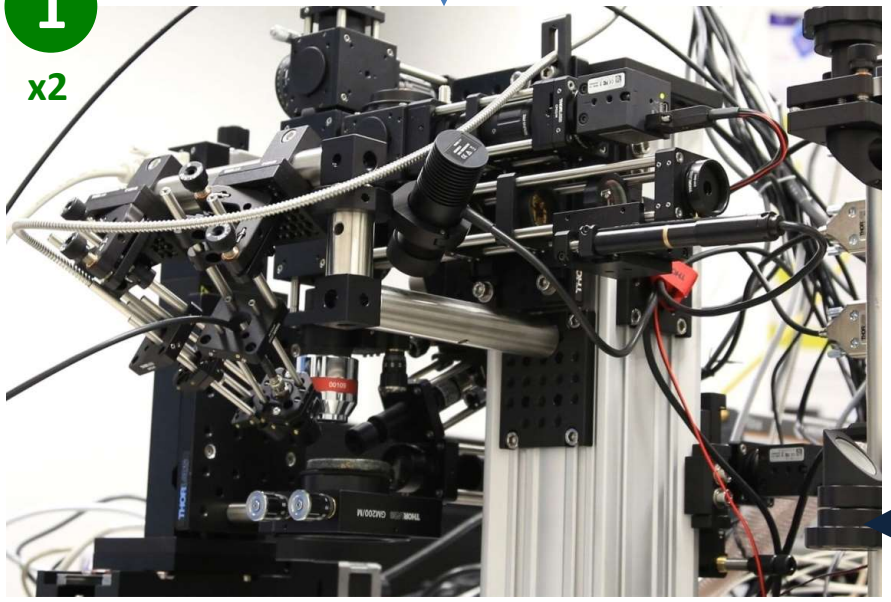
OptoLYSE

Optical analysis platform financed by the CPER2016

Project led by Christophe Dujardin, and implemented by Sylvain Hermelin.

1

x2



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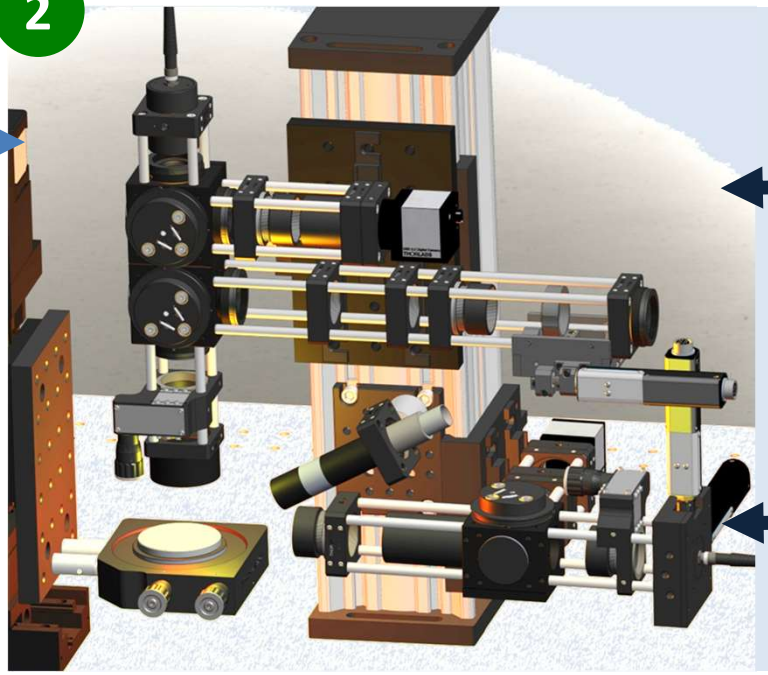


Optical Parametric Oscillator (ns, 50 Hz, UV-Vis)

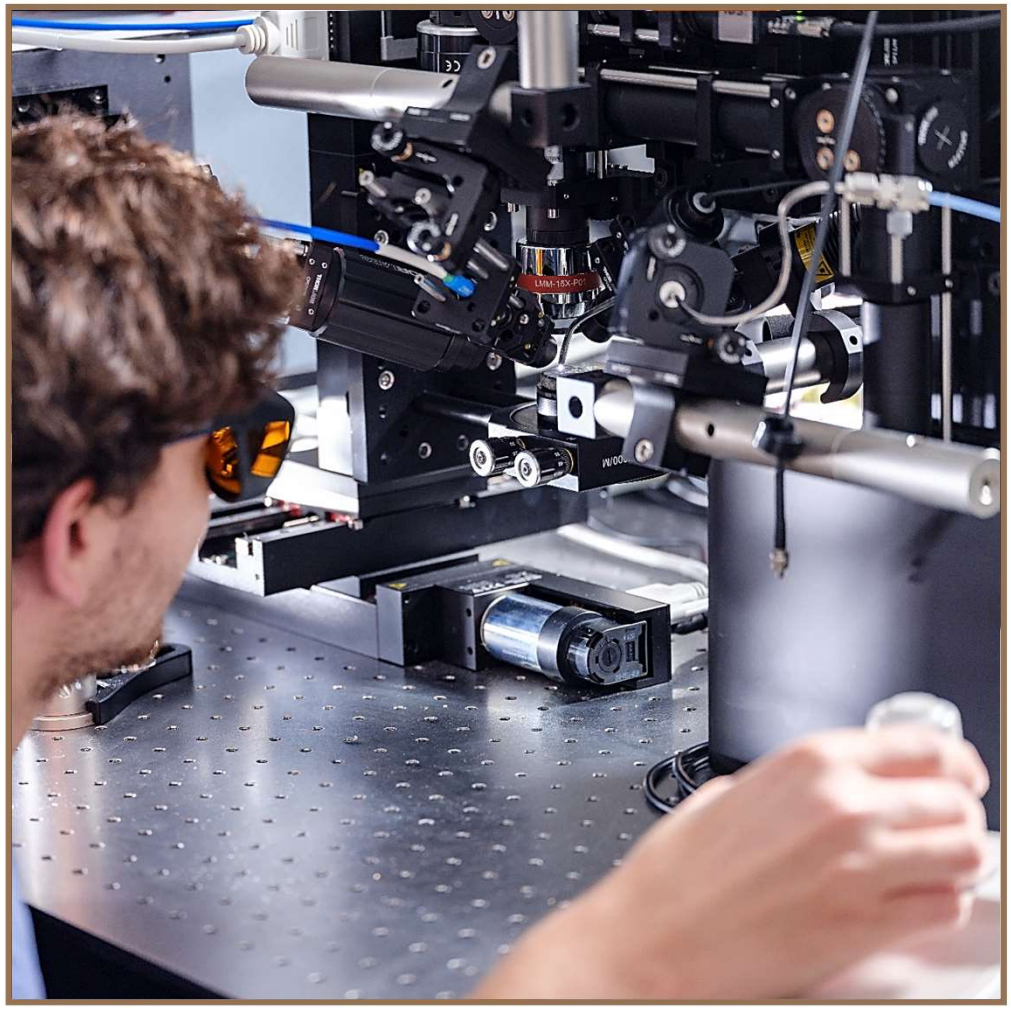
200 – 1000 nm

Ablation UV

Ablation IR, 100 Hz

Plan

Imagerie élémentaire par LIBS



µ-LIBS *v.s.* macro LIBS

Configurations géométriques typiques

Macro

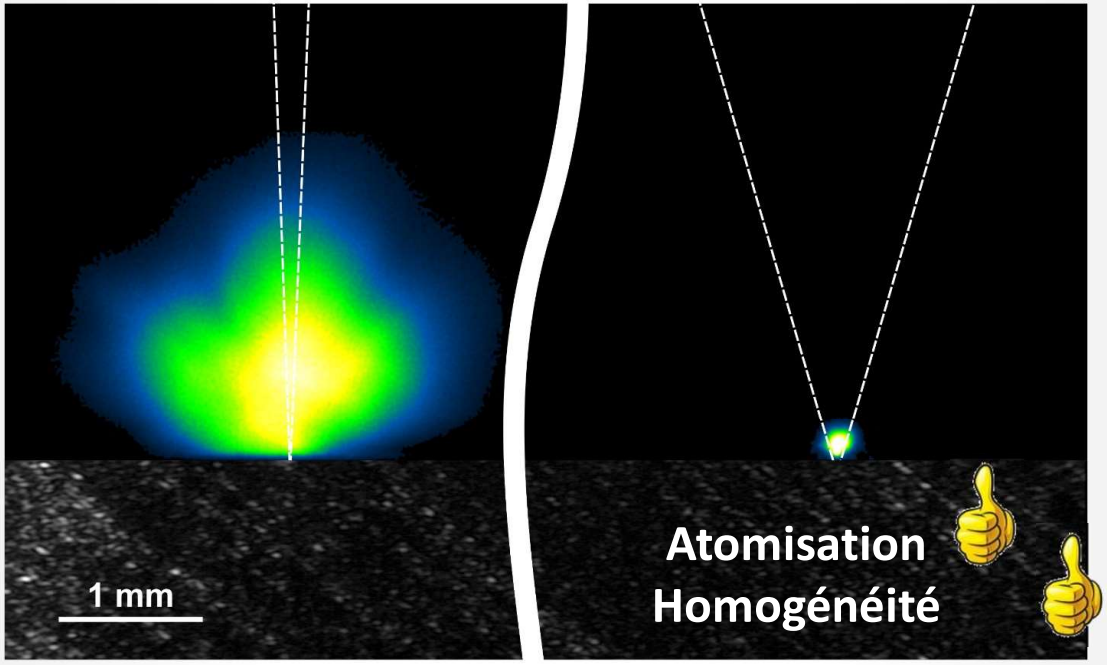
30 mJ

f = 75 mm

NA = 0.05

~ 30 µm	Spot size	~ 3 µm
> mm	Plasma size	~ 200 µm
~ mm	Rayleigh ℓ	~ 20 µm
~ µg	Ablated Mass	< ng

(at equivalent fluence)



Micro

500 µJ

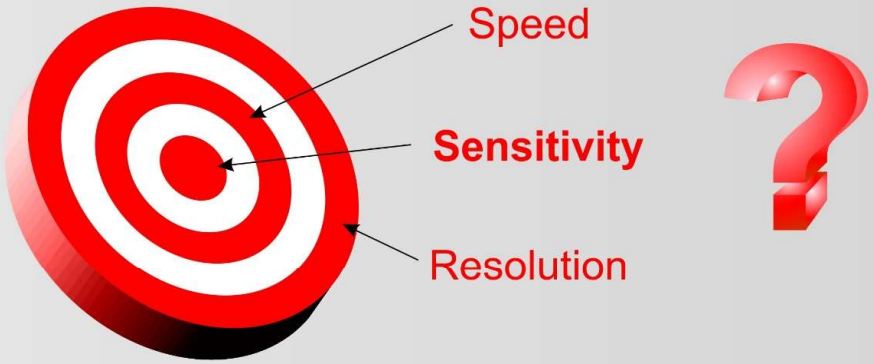
LMM-15X

f = 13 mm

NA = 0.3

Imagerie µ-LIBS

En ce qui concerne les performances !?

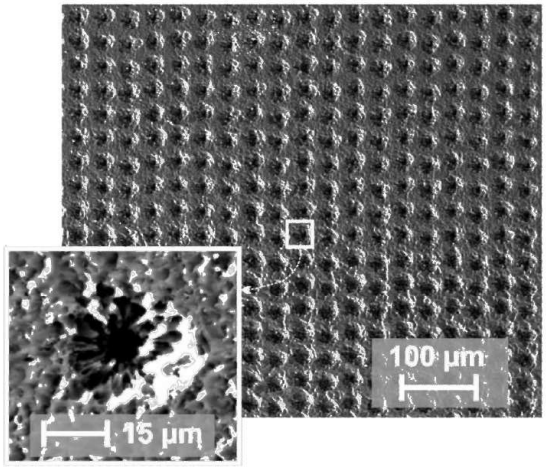


Resolution - Step Size

No overlap between consecutive laser shots to improve the repeatability

The accessible resolution (or step size) is ultimately governed by the laser-induced damage (crater size, damage induced by the shock wave, etc.)

M ~ 0.3 ng

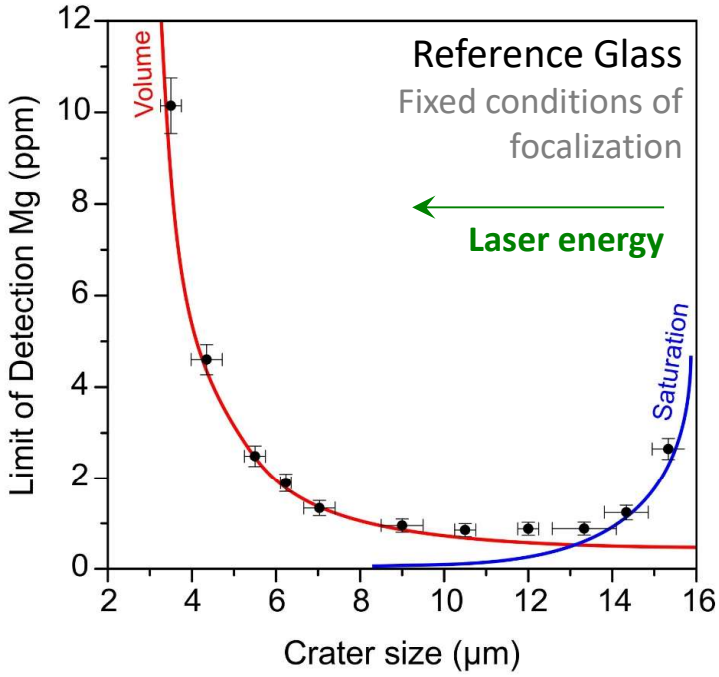


Detection Limits

LIBS signal $\sim f \cdot m_{abl}$

Reducing the crater size (i.e. volume) decreases the ablated mass (plasma density), and so the LIBS signal…

→ **Balance between resolution and LoDs**



Sensibilité

Limite de détection

< ppm
< 20 ppm
> 500 ppm

Periodic Table

And estimated
LIBS LOD (ppm)

1 H hygrogen 200																	2 He helium n.c.
3 Li lithium 0.1	4 Be berylium 0.1											5 B boron 1	6 C carbon 500	7 N nitrogen 10 000	8 O oxygen 10 000	9 F fluorine 100 000	10 Ne neon n.c.
11 Na sodium 0.7	12 Mg magnesium 0.3											13 Al aluminum 2	14 Si silicon 10	15 P phosphorous 70	16 S sulphur 100	17 Cl cholrine 20 000	18 Ar argon n.c.
19 K potassium 4	20 Ca calcium 0.5	21 Sc scandium 2	22 Ti titanium 5	23 V vanadium 5	24 Cr chromium 4	25 Mn manganese 4	26 Fe iron 20	27 Co cobalt 5	28 Ni nickel 12	29 Cu copper 2	30 Zn zinc 5	31 Ga gallium 3	32 Ge germanium 7	33 As arsenic 8	34 Se selenium 100	35 Br bromine n.c.	36 Kr krypton n.c.
37 Rb rubidium 10	38 Sr strontium 0.8	39 Y yttrium 4	40 Zr zirconium 12	41 Nb niobium 20	42 Mo molybdenum 8	43 Tc technetium n.c.	44 Ru ruthenium 12	45 Rh rhodium 10	46 Pd palladium 5	47 Ag silver 2	48 Cd cadmium 5	49 In indium 6	50 Sn tin 20	51 Sb antimony 5	52 Te tellurium 30	53 I iodine n.c.	54 Xe xenon n.c.
55 Cs caesium 1 000	56 Ba barium 3	R.E.E.	72 Hf hafnium 3	73 Ta tantalum 10	74 W tungsten 90	75 Re rhenium 20	76 Os osmium 21	77 Ir iridum 14	78 Pt platinum 70	79 Au gold 12	80 Hg mercury 150	81 Tl thallium 5	82 Pb lead 8	83 Bi bismuth 4	84 Po polonium n.c.	85 At thallium n.c.	86 Rn radon n.c.
19 Fr francium n.c.	88 Ra radium n.c.																

57 La lanthanum 18	58 Ce cerium 500*	59 Pr praseodymium 200*	60 Nd neodymium 150	61 Pm promethium n.c.	62 Sm samarium 60	63 Eu europium 6	64 Gd gadolinium 40*	65 Tb terbium 40	66 Dy dysprosium 40*	67 Ho holmium 30	68 Re erbium 20	69 Tm thulium 20	70 Yb ytterbium 10	71 Lu lutetium 20
89 Ac actinium n.c.	90 Th thorium 10*	91 Pa proactinium n.c.	92 U uranium 10*	93 Np neptunium n.c.	94 Pu plutonium n.c.	95 Am americium n.c.	96 Cm curium n.c.	97 Bk berkelium n.c.	98 Cf californium n.c.	99 Es einsteinium n.c.	100 Fm fermium n.c.	101 Md mendelevium n.c.	102 No nobelium n.c.	103 Lr lawrencium n.c.

** Very dense spectral structure*
n.c. not present in the database

Spectroscopie d'émission

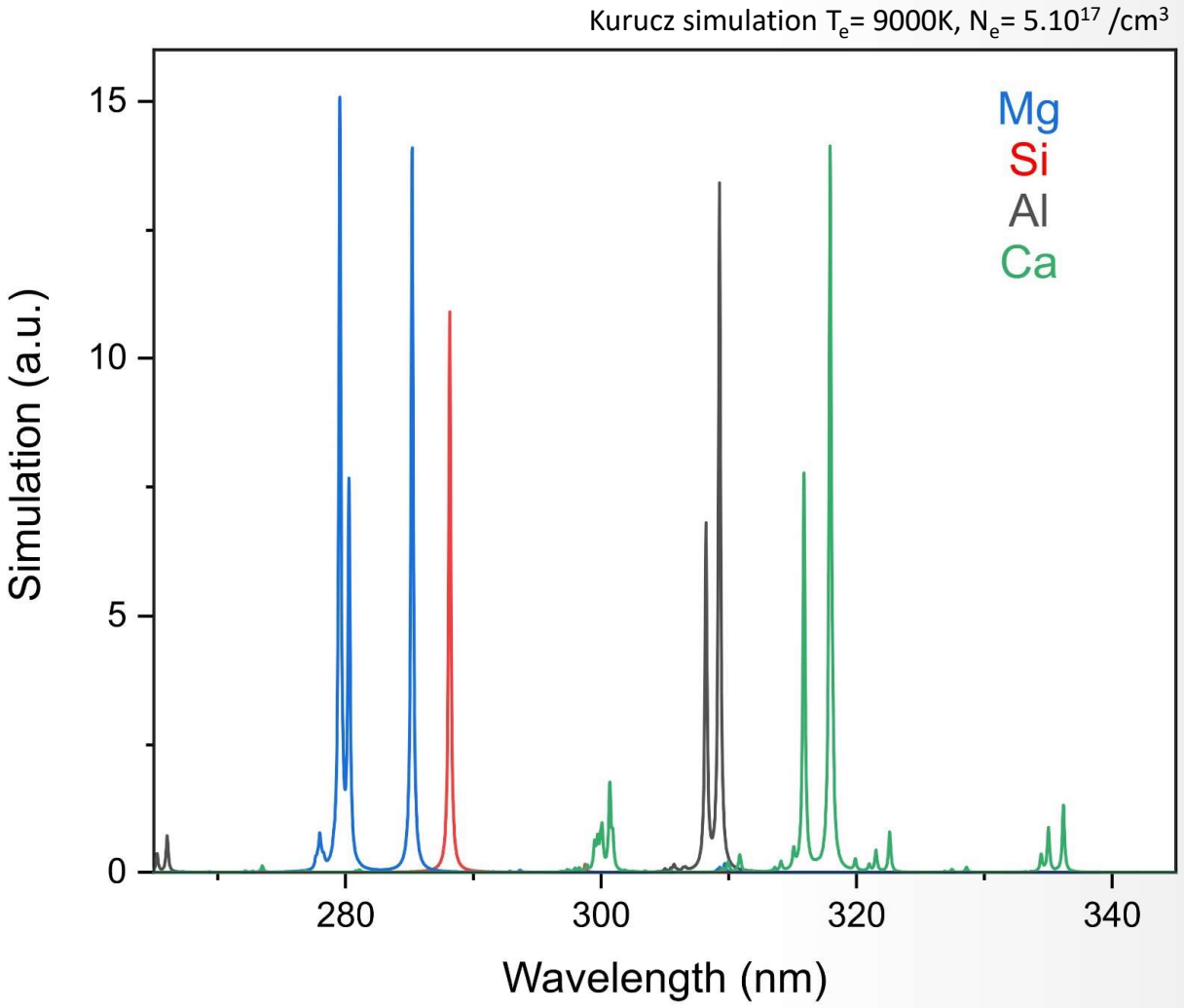
Quelques généralités

Structure spectrale complexe

Certains éléments peuvent avoir un nombres de raies très importantes donnant lieu a des interférences spectrales

Hétérogénéité des échantillons

Dans le cas des échantillons hétérogènes le traitement des données peut devenir très complexe



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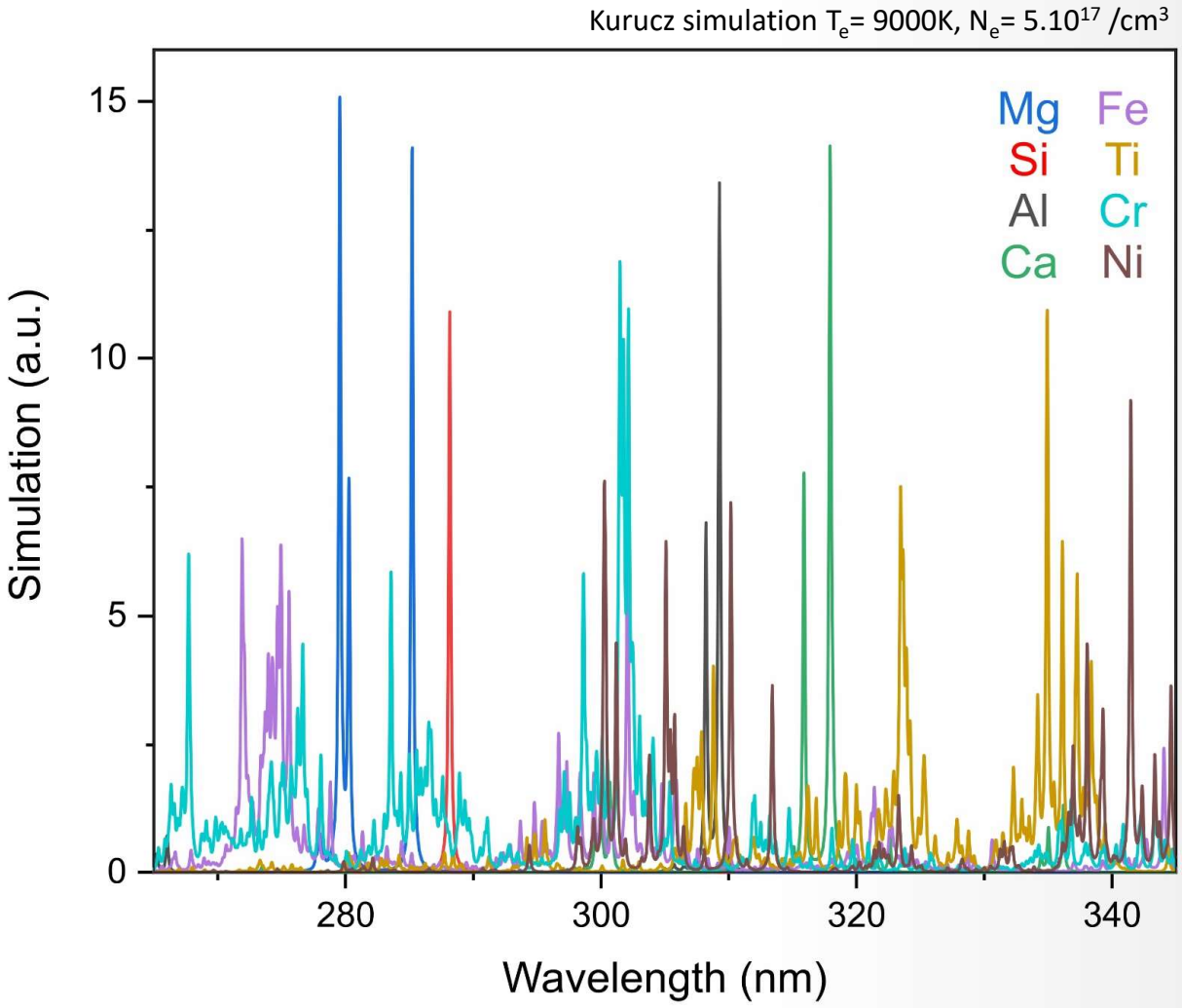

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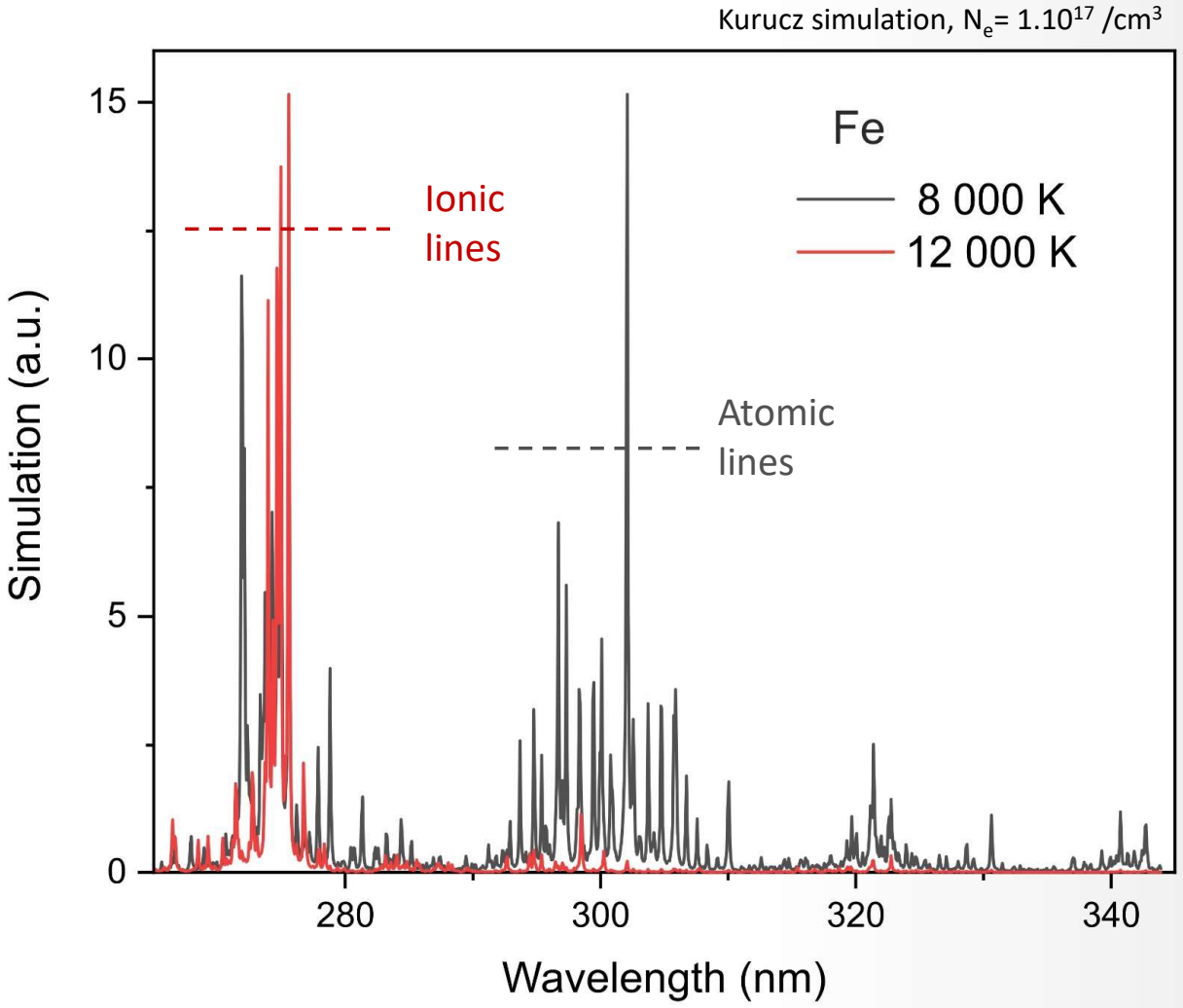
Dans le cas des échantillons hétérogènes le traitement des données peut devenir très complexe

Effets de matrice – dépendance des paramètres du plasma



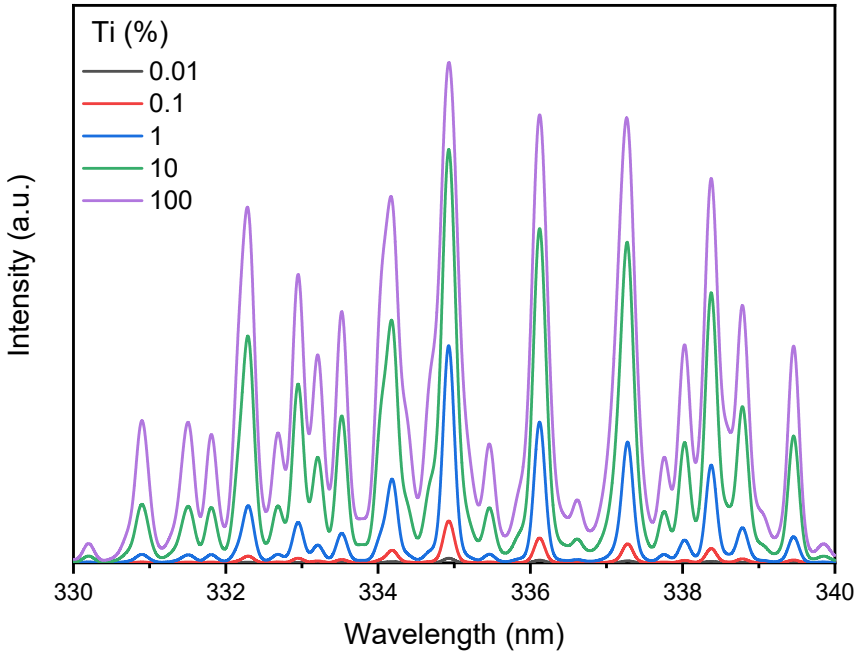
Spectroscopie d'émission

Quelques généralités

Gamme dynamique de mesure

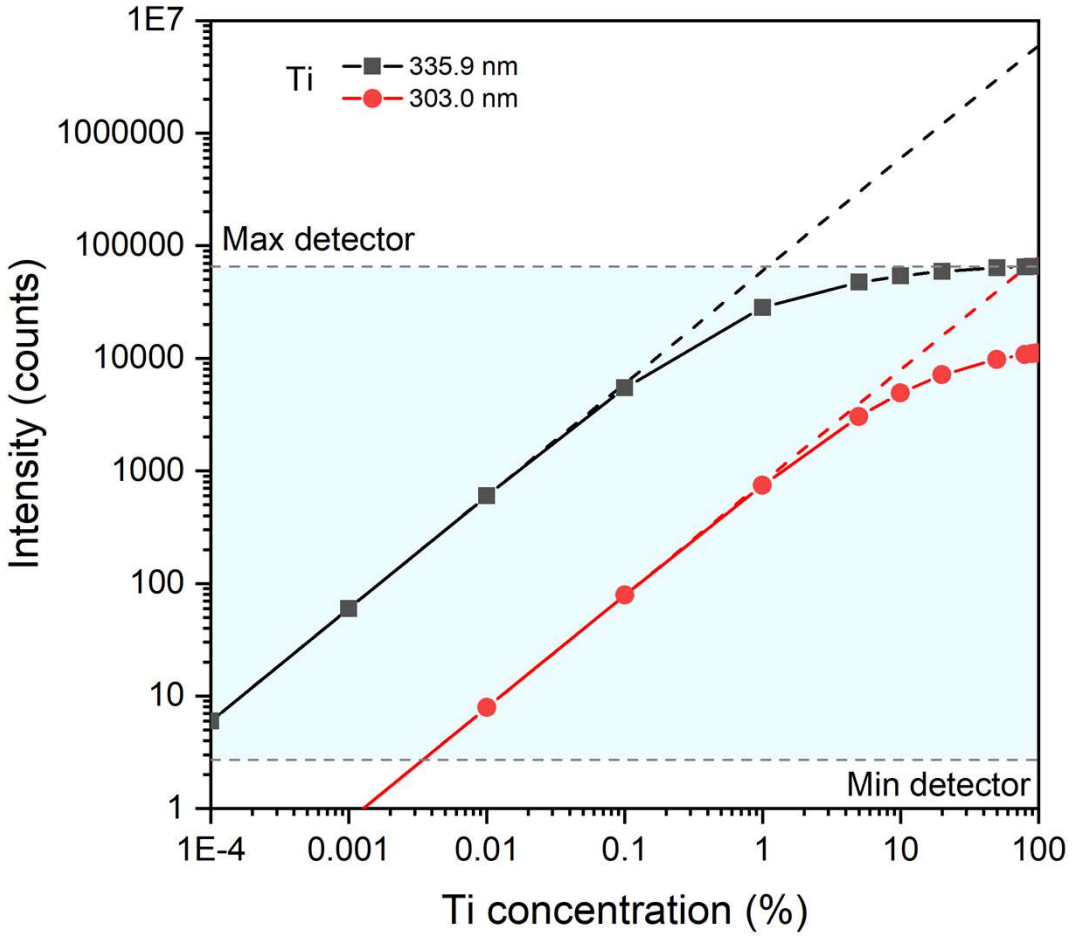
L'auto-absorption a pour effet de saturer les hautes concentrations

→ Extension de la gamme dynamique de mesure ~ 4/5 ordres de grandeurs



Simulation J. Hermann
(LP3, Marseille)

Ti dans SiO_2



Spectroscopie d'émission

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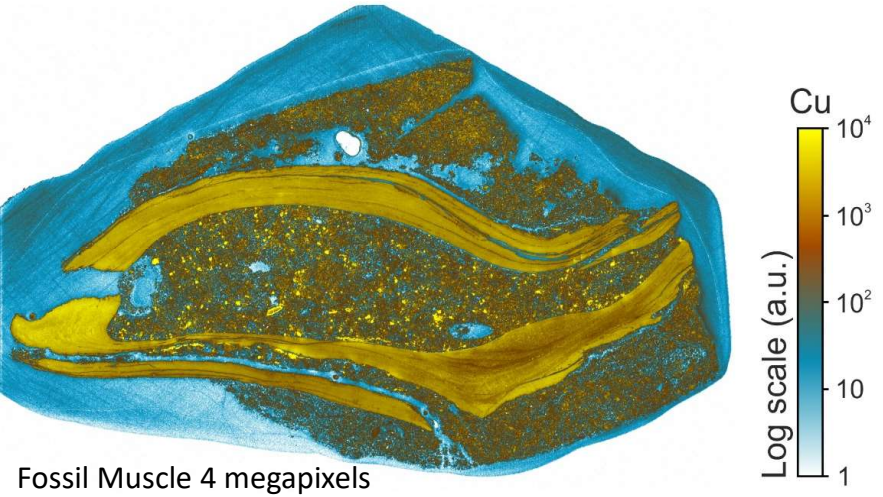
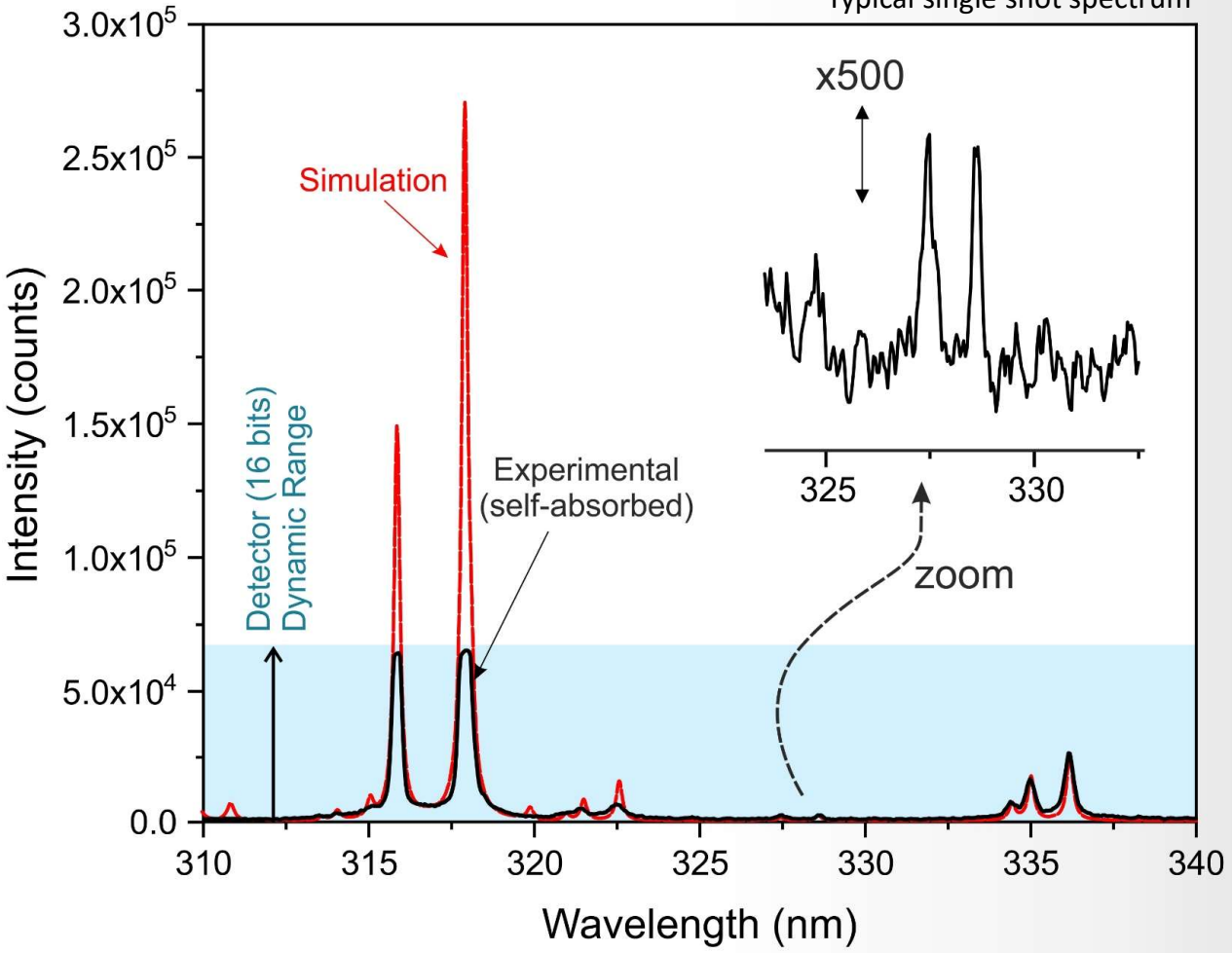


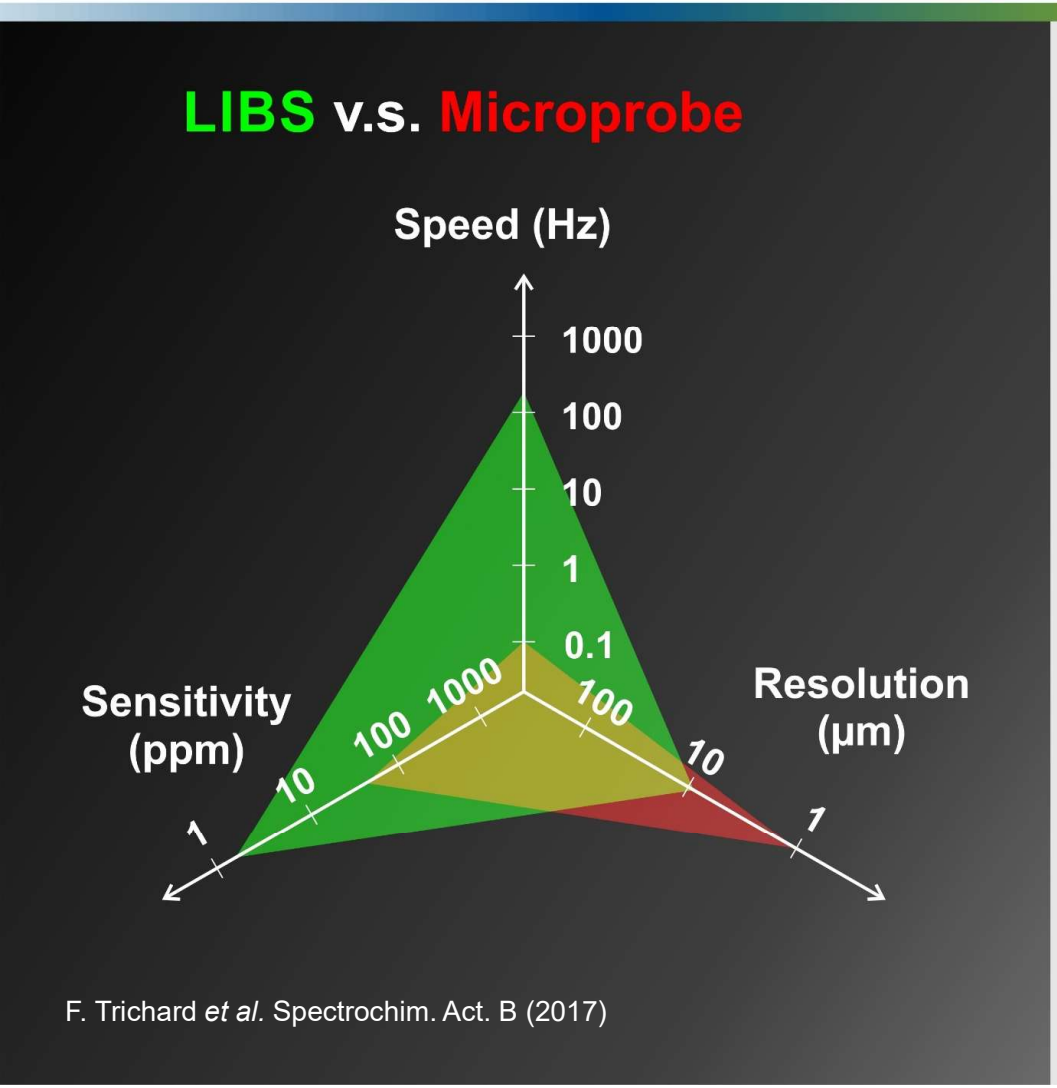
Fossil Muscle 4 megapixels

Typical single shot spectrum

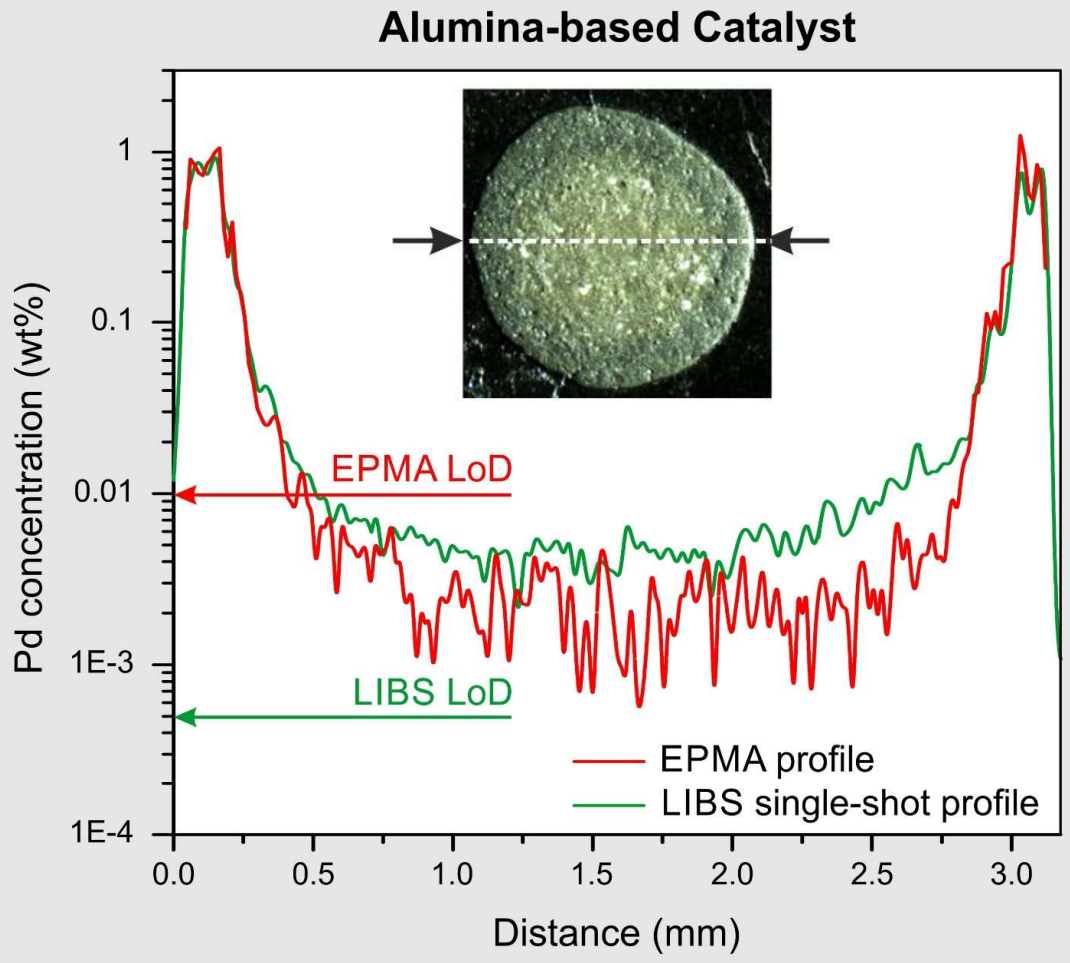


Imagerie LIBS parmi les techniques élémentaire

LIBS *v.s.* EPMA



F. Trichard *et al.* Spectrochim. Act. B (2017)



Time for the analysis: EPMA 1,5 hour / LIBS 2 seconds

Imagerie LIBS

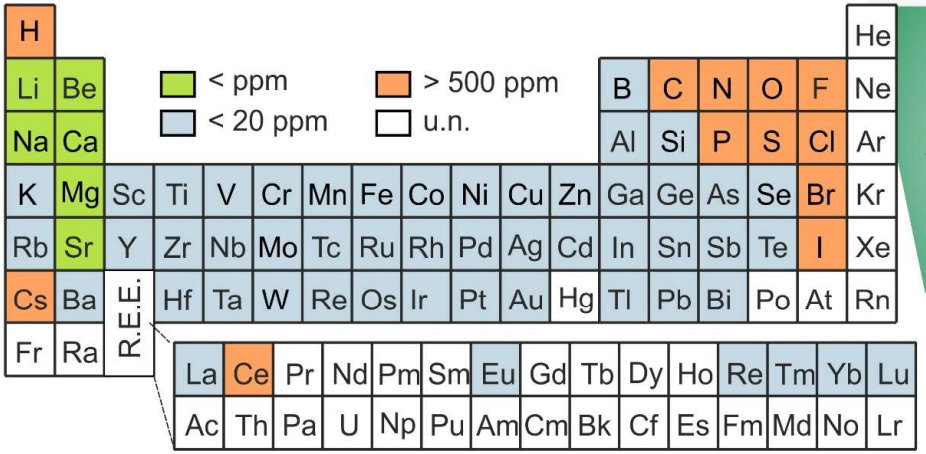
Etat des lieux

Performances

Vitesse: 100 Hz

Résolution: 10 µm

LoDs: 1-10 ppm



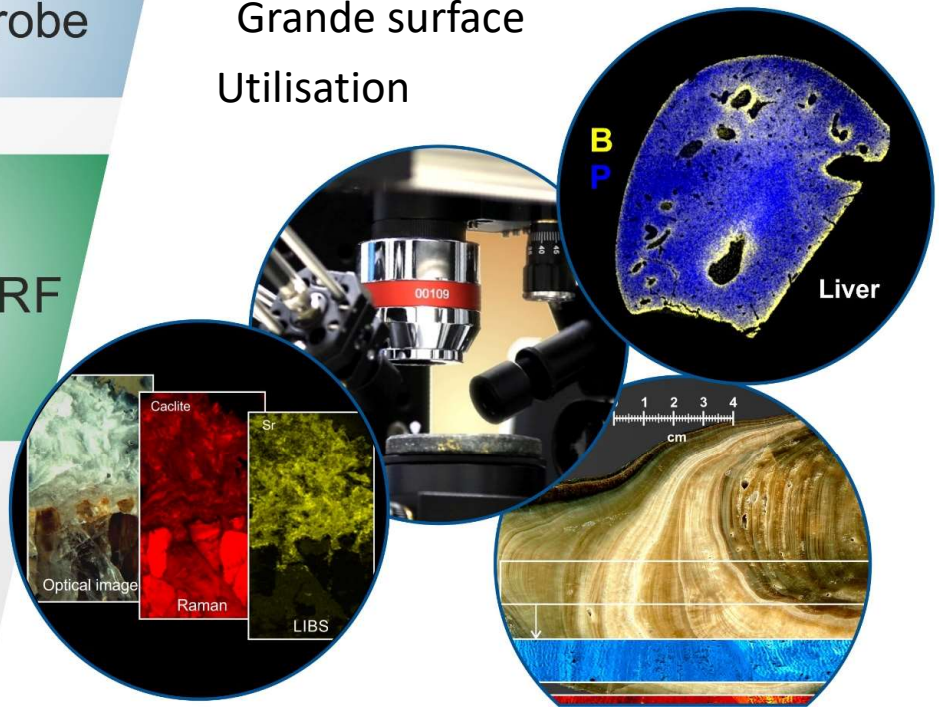
Parmi les techniques d'imagerie élémentaire

SEM-EDX
Electron Microprobe

LA-ICP-MS
Synchroton µXRF
LIBS

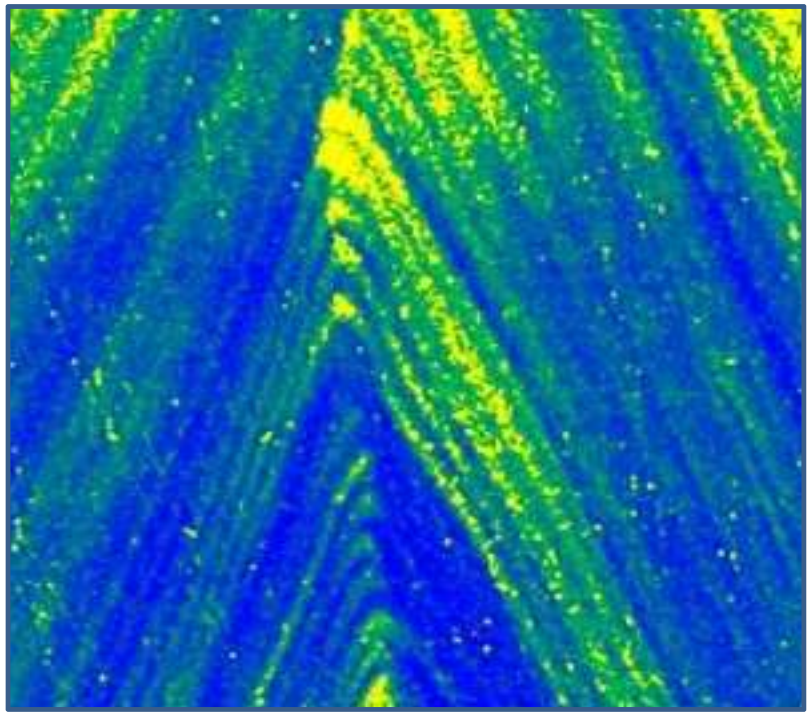
Spécificités

Conditions ambiantes
éléments légers
Tout-optique
Grande surface
Utilisation



Plan

Imagerie élémentaire par LIBS



Imagerie LIBS pour les cristaux à l'ILM

Collaborateurs

Guillaume Alombert-Goget

Kheirreddine Lebbou

} Saphirs Al_2O_3

Philippe Veber

} Cristaux Piézoélectrique $BaTiO_3$

Matias Velazquez

} LMO Li_2MoO_4

Christophe Dujardin

Sylvain Hermelin

} OPTOLYSE

Exemples de résultats

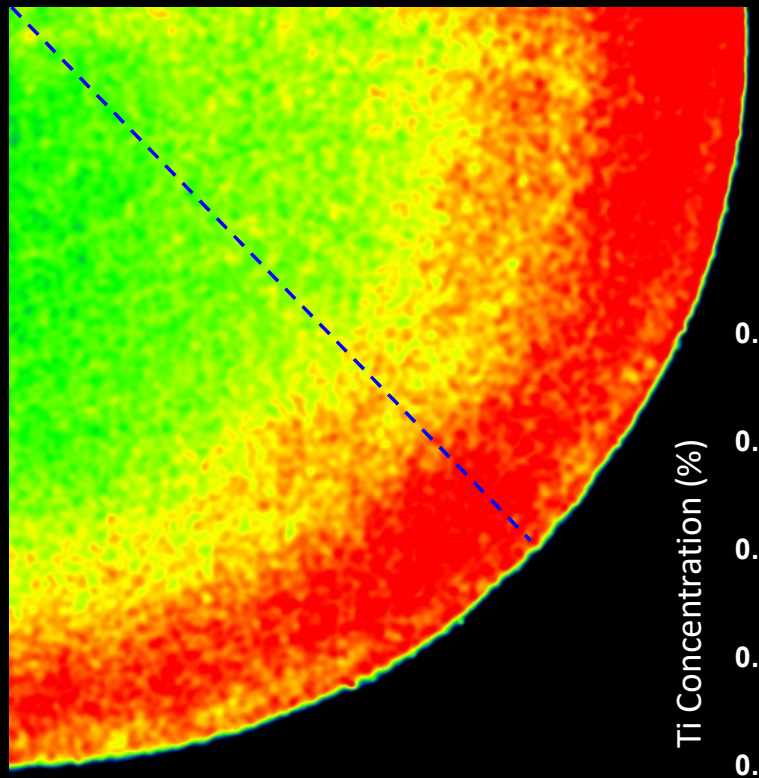
Saphirs

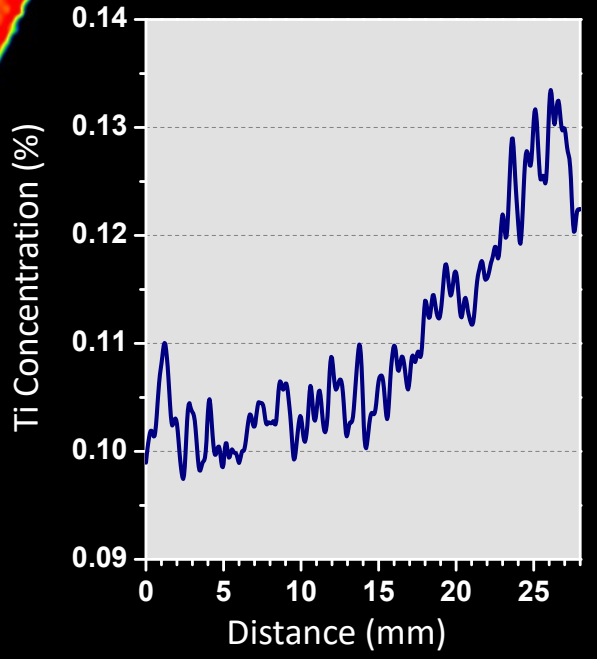
G. Alombert-Goget et al.
Titanium distribution profiles obtained by luminescence and LIBS measurements on Ti: Al2O3 grown by Czochralski and Kyropoulos techniques, Optical Materials, (2016).

ILM *G. Alombert-Goget, H. Li, K. Lebbou*

RSA le RUBIS

Images du Titane dans un saphir





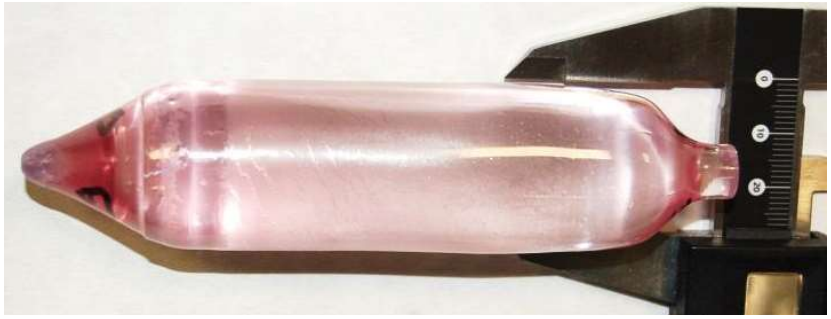
Résolution : 50 µm
Image : 340x340 pixels
Temps d'analyse ~ 20 minutes

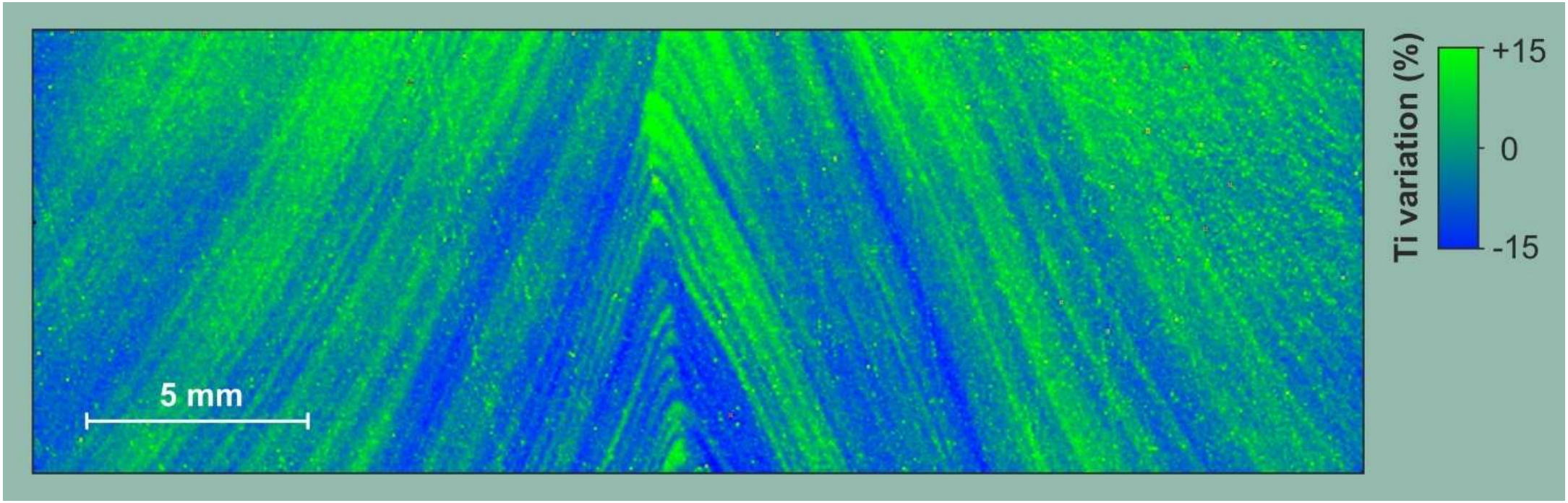
Exemples de résultats

Saphirs

ILM *Alombert-Goget, H. Li, K. Lebbou*

RSA le RUBIS



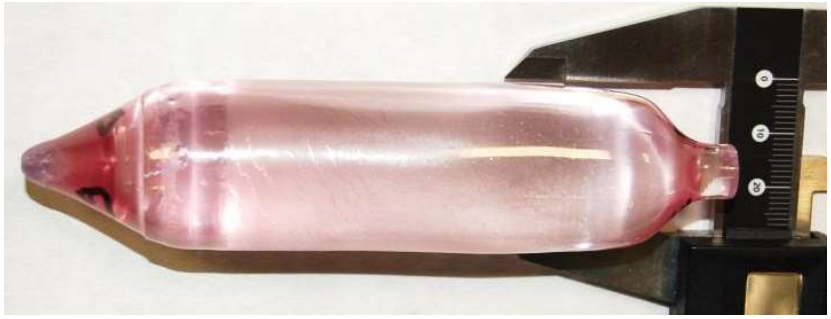


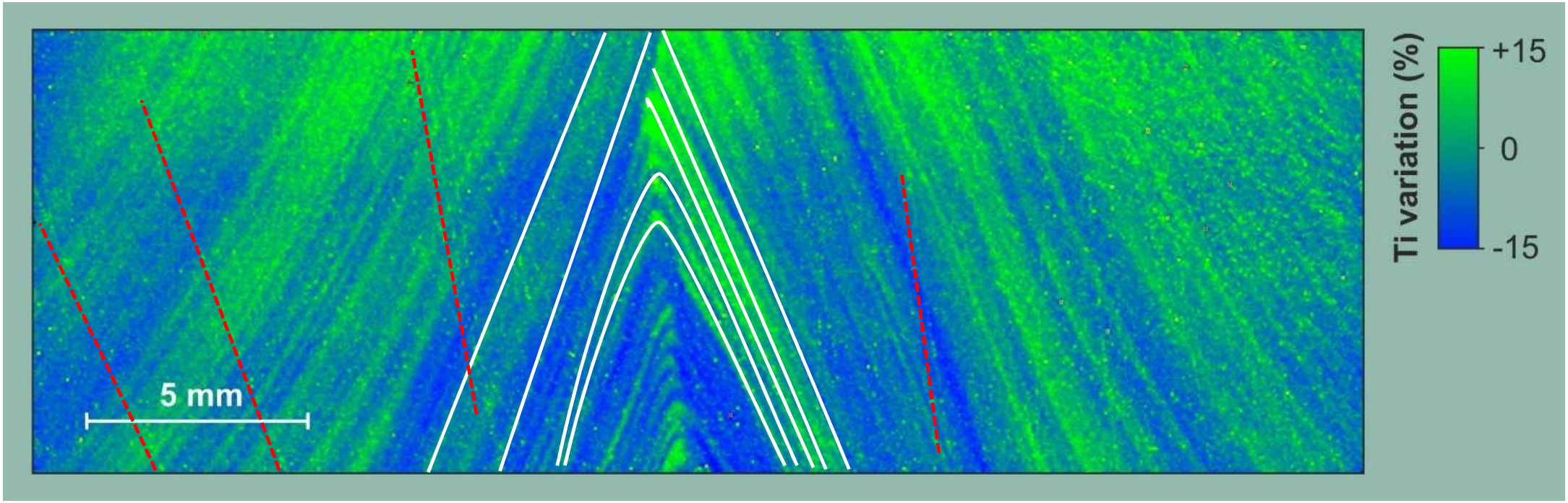
Exemples de résultats

Saphirs

ILM *Alombert-Goget, H. Li, K. Lebbou*

RSA le RUBIS





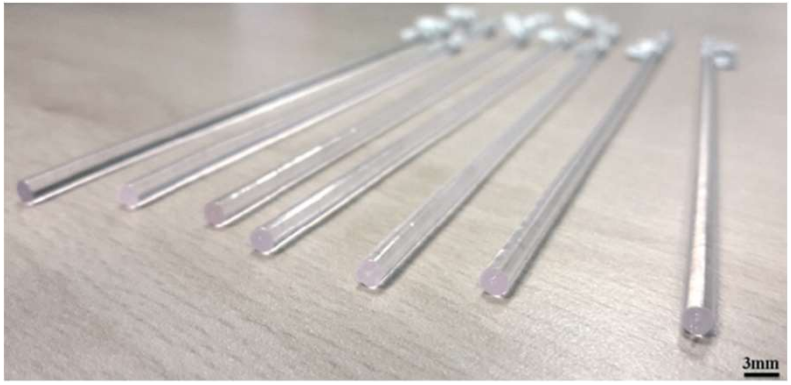
* Contamination de surface

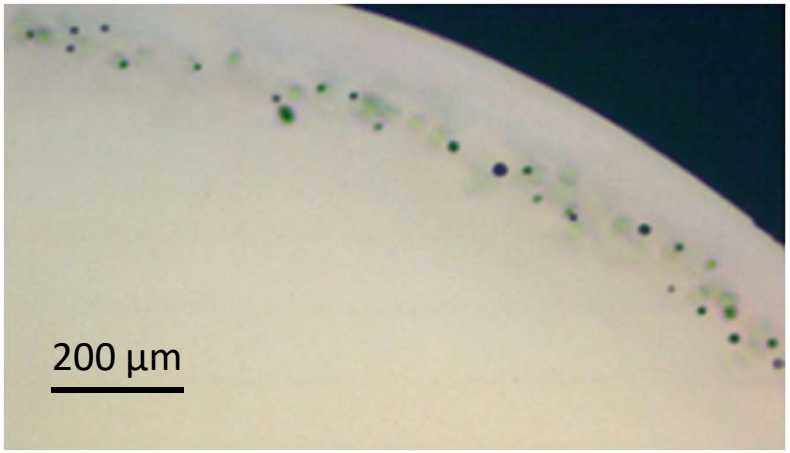
Exemples de résultats

Saphirs

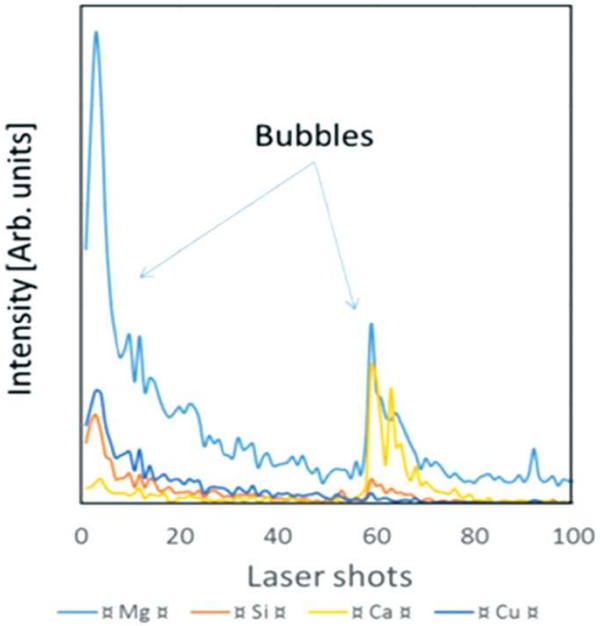
R. Bouaita et al.
Seed orientation and pulling rate effects on bubbles and strain distribution on a sapphire crystal grown by the micro-pulling down method, CrystEngComm 21(25), (2019).

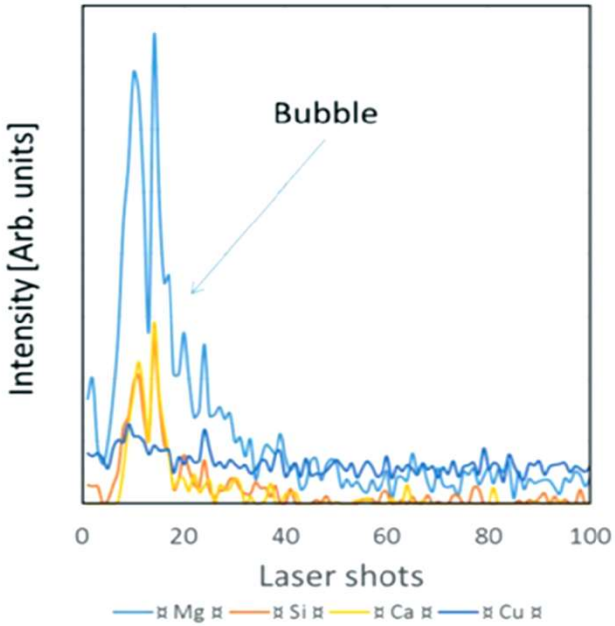
ILM *Alombert-Goget, R. Bouita, K. Lebbou*





Ablation : ~1 µm / tir



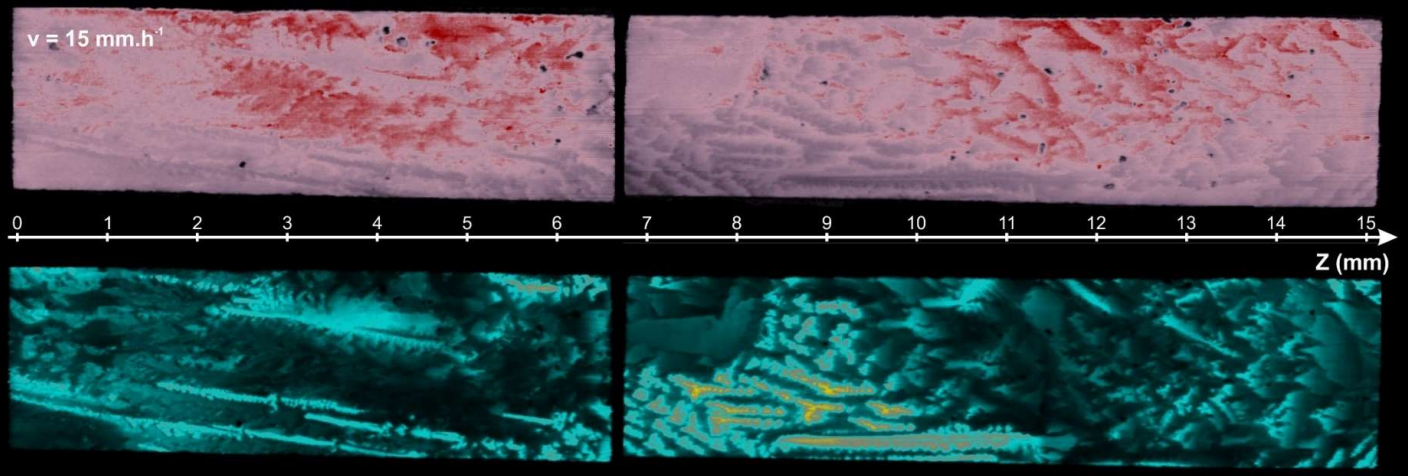


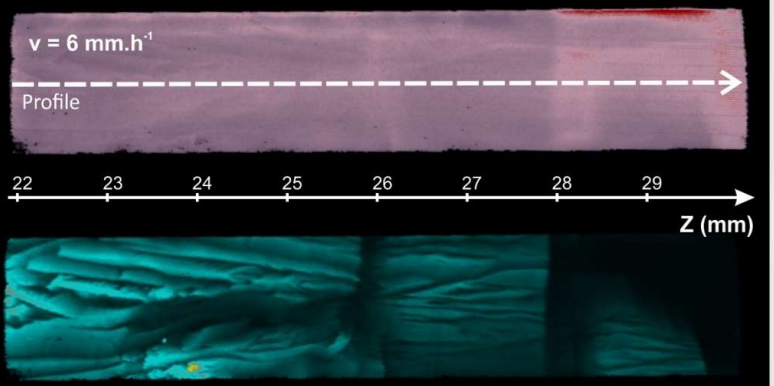
Exemples de résultats

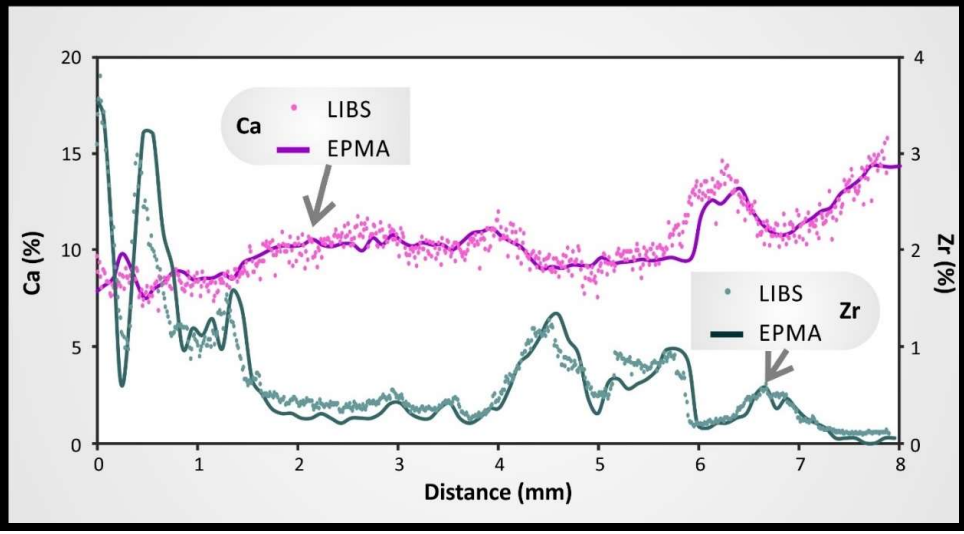
Cristaux piézoélectriques

P. Veber et al.
Lead-free piezoelectric crystals grown by the micro-pulling down technique in the BaTiO3– CaTiO3–BaZrO3 system, CrystEngComm 21, 3844 (2019).

ILM *P. Veber*





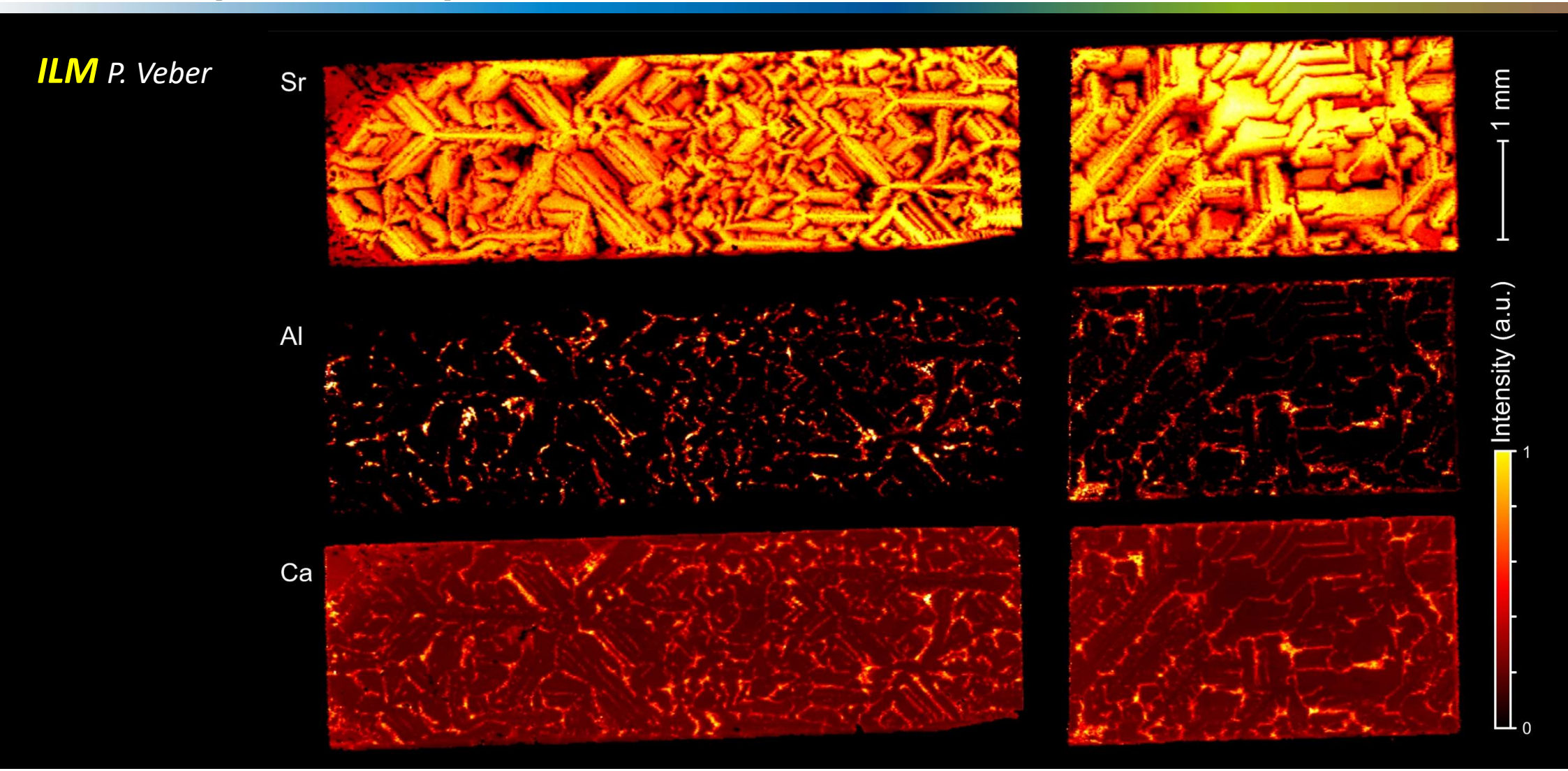


Exemples de résultats

Cristaux piézoélectriques

P. Veber et al.
Highly textured lead-free piezoelectric polycrystals grown by the micro-pulling down freezing technique in the BaTiO3-CaTiO3system, CrystEngComm 22 (30) (2020).

ILM *P. Veber*



Exemples de résultats

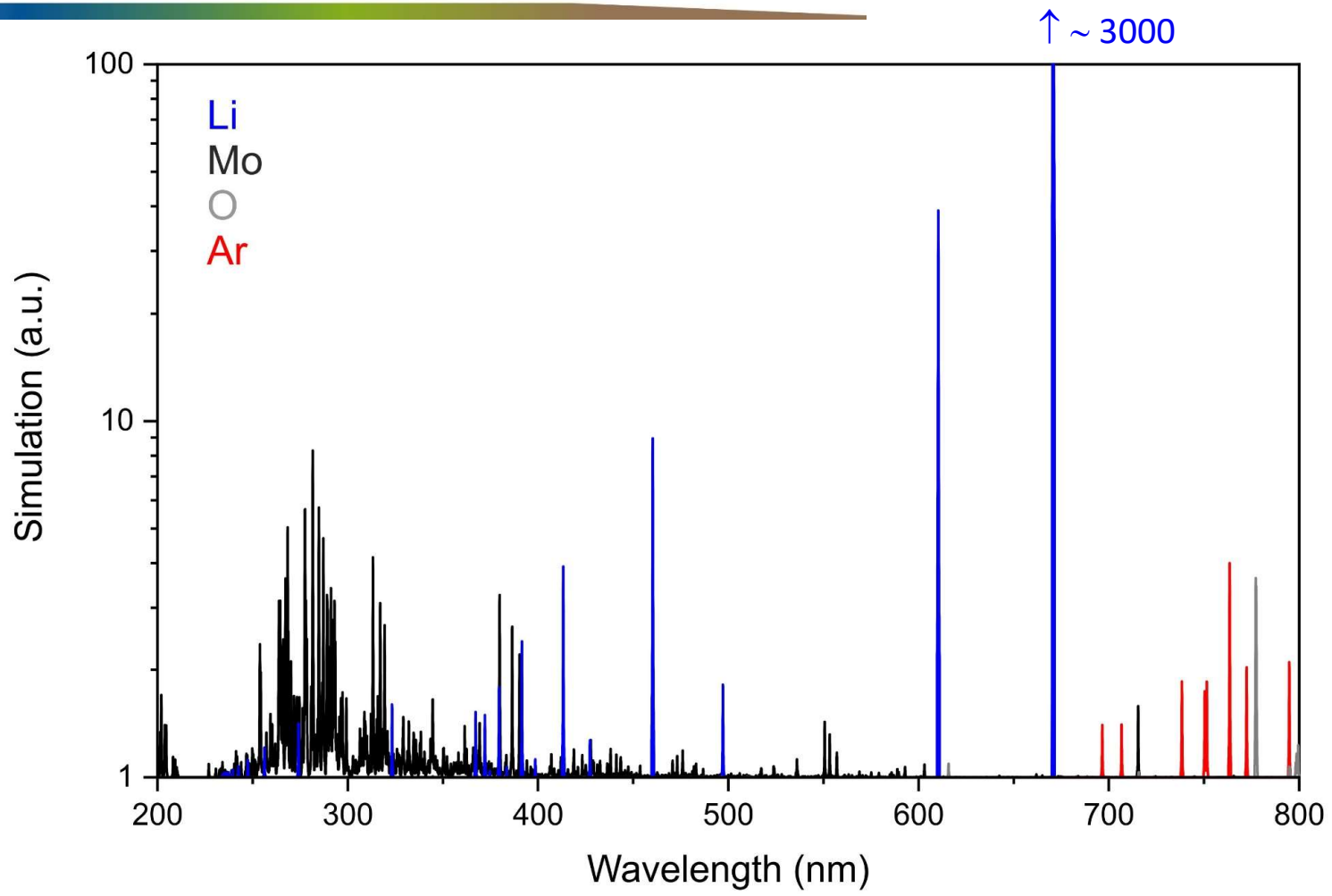
LMO – préparation de l'expérience

M. Velazquez

Li_2MoO_4

Traces recherchées :

K et W



Kurucz simulation

T_e= 10000K

N_e= 5.10^{17} /cm^3

Exemples de résultats

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Li_2MoO_4

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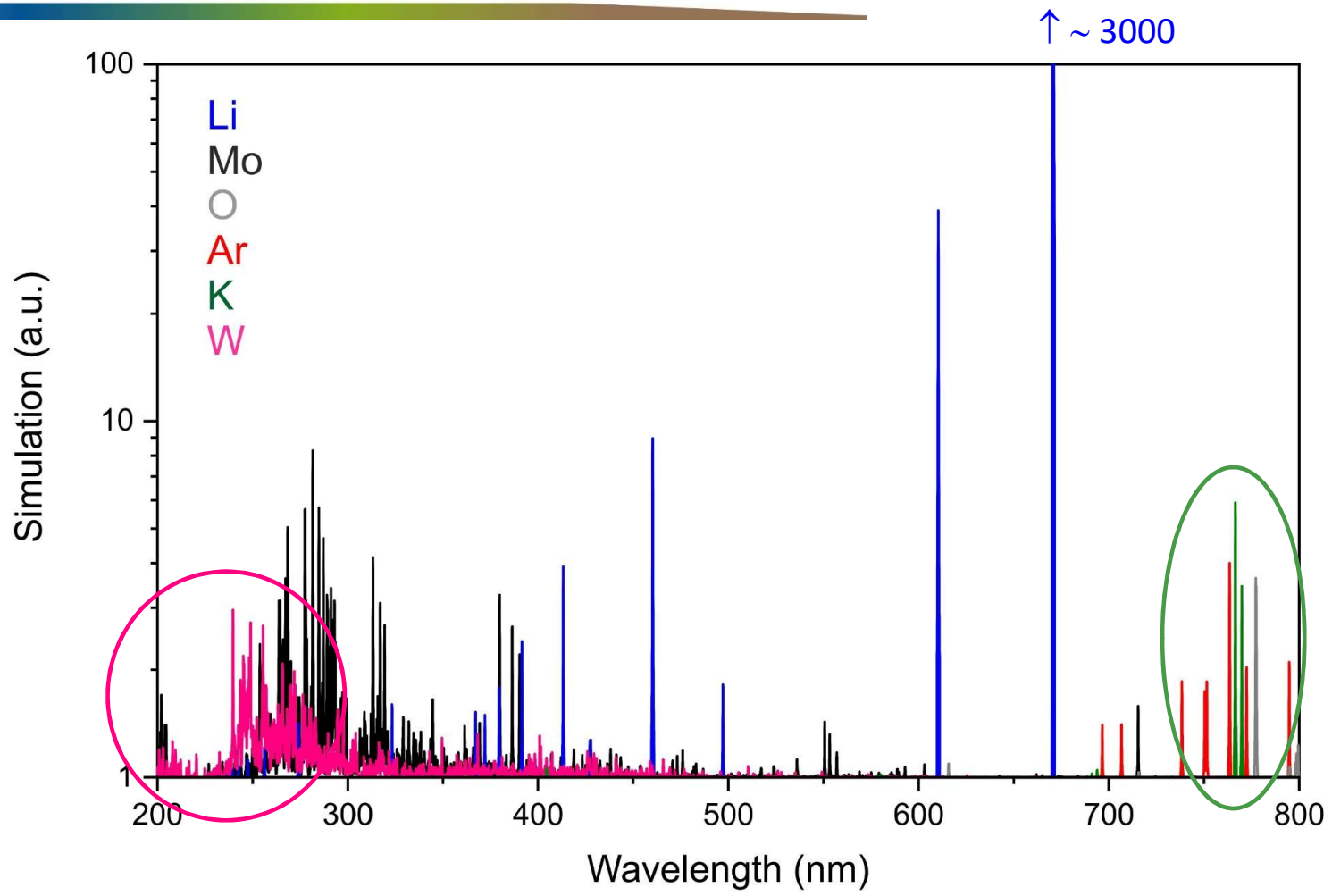


Kurucz simulation
T_e= 10000K
N_e= 5.10^{17} /cm^3

Système de détection actuel peu sensible!

Exemples de résultats

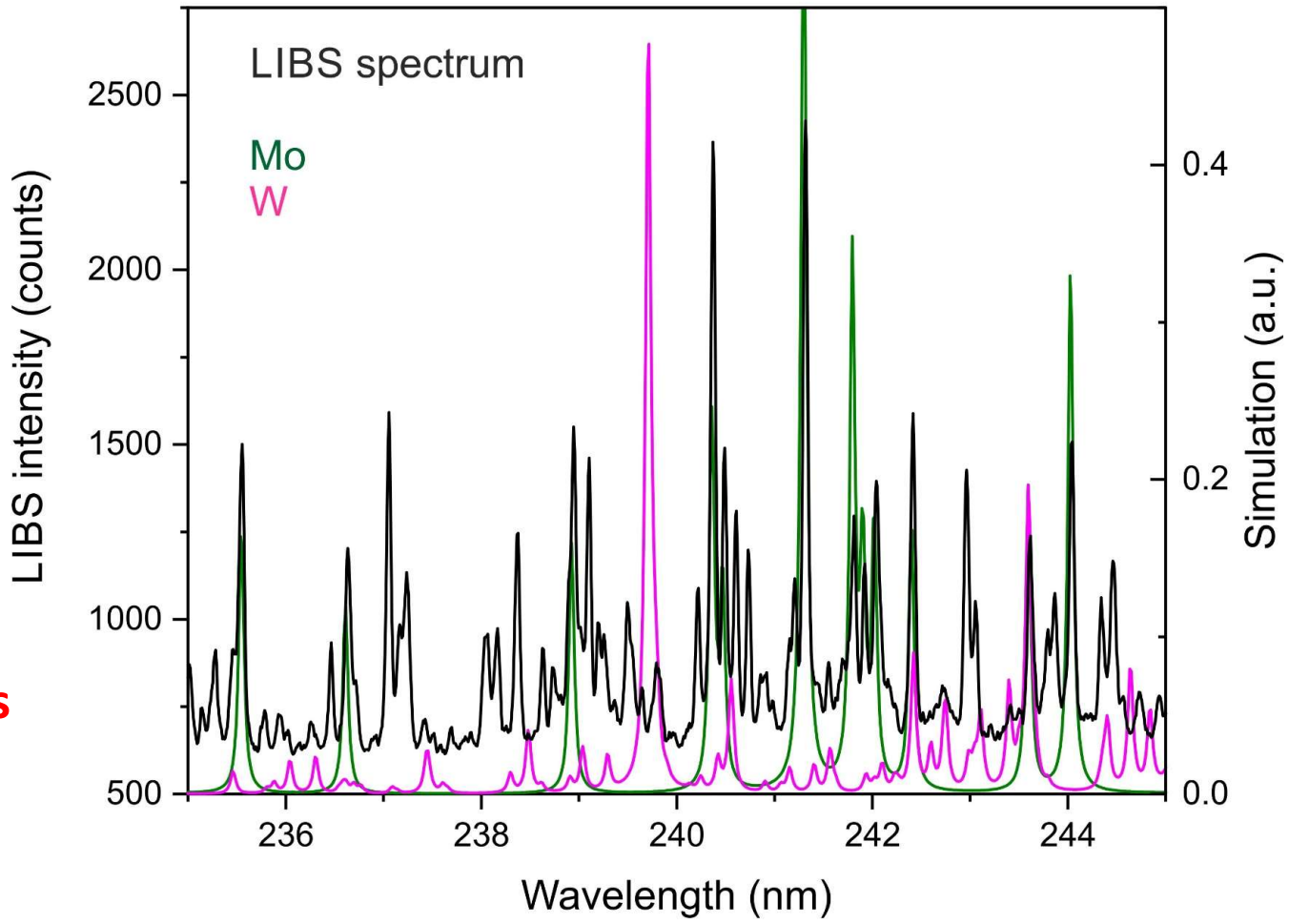
LMO – Résultats

M. Velazquez

Li_2MoO_4

Traces recherchées :

K et W



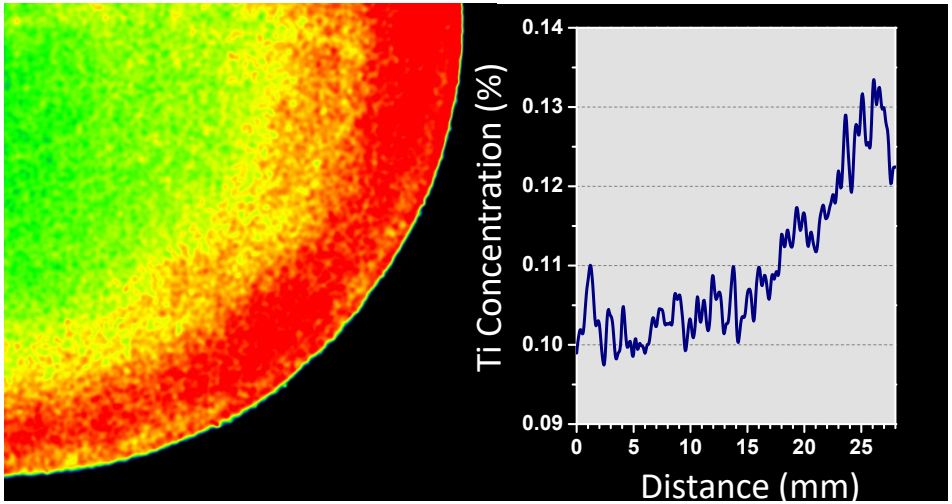
Bases de données non complètes…

Pour finir

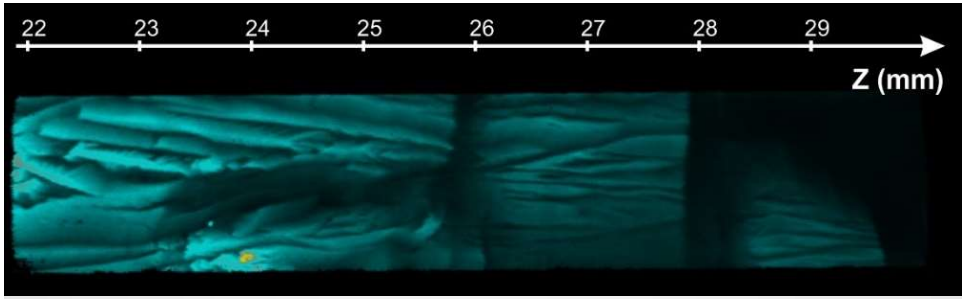
Et à propos de la quantification?

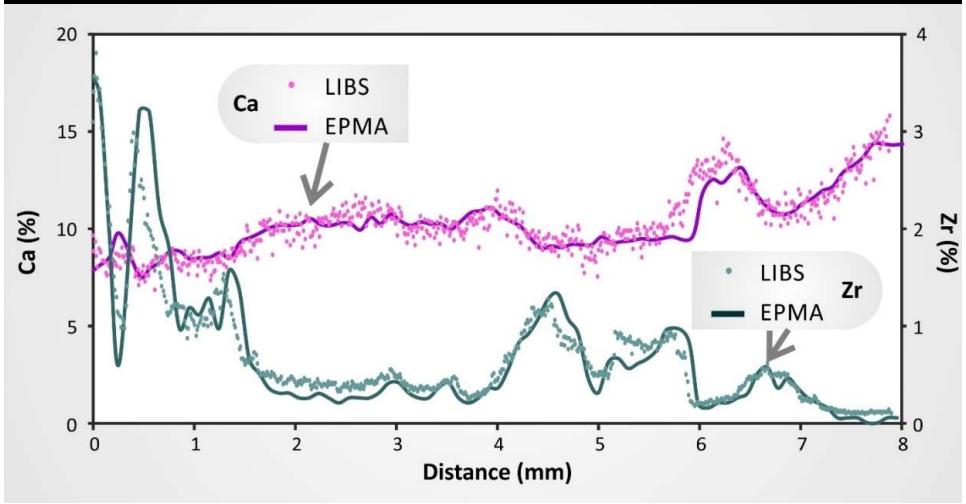
1) Comme les méthodes « classiques » besoin d'étalons… mais…

2) Hypothèse que les données de surface sont représentatives du volume



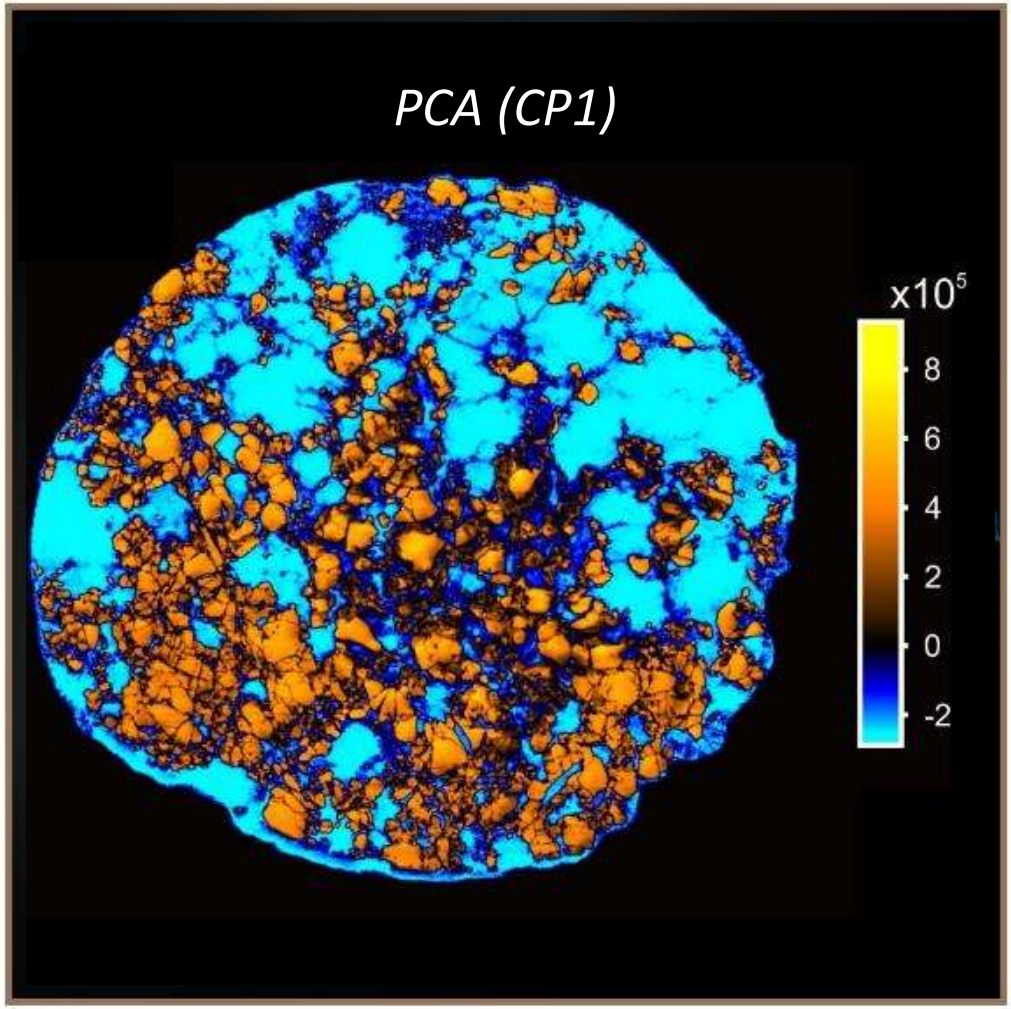
3) Utilisation d'autres techniques





Plan

Imagerie élémentaire par LIBS

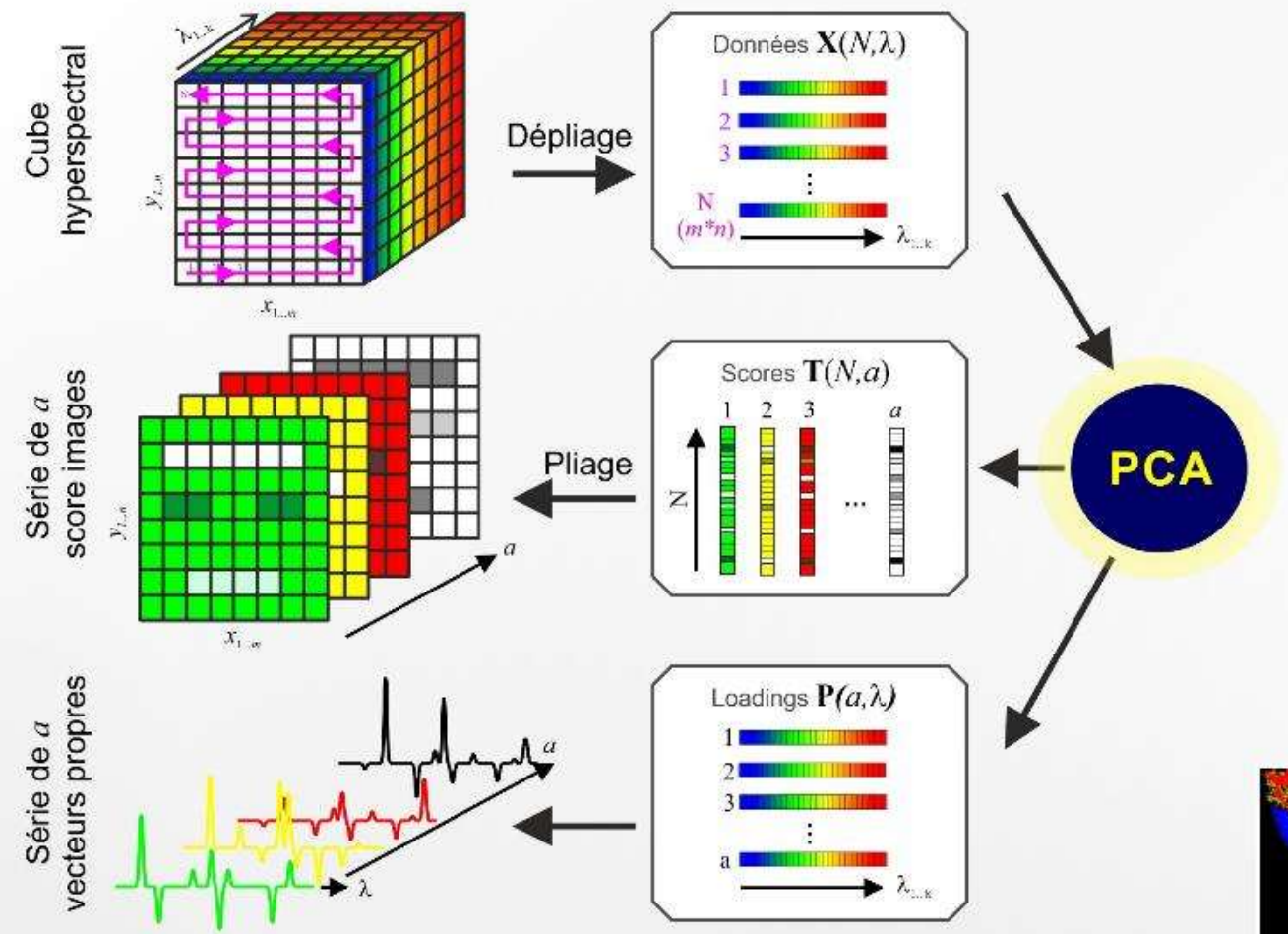


Perspectives

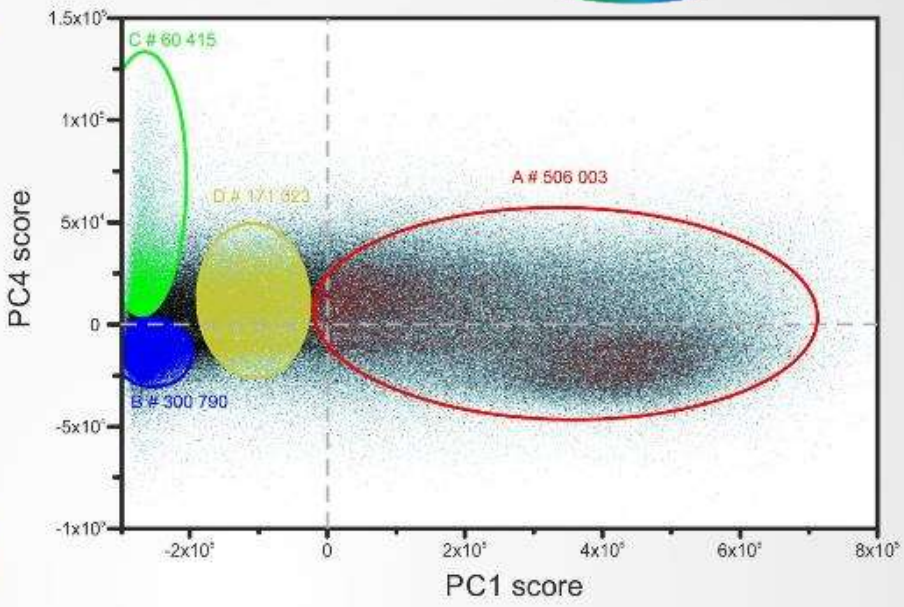
Utilisation de la chimiométrie

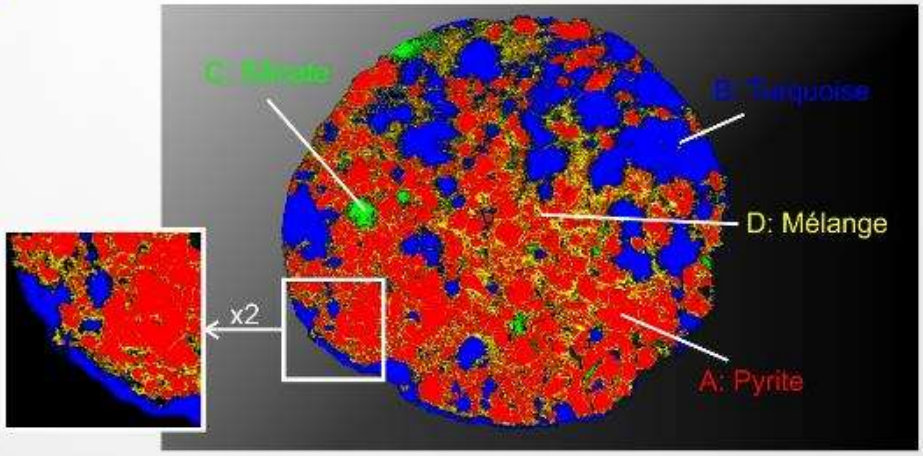
Collaboration L. Duponchel

LASIR



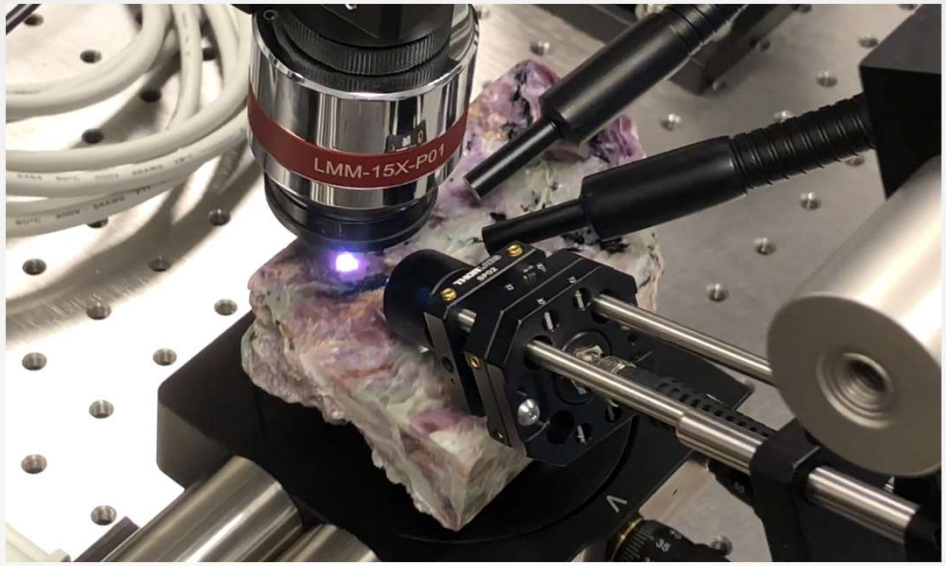
S. Moncayo *et al.* JAAS (2018)



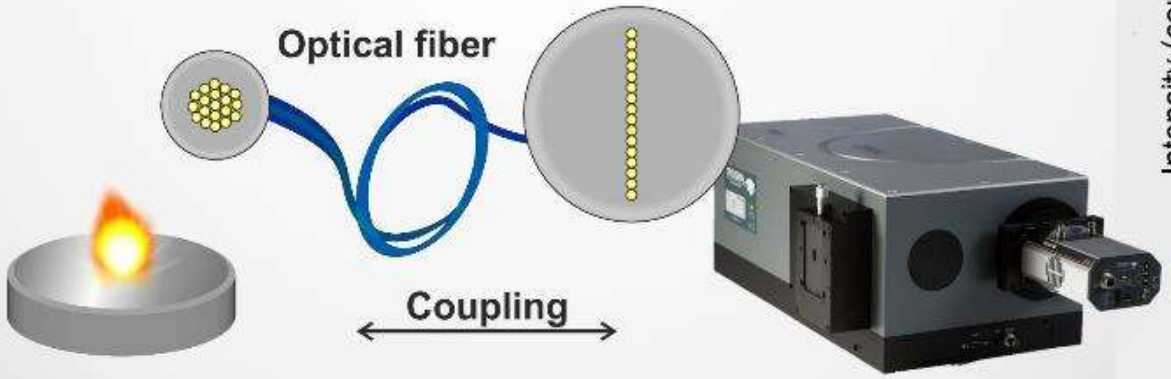


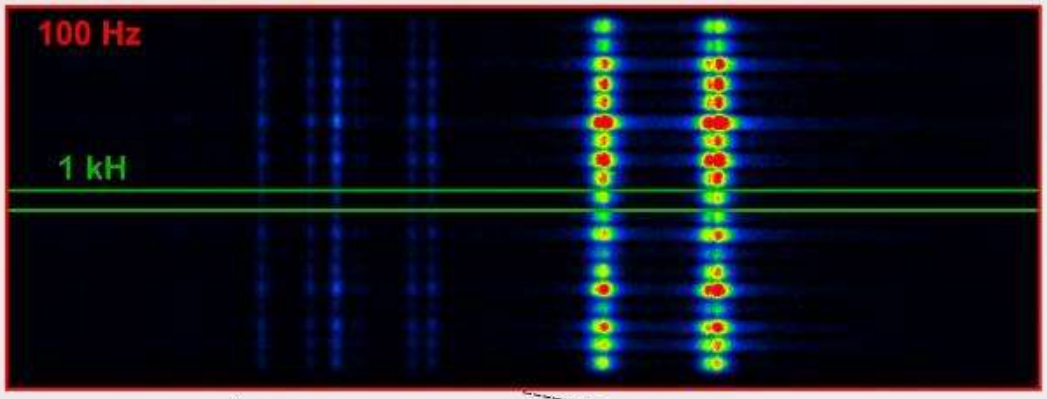
Perspectives

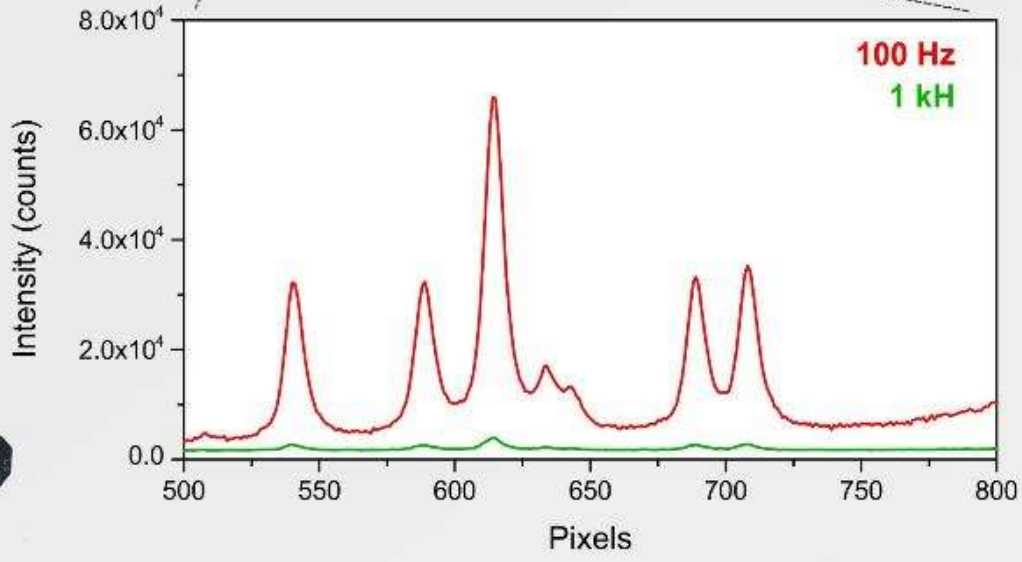
Amélioration de la vitesse d'acquisition



1 megapixels in 17 min!





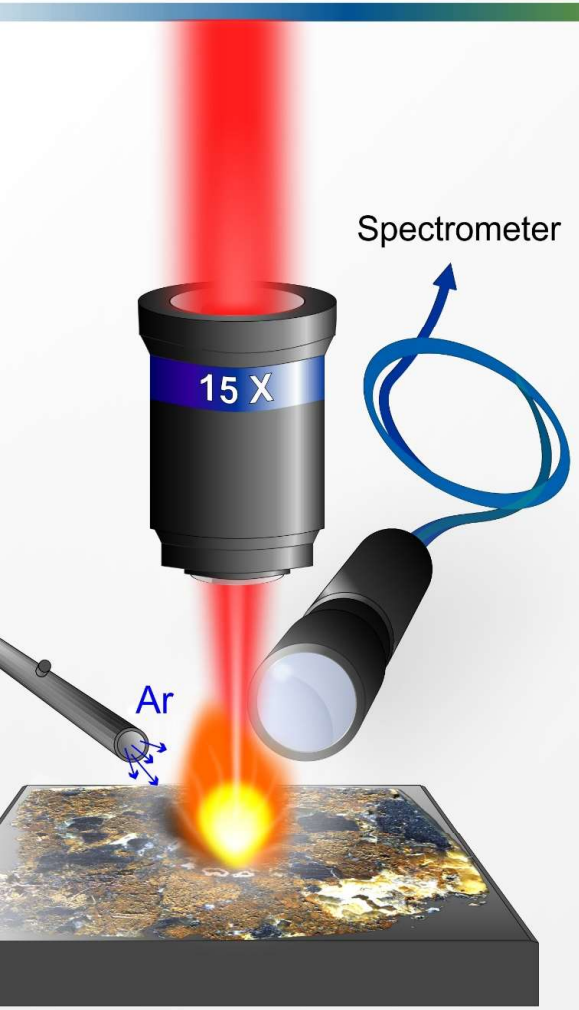


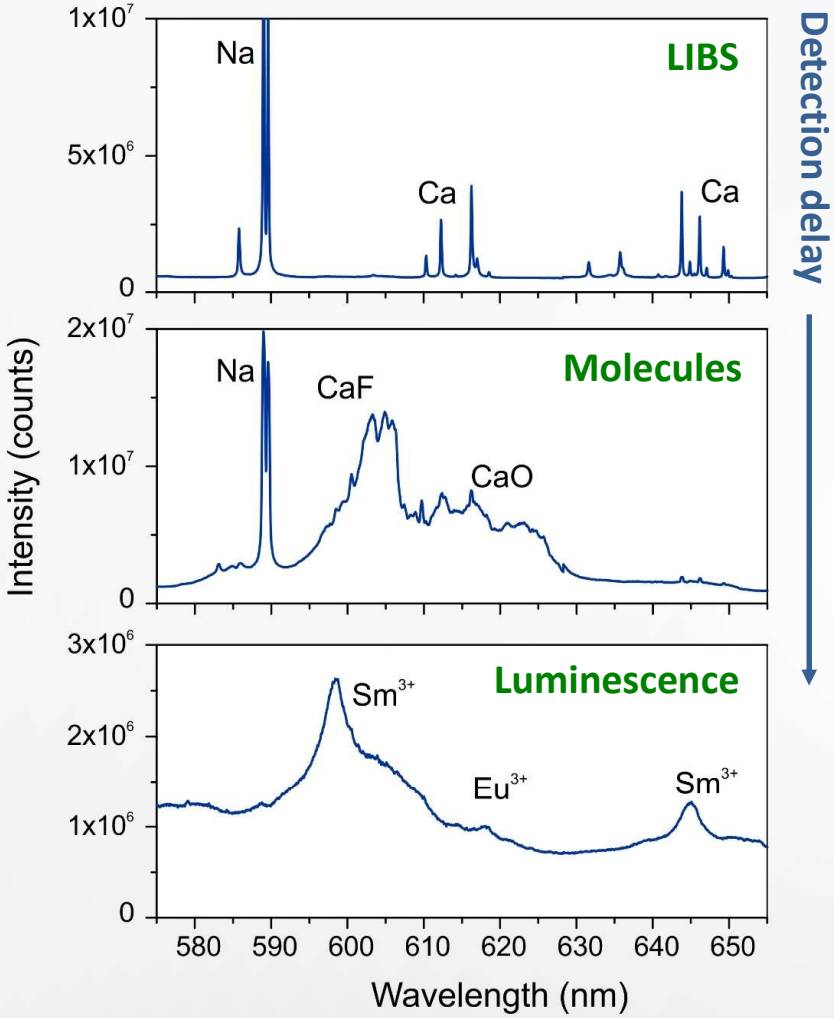
Perspectives

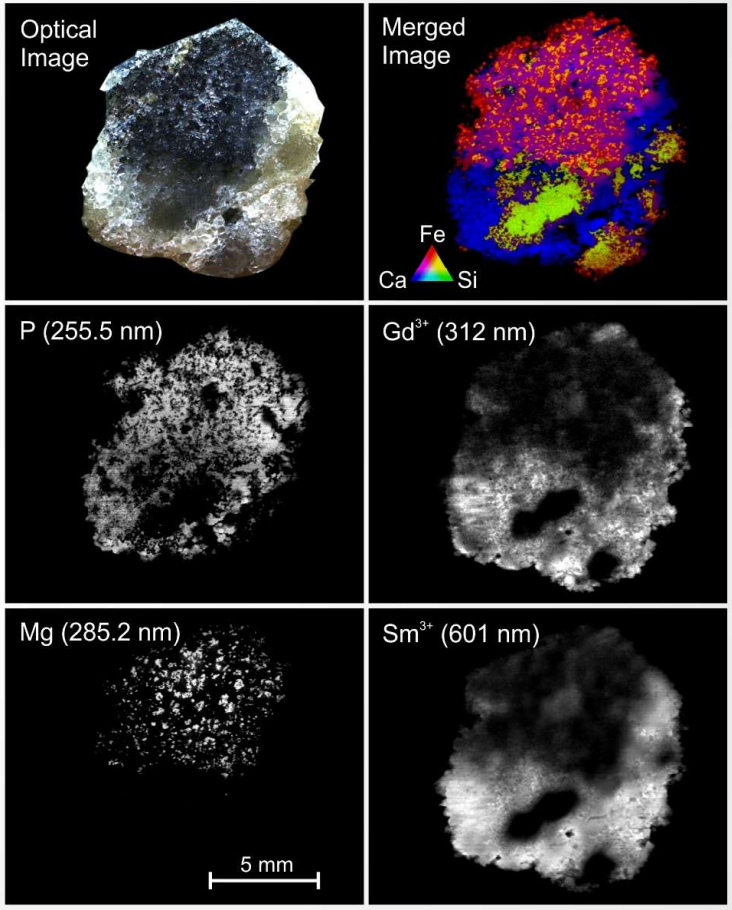
Amélioration des limites de détections

Collaboration M. Gaft

ARIEL UNIVERSITY







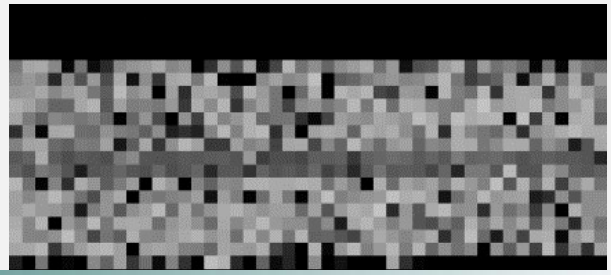
M. Gaft *et al.* SAB (2018)

Perspectives

Configuration LIBS - LIF

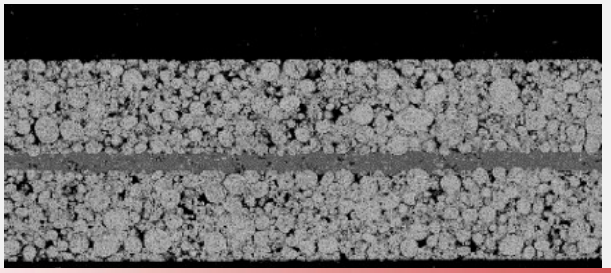
Actual performances (10 µm)

SEM image of a commercial cathode



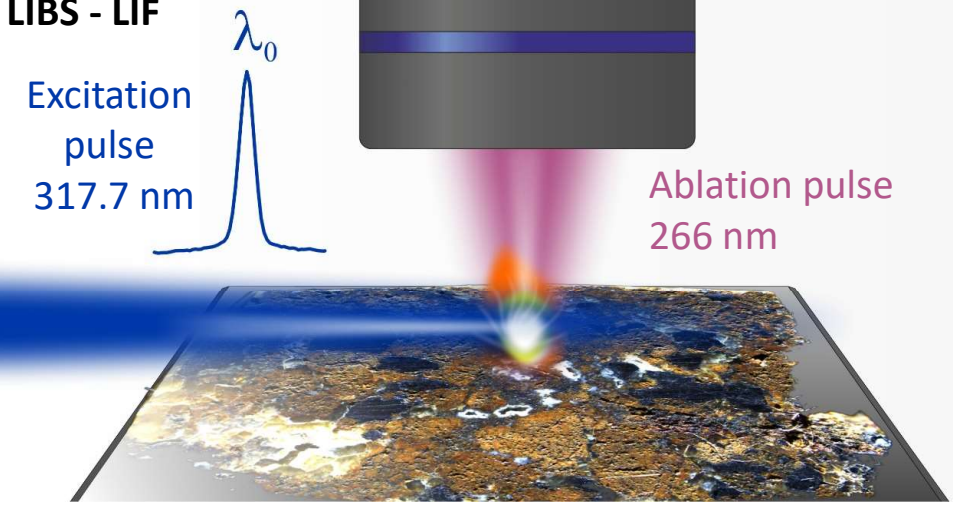
100 µm

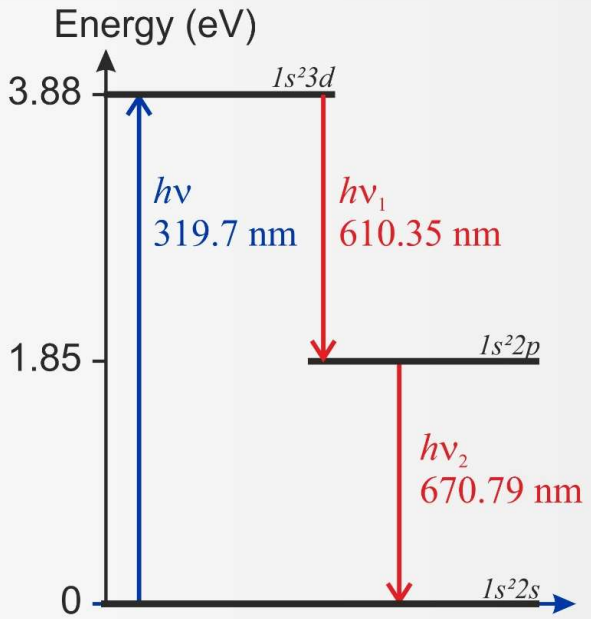
Objective (1 µm)



Ablated volume: **~ 1000 µm³** **~ 1 µm³**

Signal enhancement LIBS - LIF





Benefits

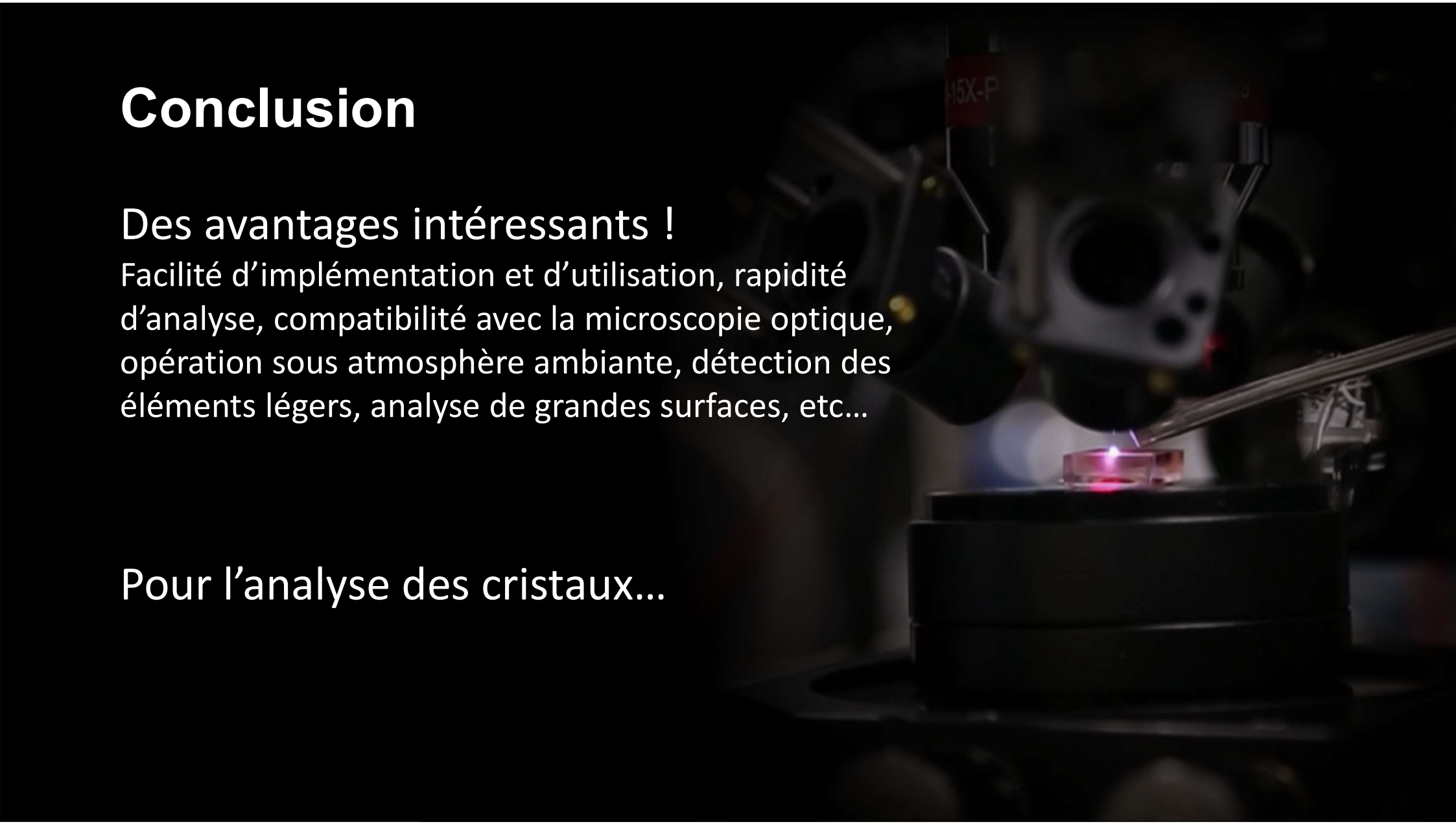
- "Low energy" ablation (no excitation)
- No continuum
- Sensitivity x $10^2/10^3$

Conclusion

Des avantages intéressants !

Facilité d'implémentation et d'utilisation, rapidité d'analyse, compatibilité avec la microscopie optique, opération sous atmosphère ambiante, détection des éléments légers, analyse de grandes surfaces, etc…

Pour l'analyse des cristaux…




S. Hermelin


C. Zerbino


C. Dujardin


D. Devismes


B. Busser


L. Sancey


F. Pelascini


F. Trichard

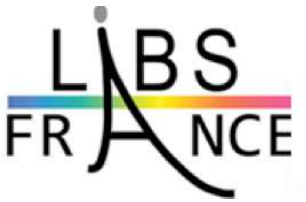

L. Duponchel

LIBS collaborations: C. Fabre, M. Baudelet, B. Bousquet, J.O. Caceres, V. Detalle, A. Di-Giacomo, F. Doucet, M. Gaft, J. Hermann

P. Veber , G. Alombert, M. Velasquez, K. Leddoux , G. Panczer, O. Tillement, V. Bonneterre, J. Cauzid, R. Chapoulie, C. P. Lienmann, S. Roux, A.M. Sfarghiu, F. Surma, L. Sorbier, Manuel Munoz, Alexandre Curgerone, etc…

Companies
J. M. Laurent, A. Feugier, M. Semenoux

Thanks for your attention!!



dIAg-EM

Spectra simulation

Assuming a uniform plasma in LTE
(Local Thermodynamic Equilibrium):

Boltzmann equation: Population density of the emitters

$$I_\alpha^z = f\frac{hc}{\lambda_\alpha^z}\frac{A_\alpha^z g_\alpha^z}{U^z(T)}N_\alpha^z \exp\left[-\frac{E_\alpha^z}{kT}\right]$$

z=0 (neutral)
z=1 (singly ionised)

Saha equation: Ionization states

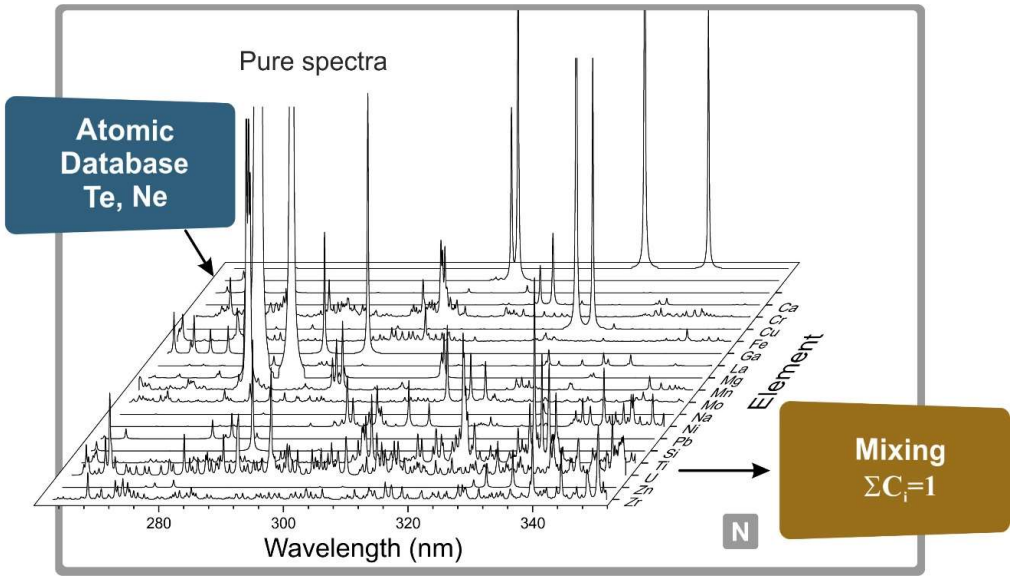
$$\frac{N_\alpha^1}{N_\alpha^0} = \frac{2}{Ne}\frac{U_\alpha^1(T)}{U_\alpha^0(T)}\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}\exp\left[-\frac{E_{ion}^1-\Delta E}{kT}\right]$$

Spectral radiance (self-absorption)

$$B_\lambda = B_\lambda^0\left(1-e^{-\tau(\lambda)}\right)$$

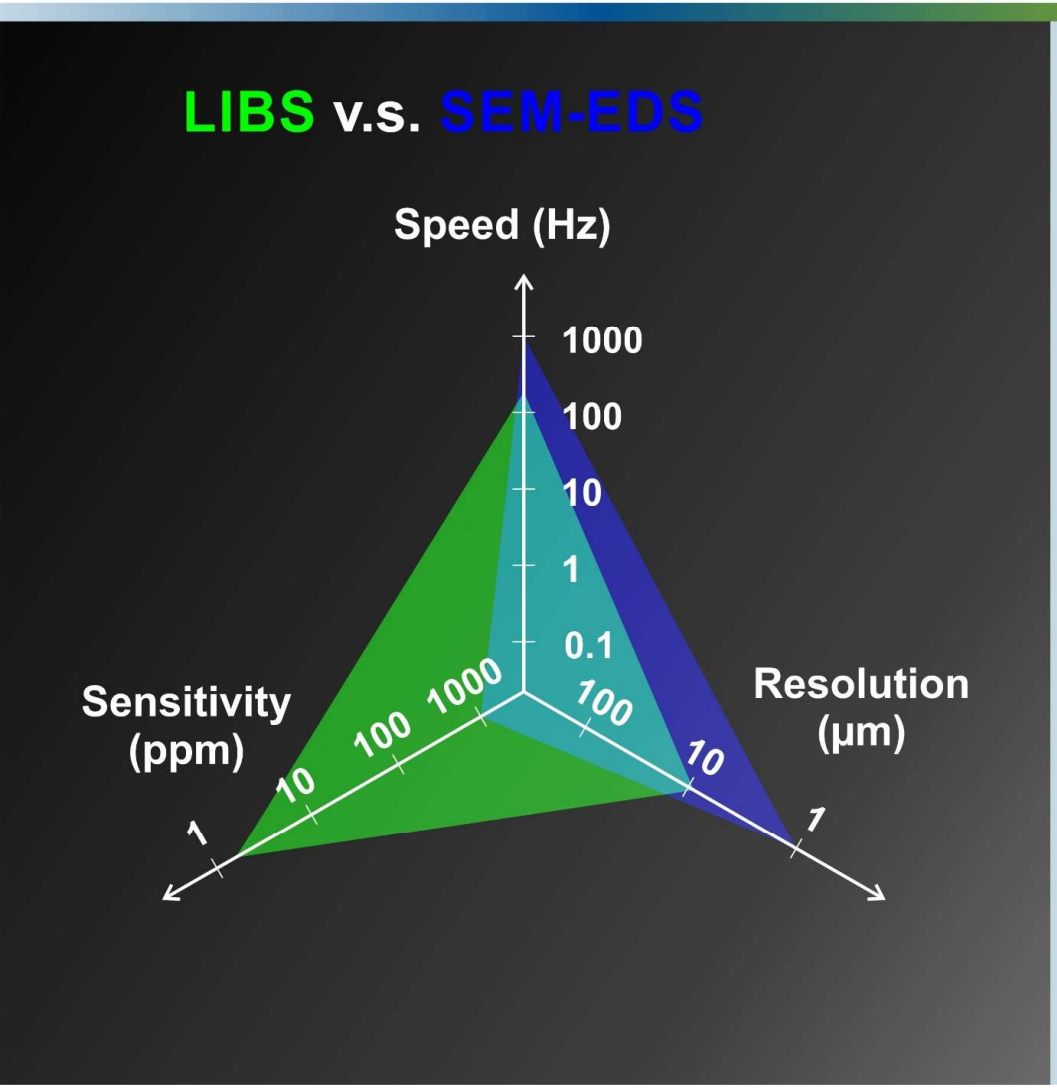
$\tau(\lambda)$ *Optical thickness*

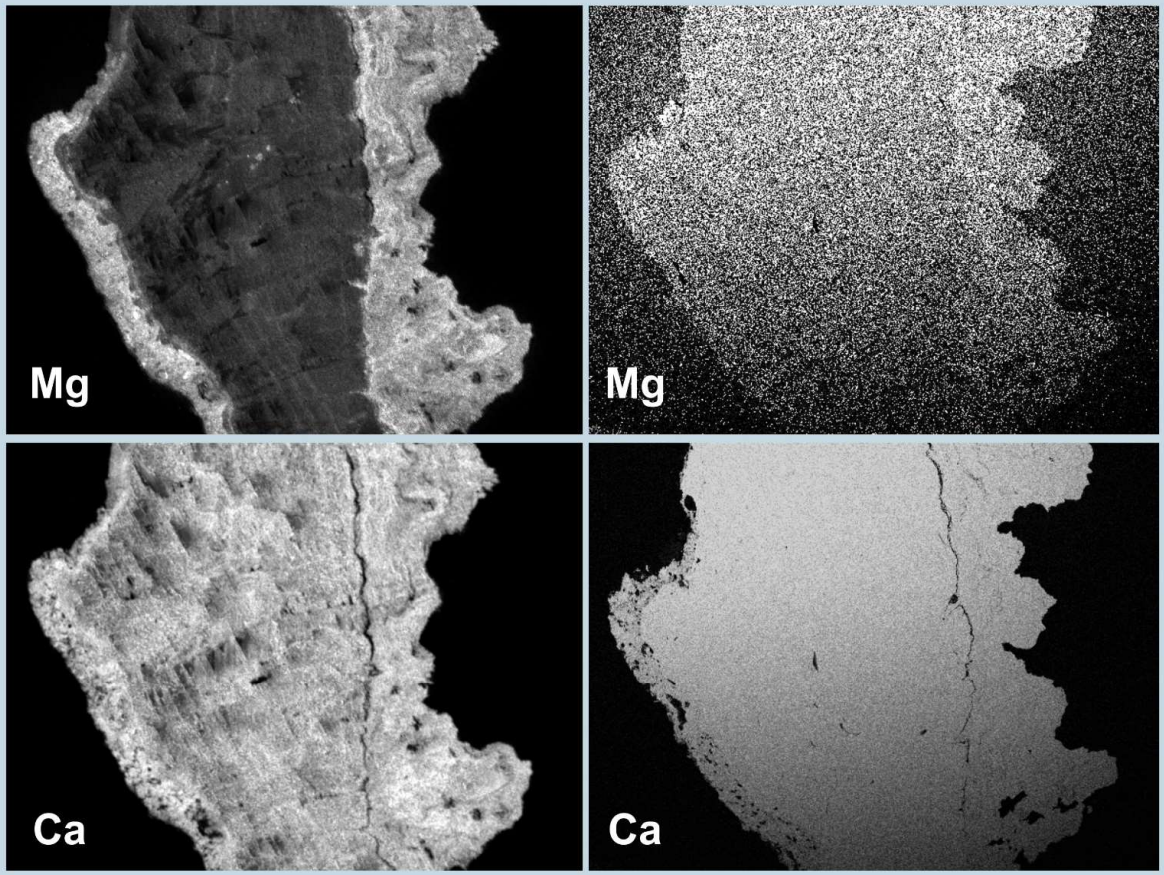
Simulation of pure elemental emissions for various T and Ne



Parmi le panel des techniques d'imagerie élémentaire

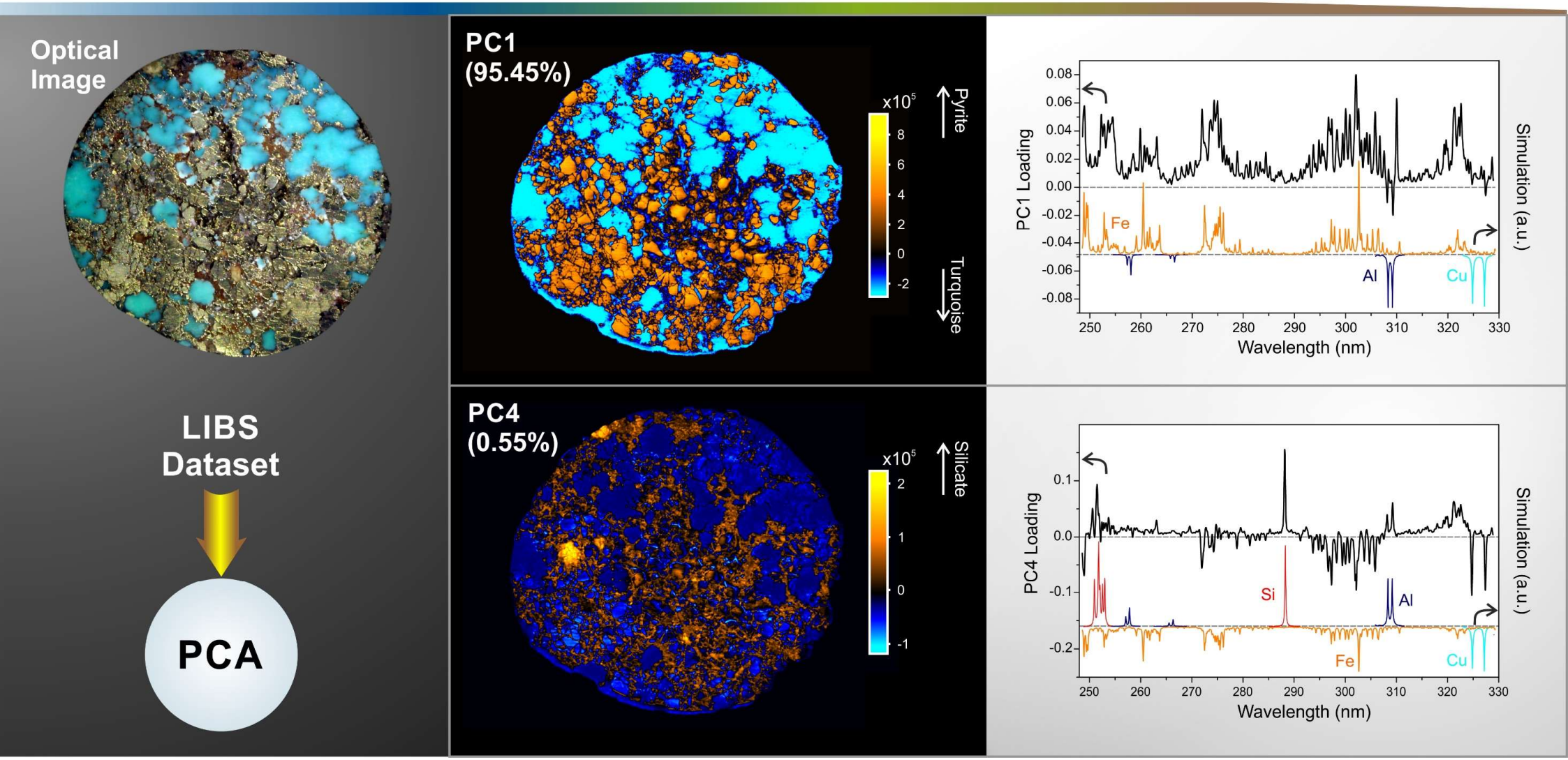
LIBS v.s. microscopie électronique





Traitement des données

Analyse en composante principale sur matrice « complexe »



Exemples de résultats

LMO – Résultats

M. Velazquez

Li_2MoO_4

Traces recherchées :

K et W