l'Imagerie LIBS hyper « mega » spectrale couplée à l'IA : un fort potentiel analytique !

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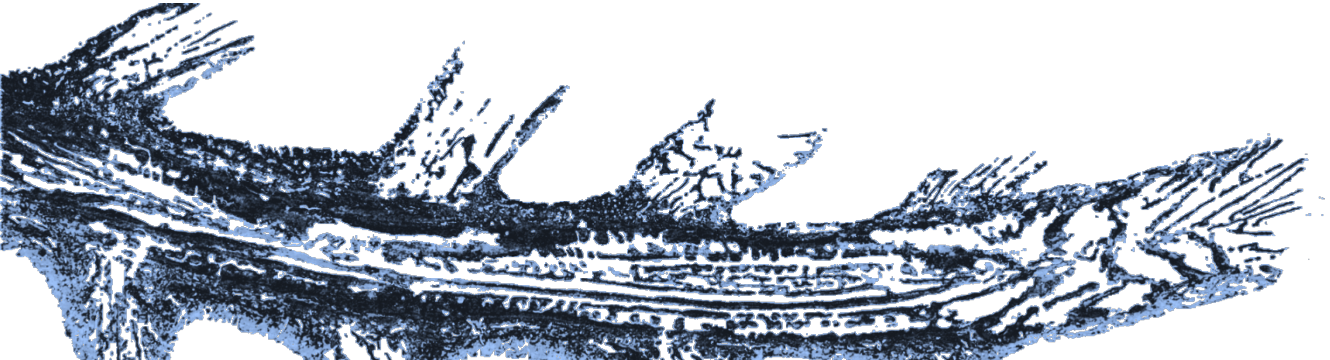
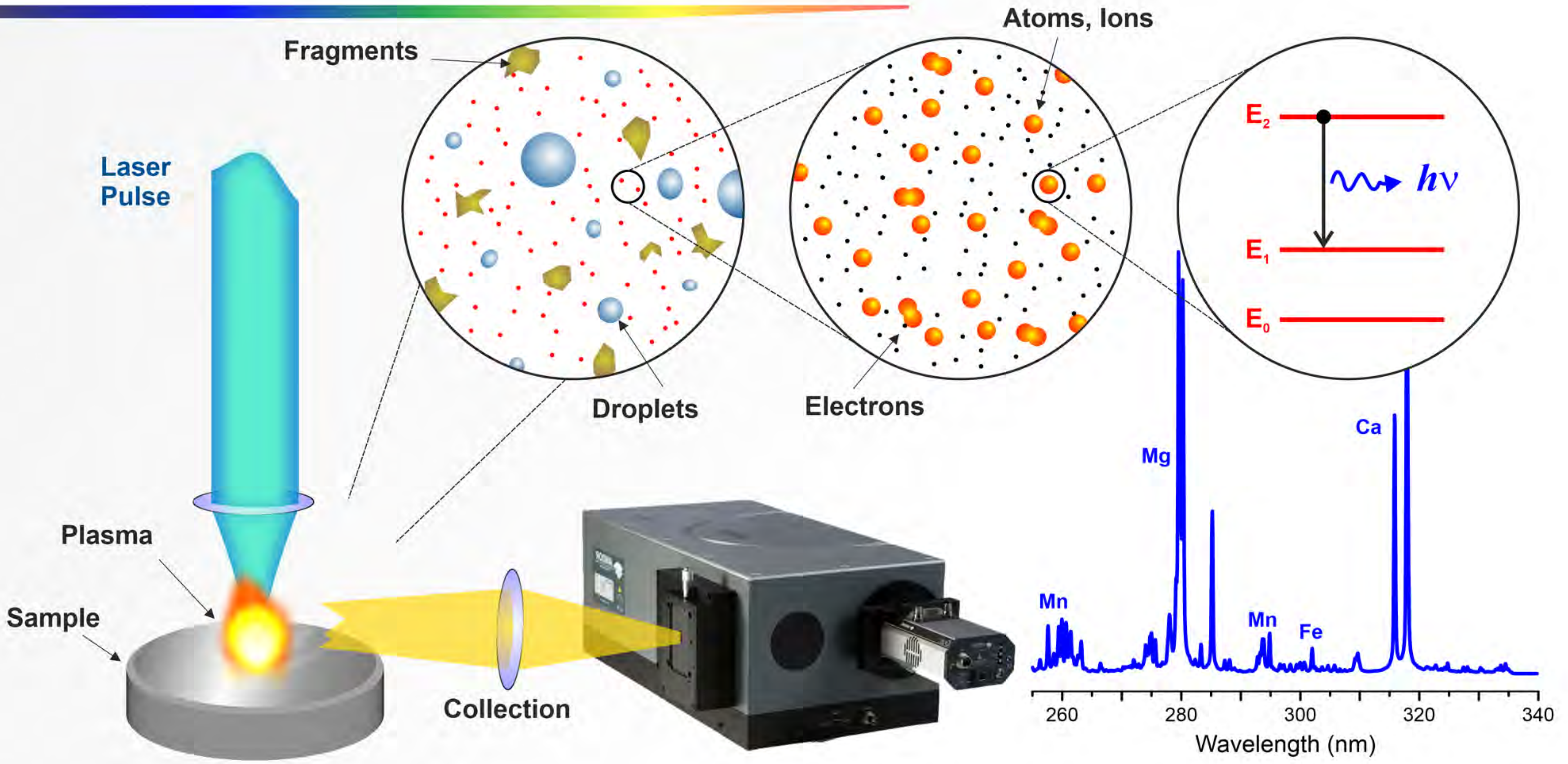


GDR Groupement de recherche
EMILI Étude des milieux ionisés
Plasmas froids créés par décharge et laser

Laser-Induced Breakdown Spectroscopy (LIBS)

Principle



Outline

1. LIBS-based imaging

   Principle & Instrumentation

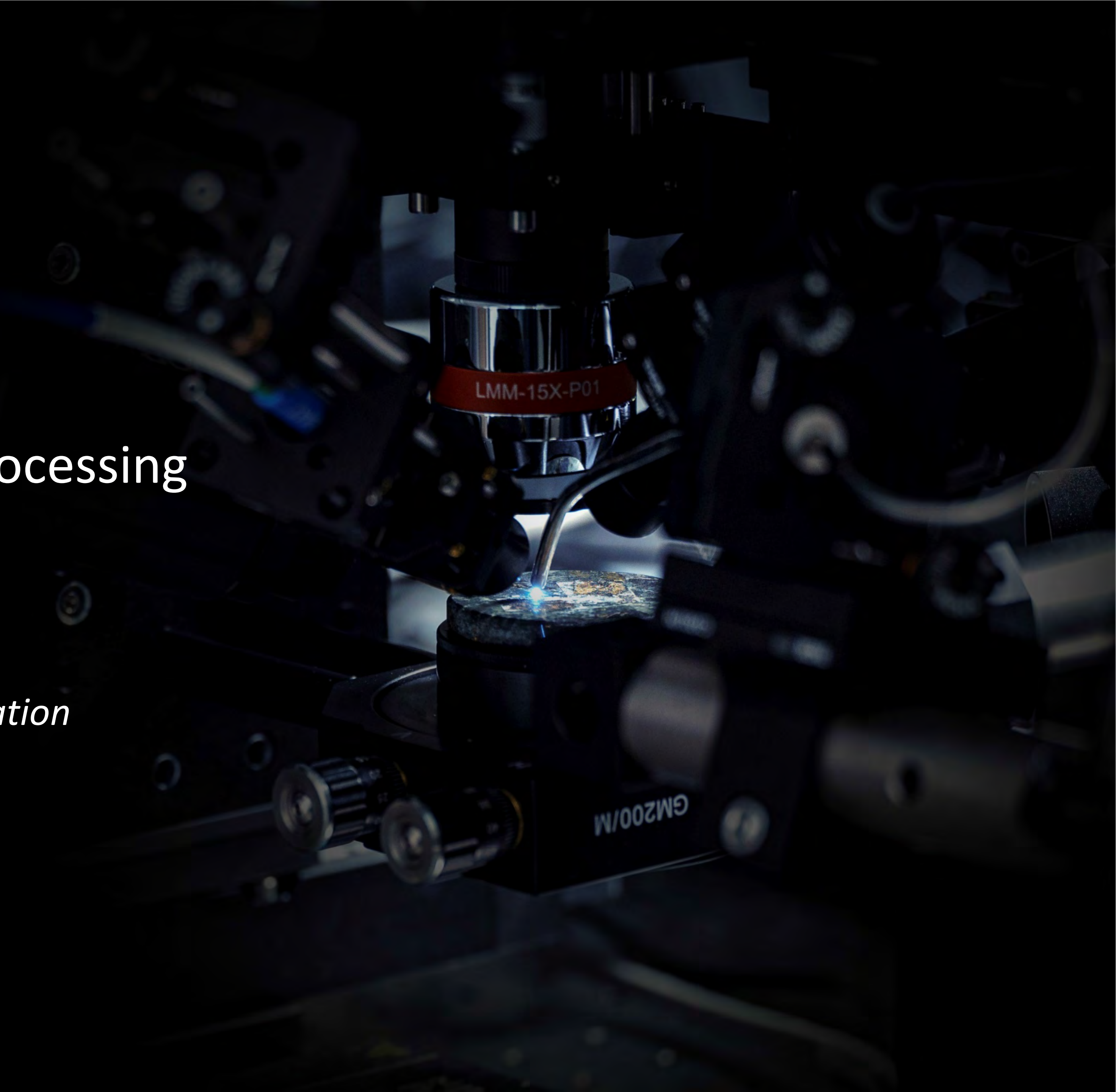
2. Specificities and Data Processing

   The good and not so good

3. Application of the ANN

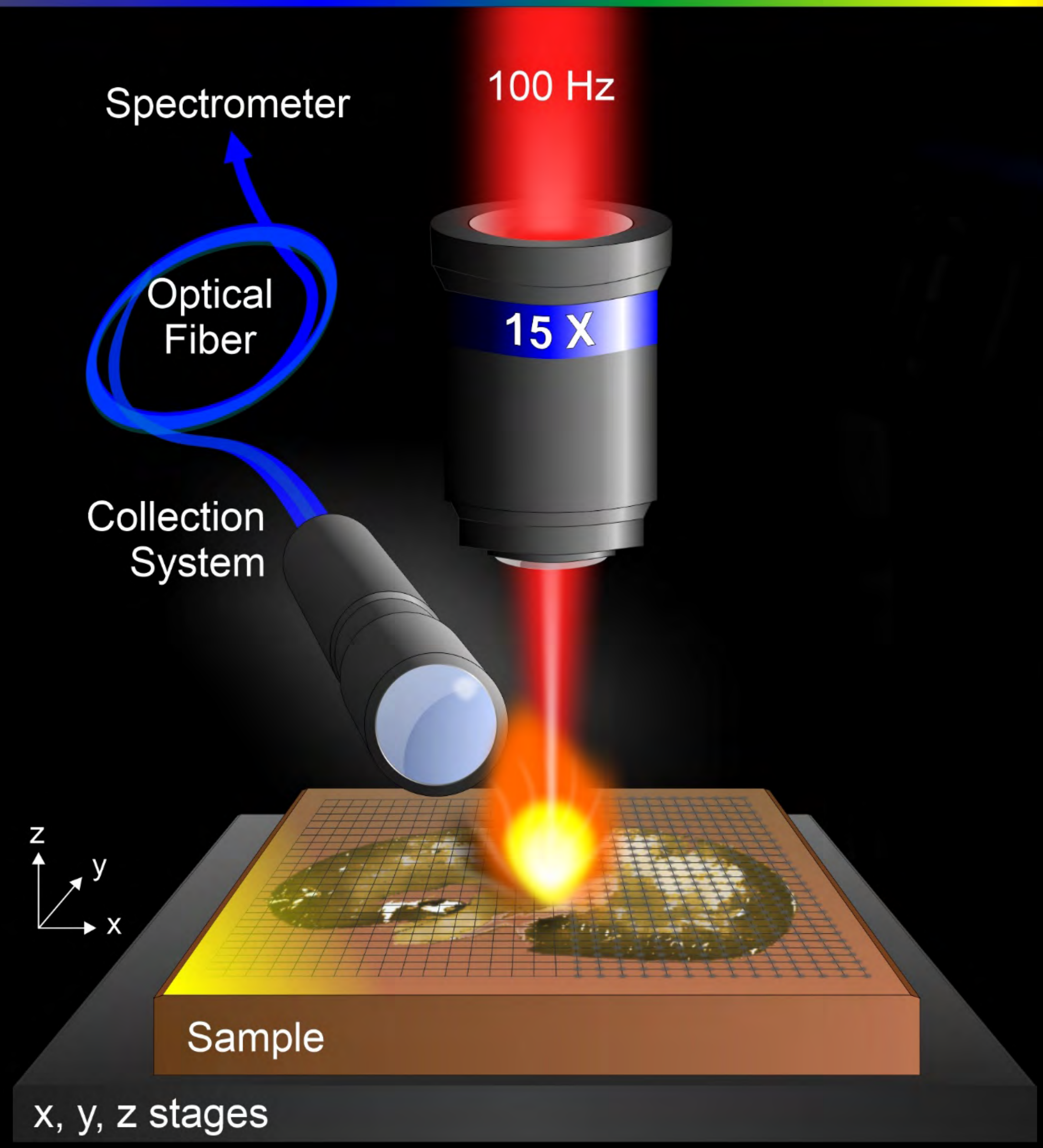
   Archeological Mortar Characterization

4. Perspectives



LIBS-based imaging

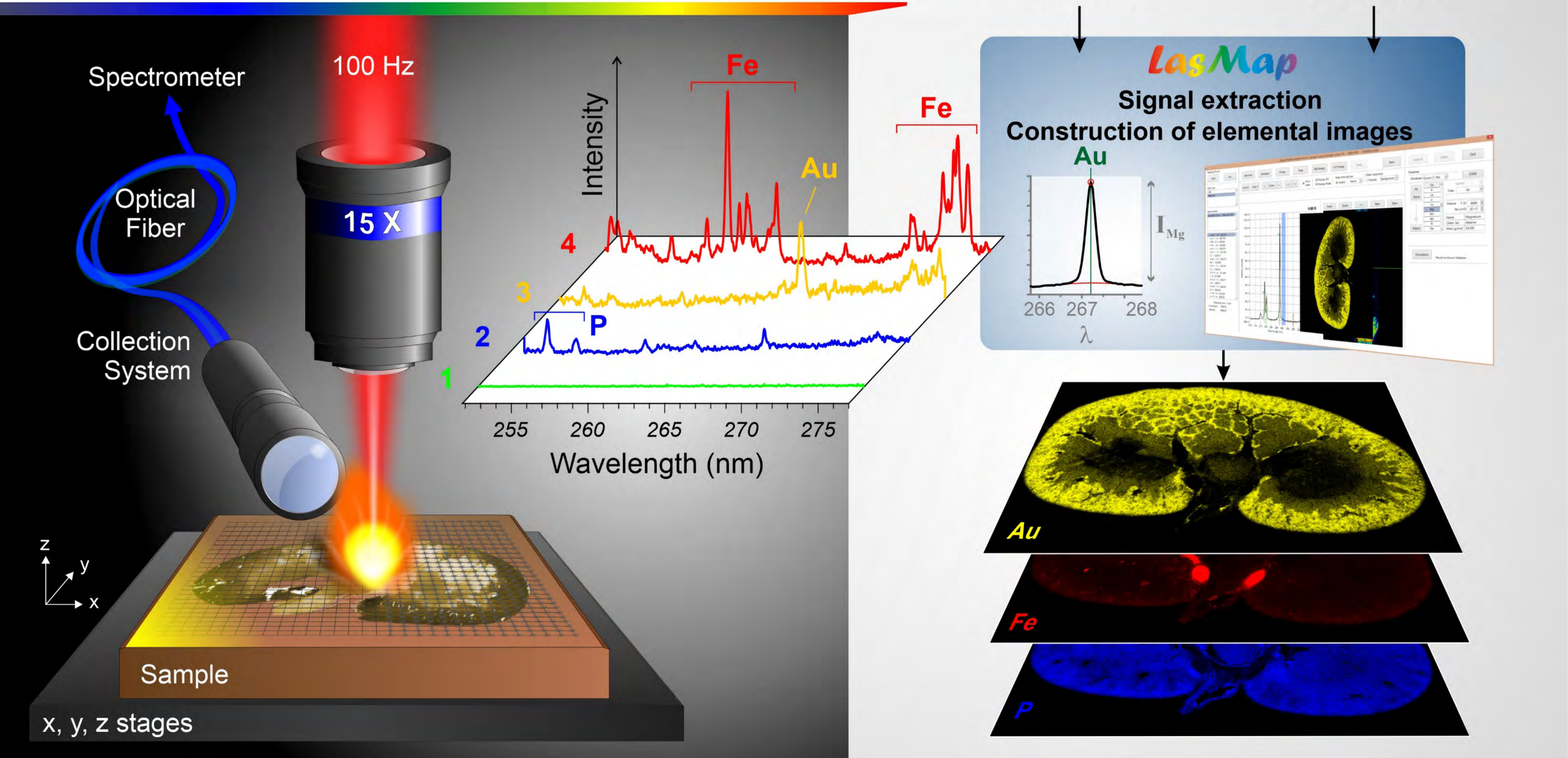
Principle

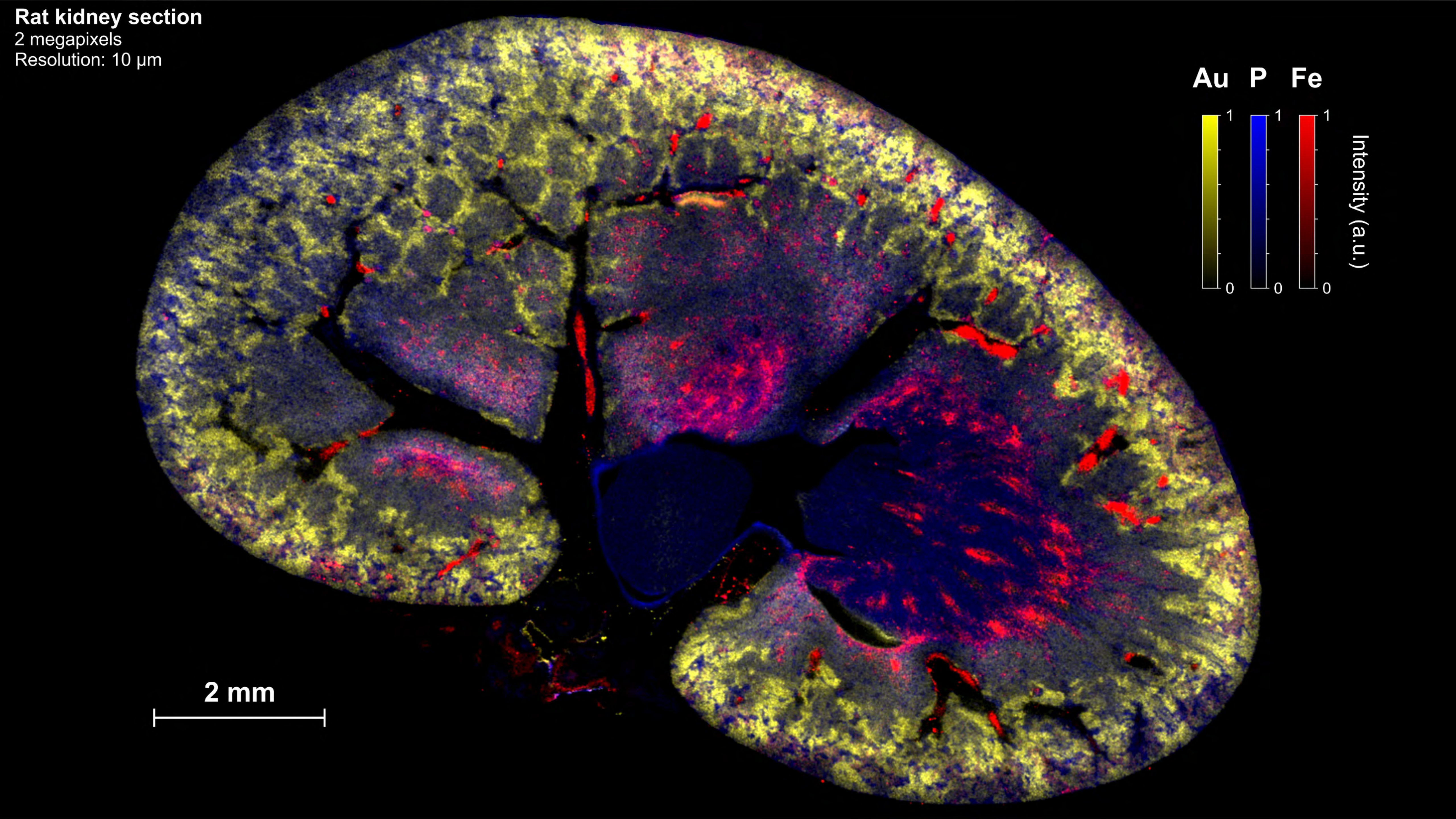


L. Jolivet, M. Leprince, S. Moncayo, L. Sorbier, et *al.* SAB 2019 (Review)
V. Gardette, V. Motto-Ros, C. Alvarez-Llamas, *et al.* Anal. Chem. 2023 (Review)

LIBS-based imaging

Principle

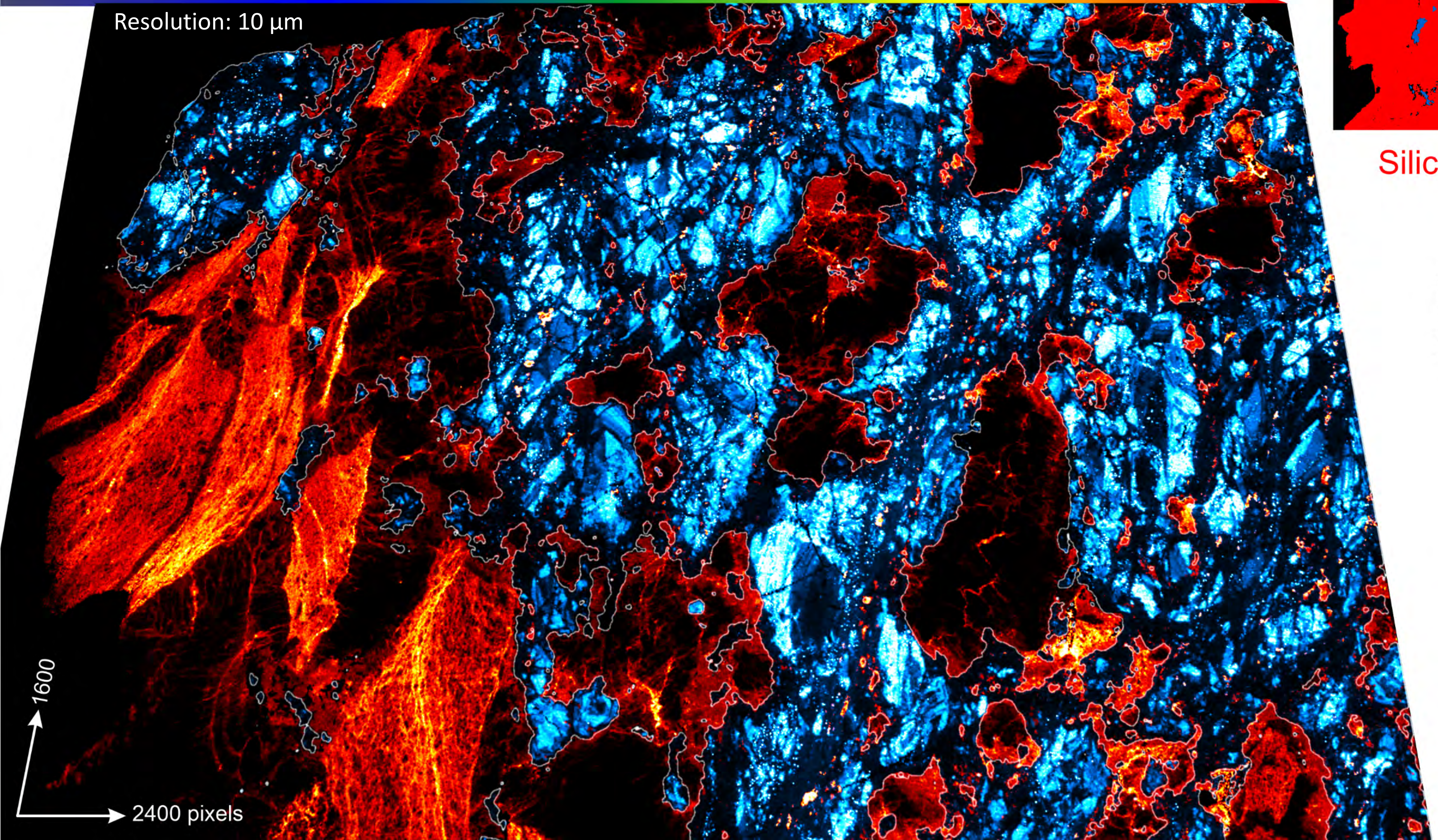


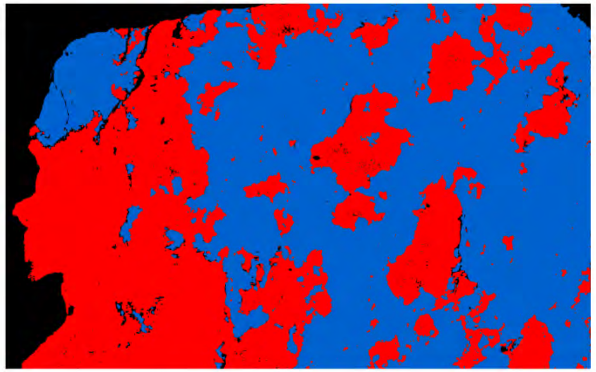

Rat kidney section
2 megapixels
Resolution: 10 μm
Au
P
Fe
1
0
1
0
1
0
Intensity (a.u.)
2 mm

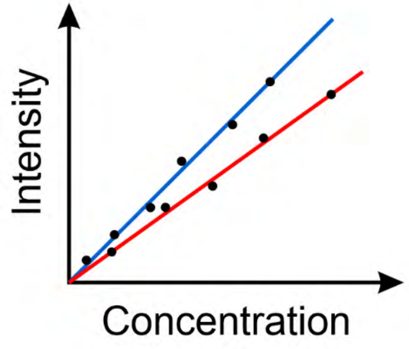
LIBS imaging

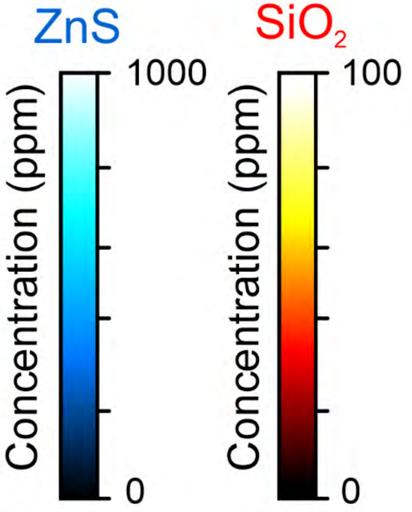
An example with a mine ore: Ge

A. Cugerone *et al.* Geology 48 (2019)









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Issues with Data Processing

Generalities

Emission Spectroscopy

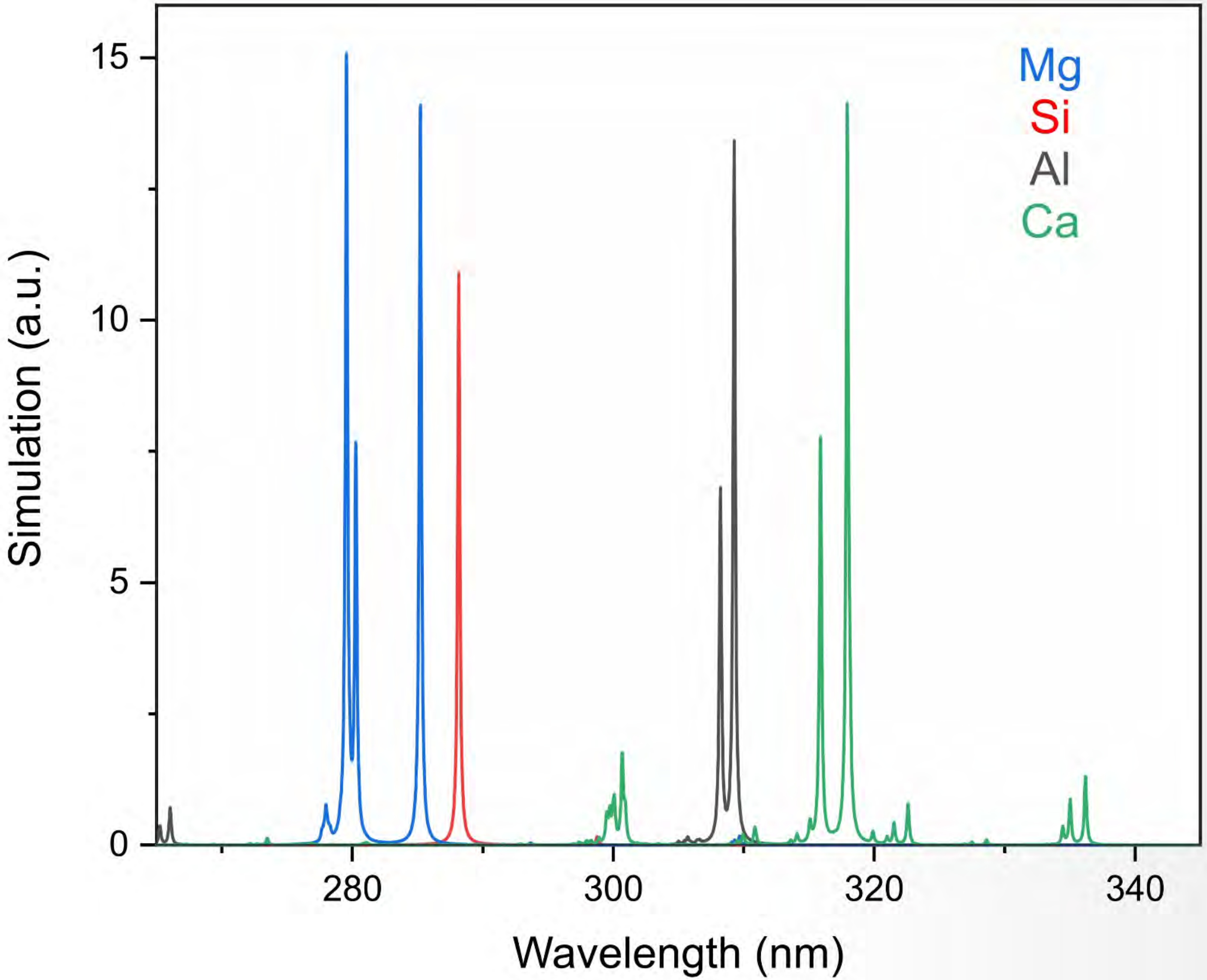
Complex spectral structure

Some elements have a very dense emission spectrum with thousands of lines (Ti, Fe, etc…)

High sample heterogeneity

By principle the aim in LIBS imaging is to reveal the heterogeneity of elements

Kurucz simulation T_e= 9000K, N_e= 5.10^{17} /cm^3



Issues with Data Processing

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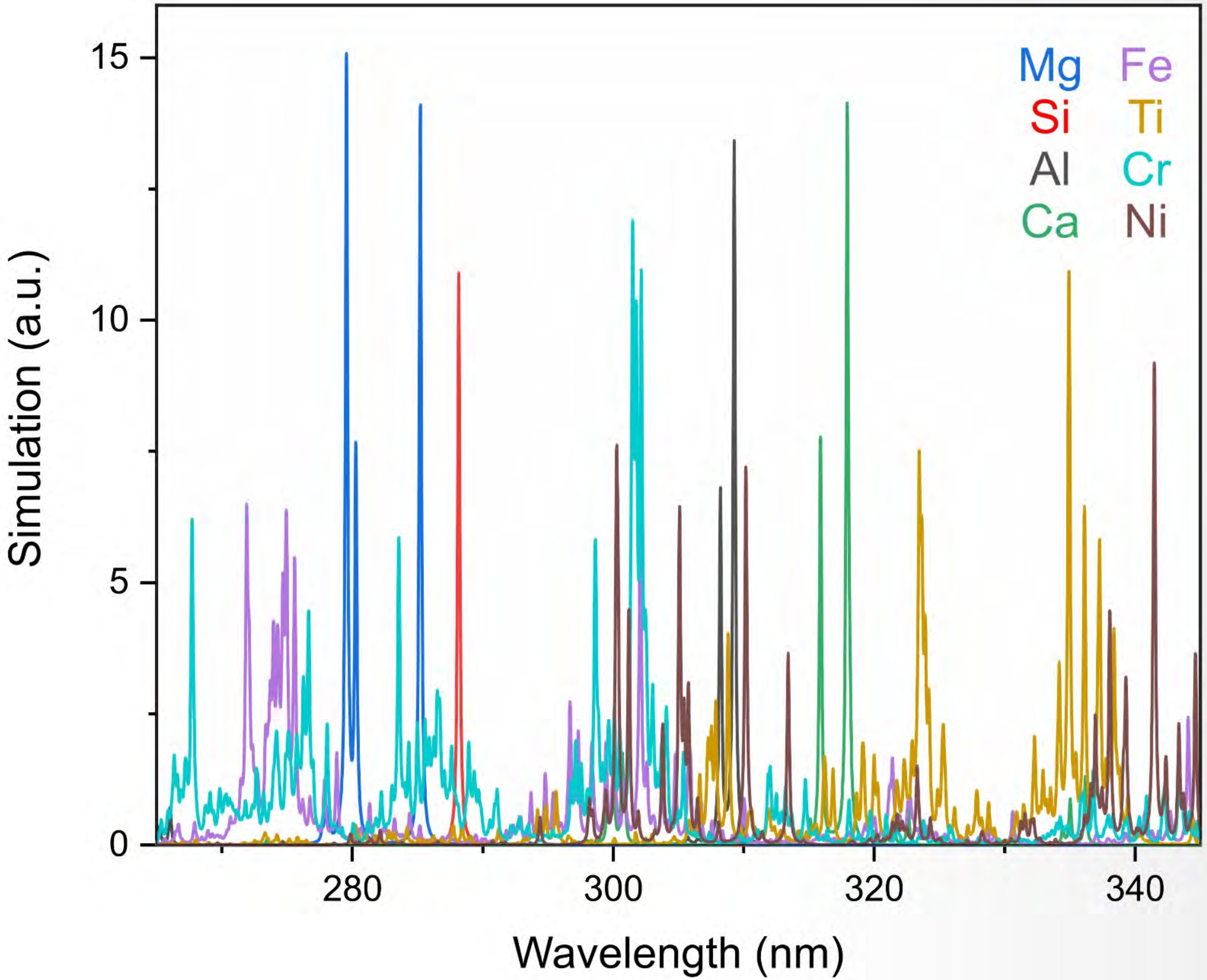


Issues with Data Processing

Generalities

Emission Spectroscopy

Complex spectral structure

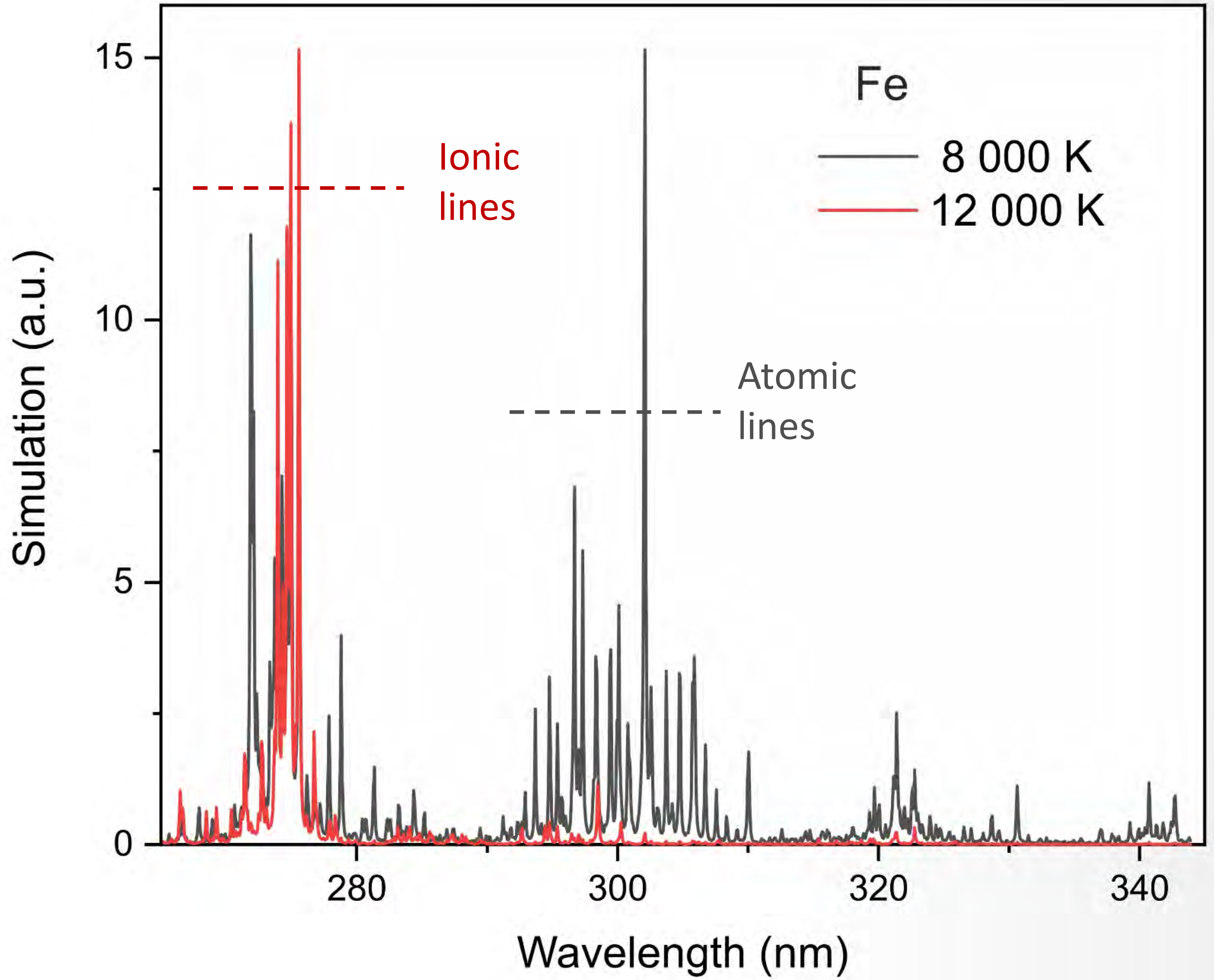
Some elements have a very dense emission spectrum with thousands of lines (Ti, Fe, etc…)

High sample heterogeneity

By principle the aim in LIBS imaging is to reveal the heterogeneity of elements

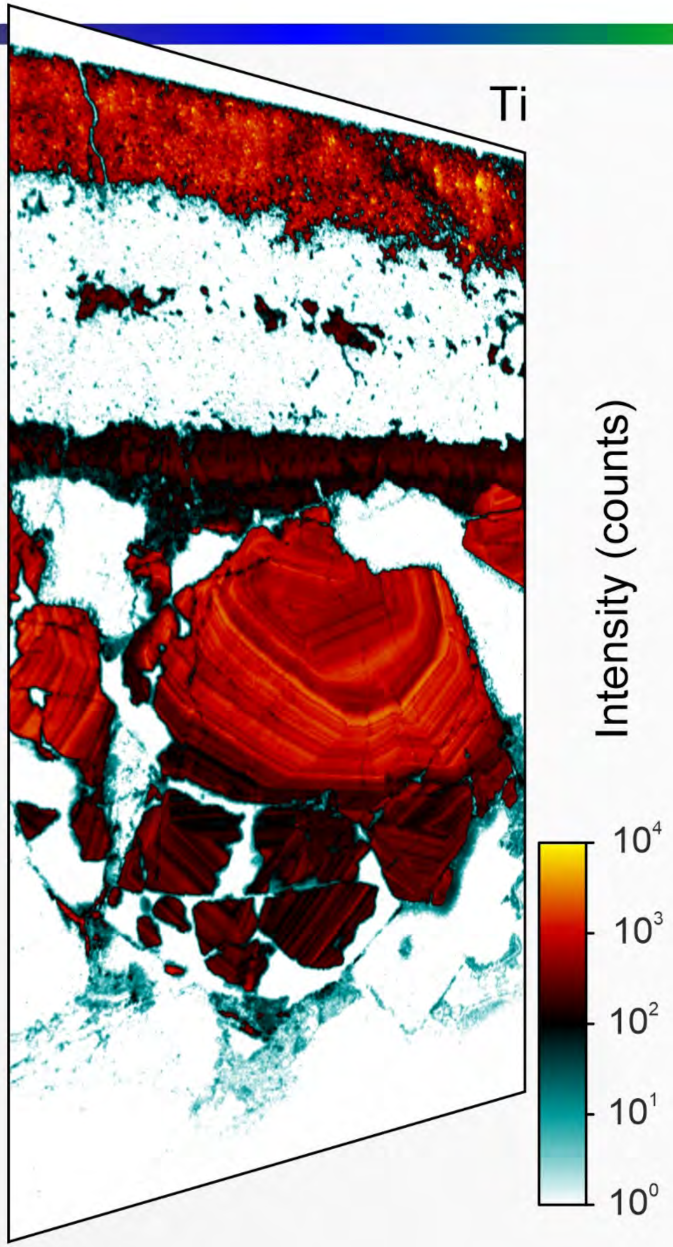
Dependence on plasma parameters

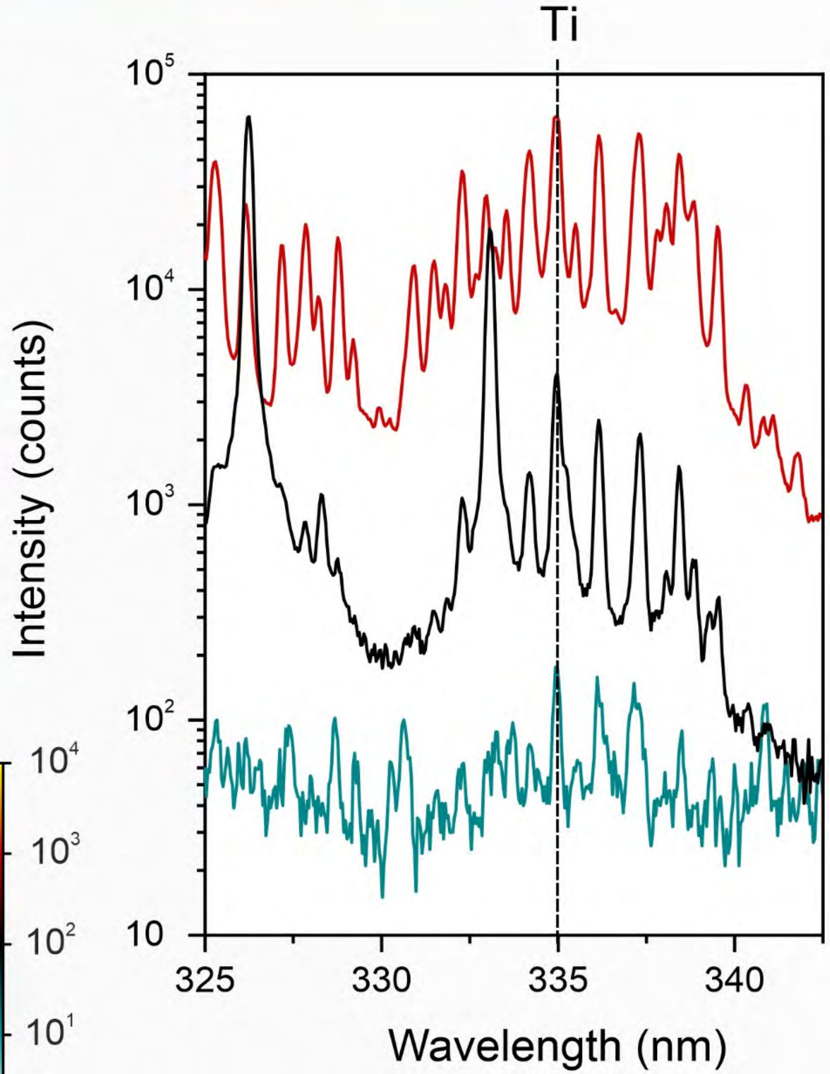
Kurucz simulation, $N_e = 1.10^{17}$ /cm^3

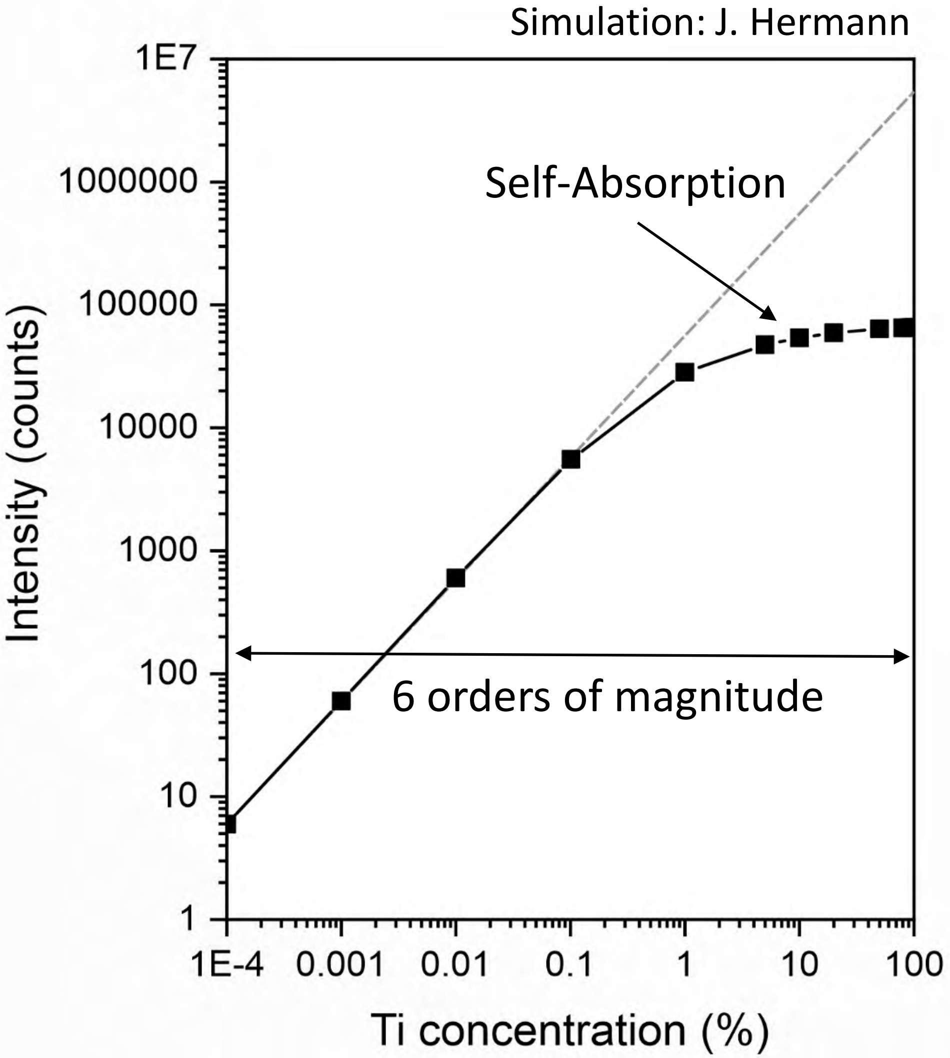


Issues with Data Processing

Dynamic range in "concentration"







Issues with Data Processing

To resume

Large Spectral Dataset

> millions of spectra

Up to 3 spectrometers (i.e. ~ 6000 wavelength channels)

Complexity of the Emission Spectra

Complex structure in wavelength (line interferences)

High dynamic range in intensity

Non linearity

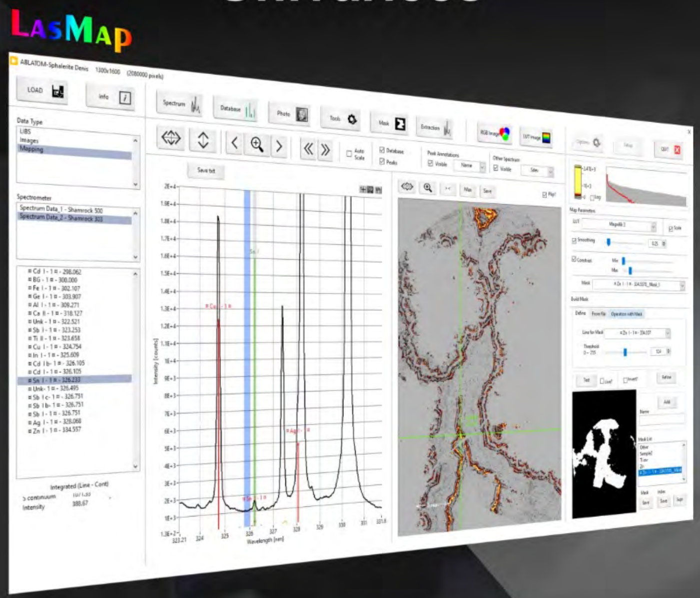
Plasma variability

Single shot analysis

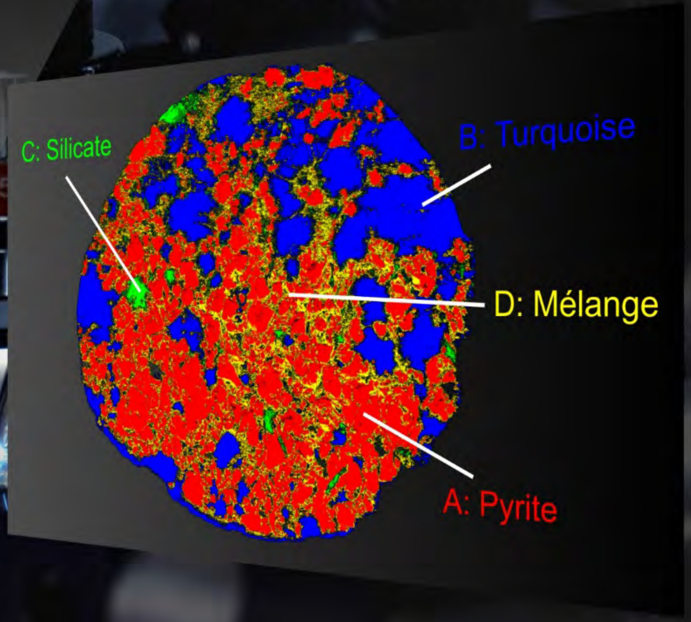
All the more challenging as the sample is complex

Data Processing

Méthodes Univariées



Méthodes Multivariées

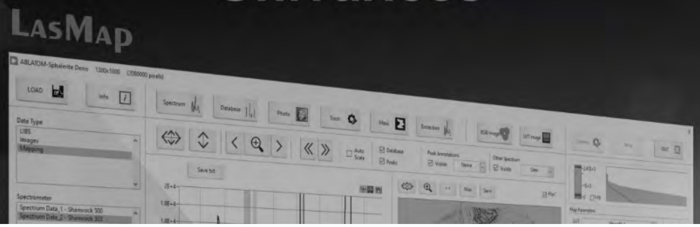


Vers un traitement automatisé?

A. Nardecchia *et al.*, Anal. Chim. Act. (2021)
A. Nardecchia *et al.*, Anal. Chim. Act. (2021)
A. Nardecchia *et al.*, Anal. Chim. Act. (2020)
V. Motto-Ros *et al.*, SAB (2019)
S. Moncayo *et al.*, JAAS (2018)

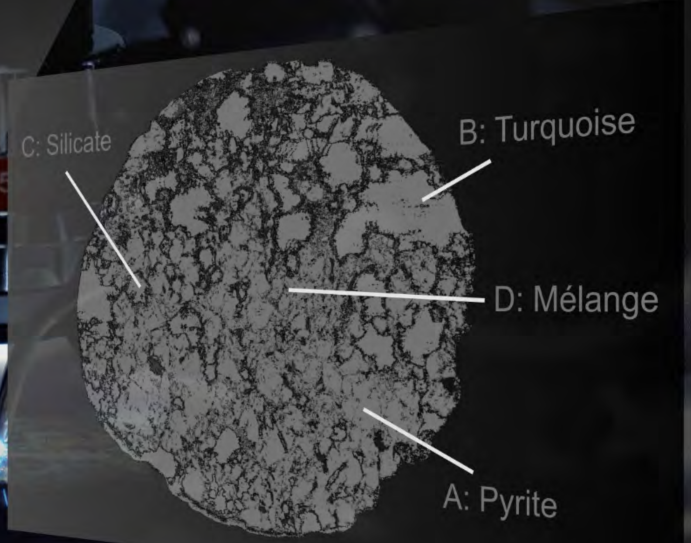
Data Processing

Méthodes Univariées



Intelligence Artificielle

Méthodes Multivariées



MITI *étape 1*

Caractérisation du mortier archéologique
Septembre 2021 - 36 Mois

UMR 5138
Archéologie et Archéométrie

LIBELUL

PEPR DIADEM
Septembre 2022

Vers un traitement automatisé?

dIAg-EM *étape 2*

Diagnostique médical par intelligence artificielle appliquée à la microscopie LIBS élémentaire
Novembre 2020 - 42 Mois

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JAAS

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Cite this: DOI: 10.1039/d2ja00389a

Artificial neural network for high-throughput spectral data processing in LIBS imaging: application to archaeological mortar†

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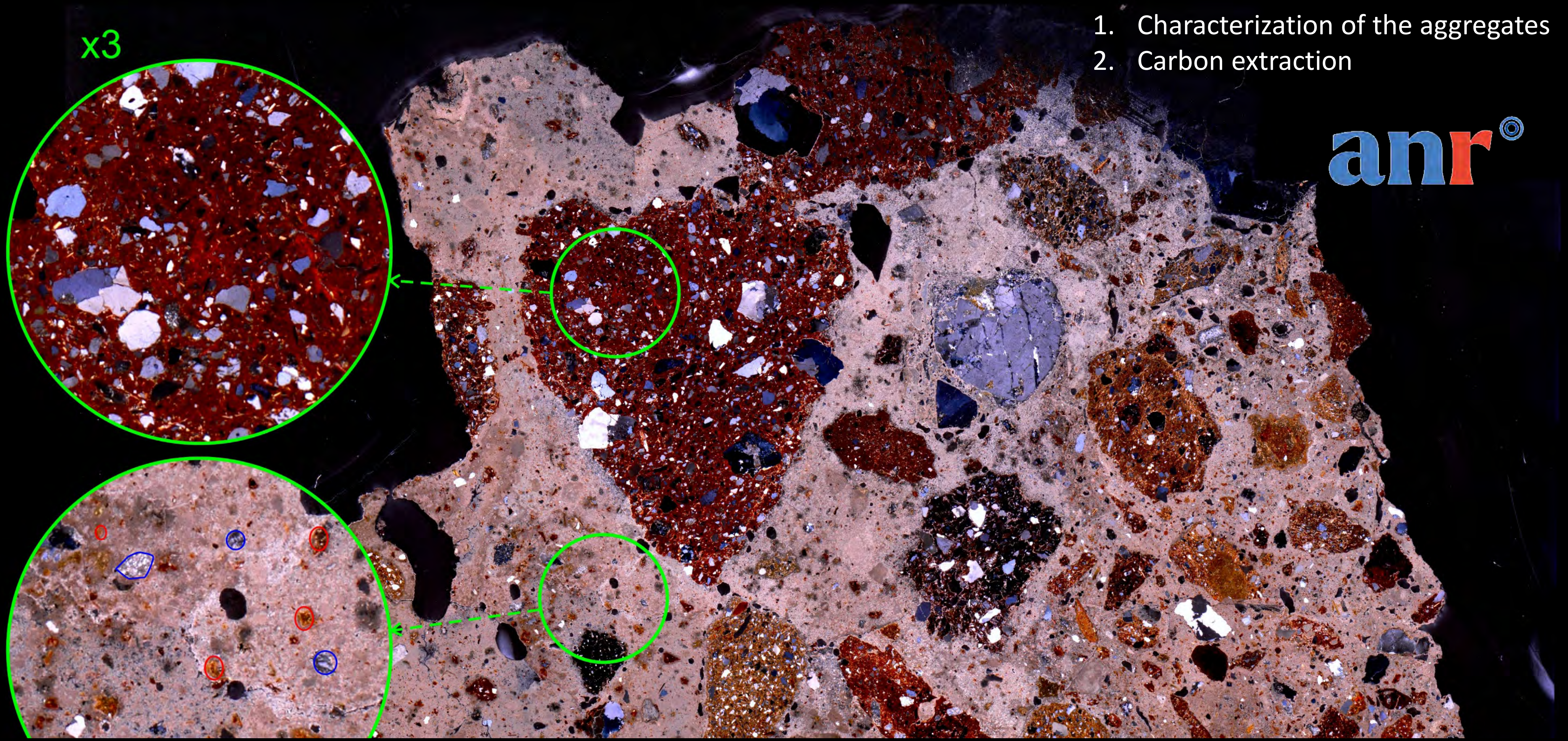
With the development of micro-LIBS imaging, the ever-increasing size of datasets (sometimes >1 million spectra) makes the processing of spectral data difficult and time consuming. Advanced statistical methods have become necessary to process these data, but most of them still require strong expertise and are not adapted to fast data treatment or a high throughput analysis. To address these issues, we evaluate, in the present work, the use of an artificial neural network (ANN) for LIBS imaging spectral data processing for the identification of different mineral phases in archaeological lime mortar. Common in ancient architecture, this building material is a complex mixture of lime with one or more aggregates, some components of which are of the same chemical nature (*e.g.* calcium carbonates). In this study, we trained an artificial neural network (ANN) for automatic detection of different phases in these complex samples. The training of such a predictive model was made possible by building a LIBS dataset of more than 1300 reference spectra, obtained from various selected materials that may be present in mortars. The ANN parameters (pre-treatment of data, number of neurons and of iterations) were optimized to ensure the best recognition of mortar components, while avoiding overtraining. The results demonstrate a fast and accurate identification of each component. The use of an ANN appears to be a strong means to provide an efficient, fast and automated LIBS characterization of archaeological mortar, a concept that could later be generalized to other samples and other scientific fields and methods.



Need of a real time processing to identify minerals

→ accurate discrimination between the carbonates

Artificial Neural Network

Through an automated processing?

Methodology

Key point

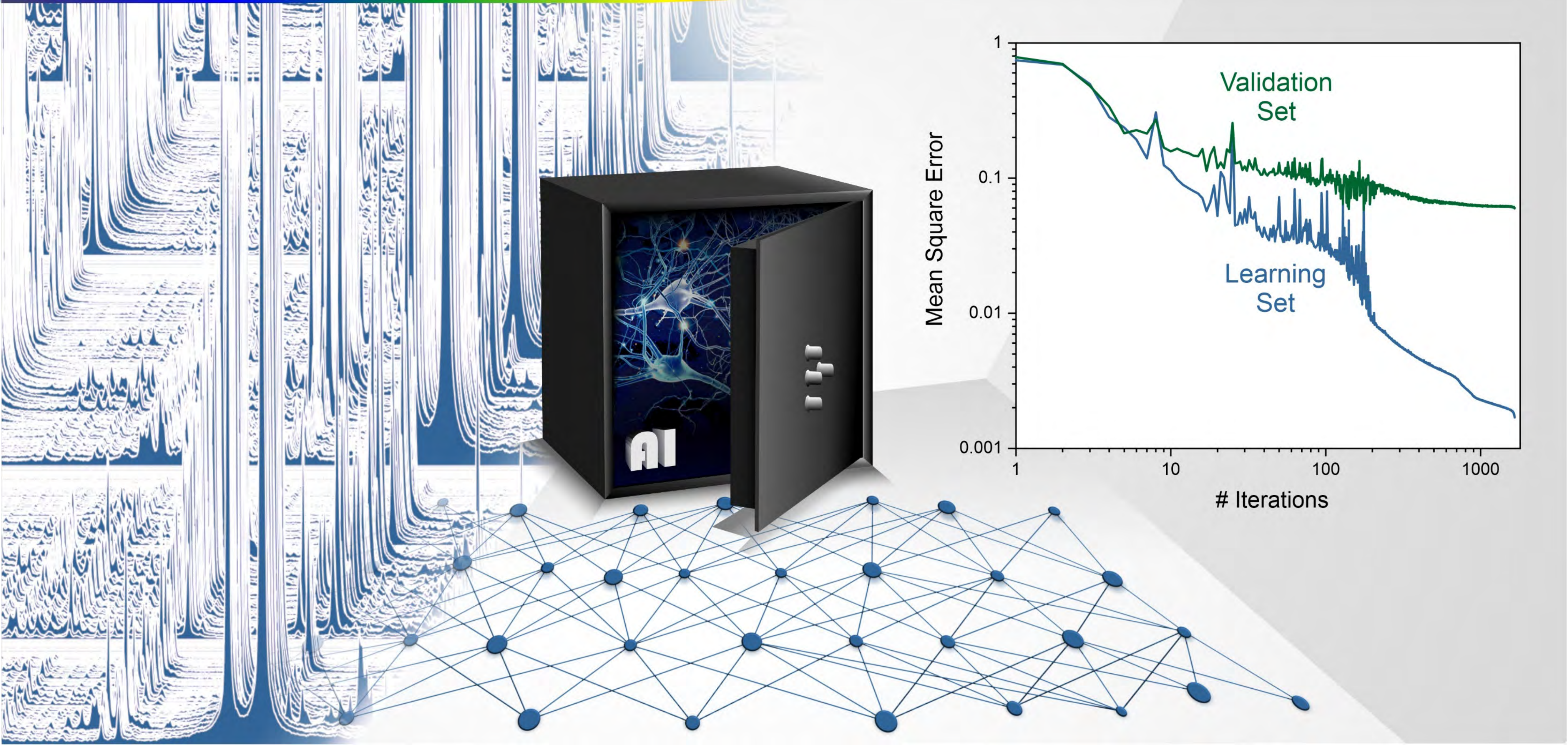
~ 1400 reference spectra
For 8 categories

3 steps

- Learning
- Validation
- Step

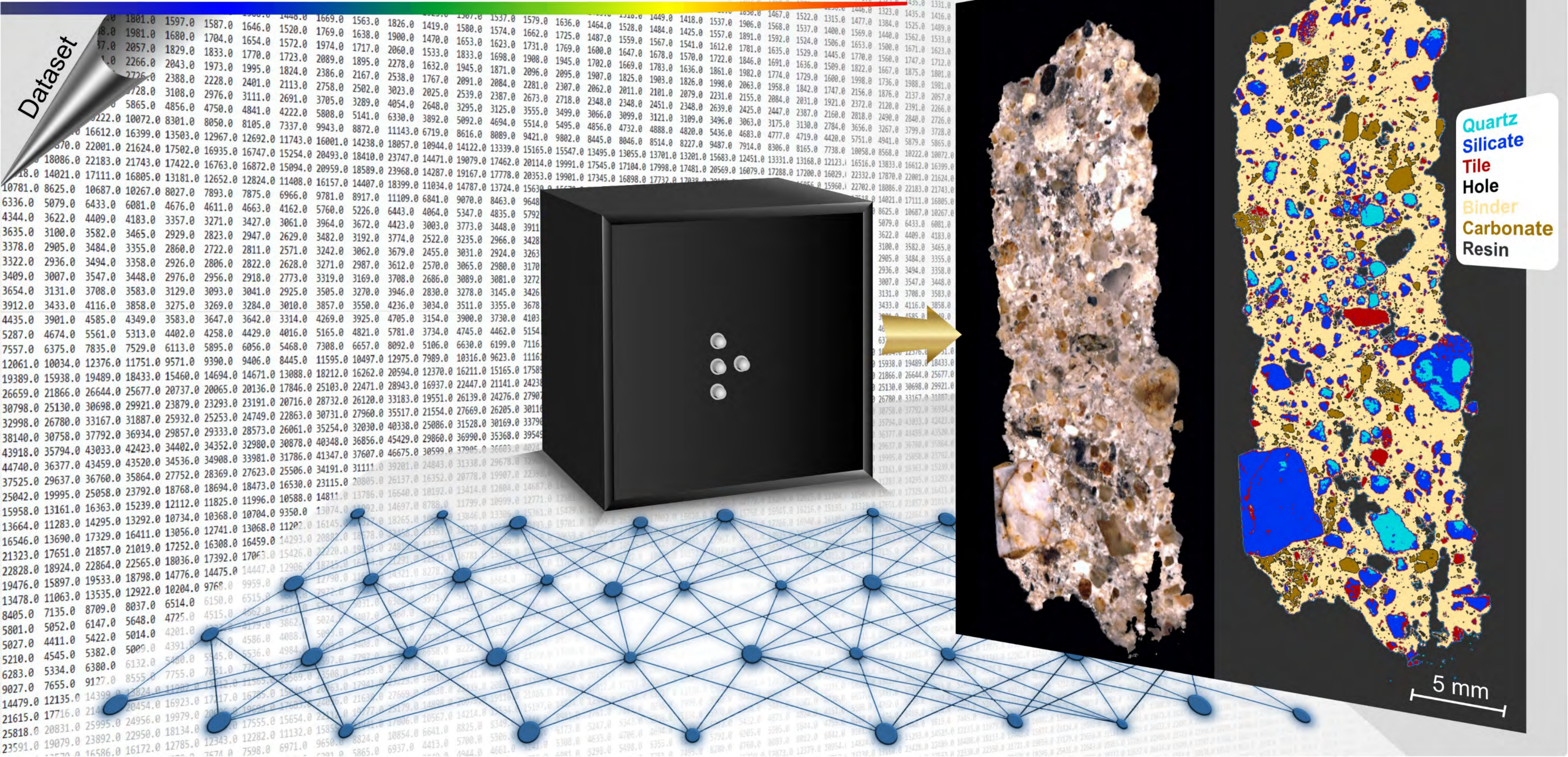
Artificial Neural Network

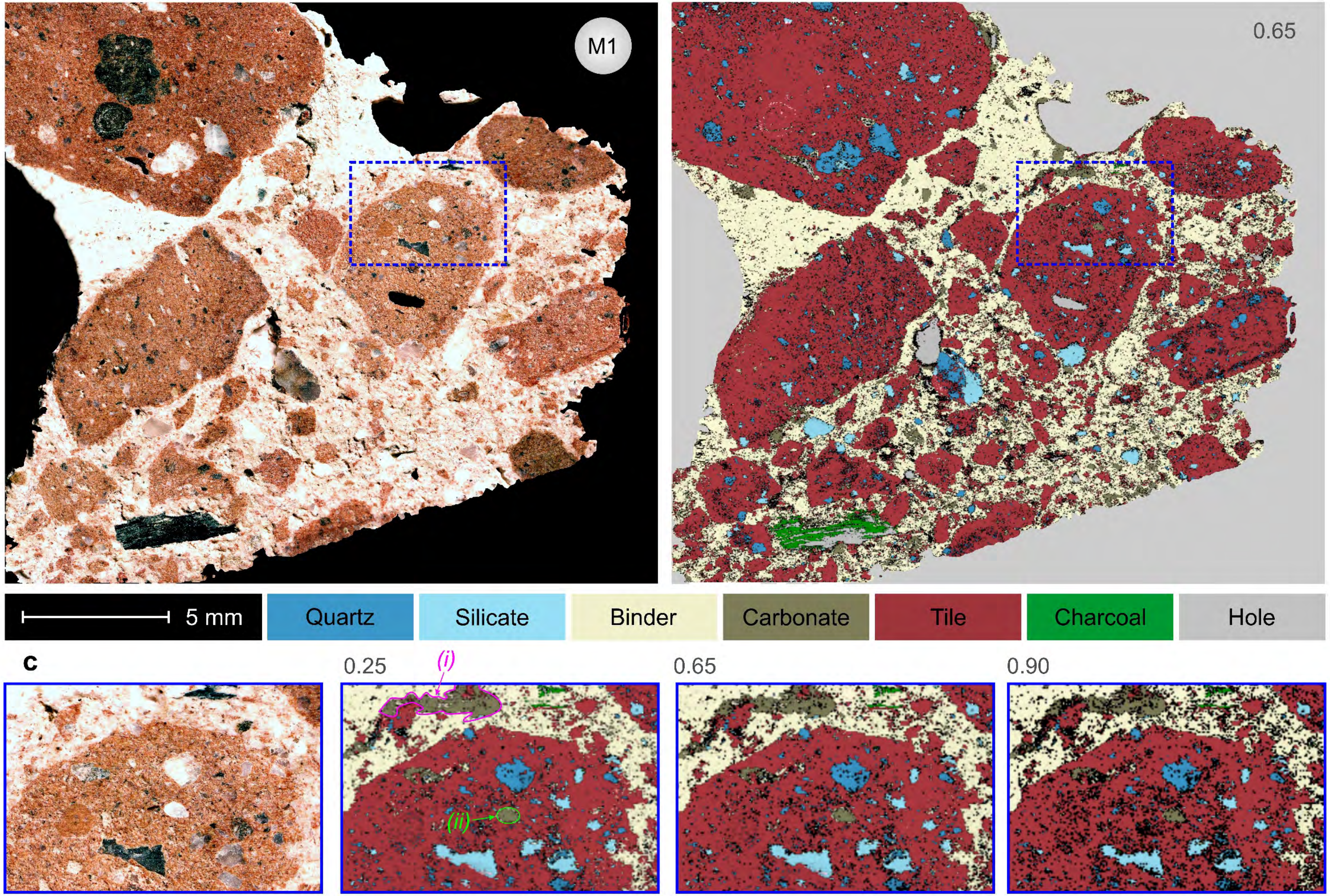
Through an automated processing?



Artificial Neural Network

Through an automated processing?





M1
0.65
5 mm
Quartz
Silicate
Binder
Carbonate
Tile
Charcoal
Hole
c
0.25
(i)
(ii)
0.65
0.90

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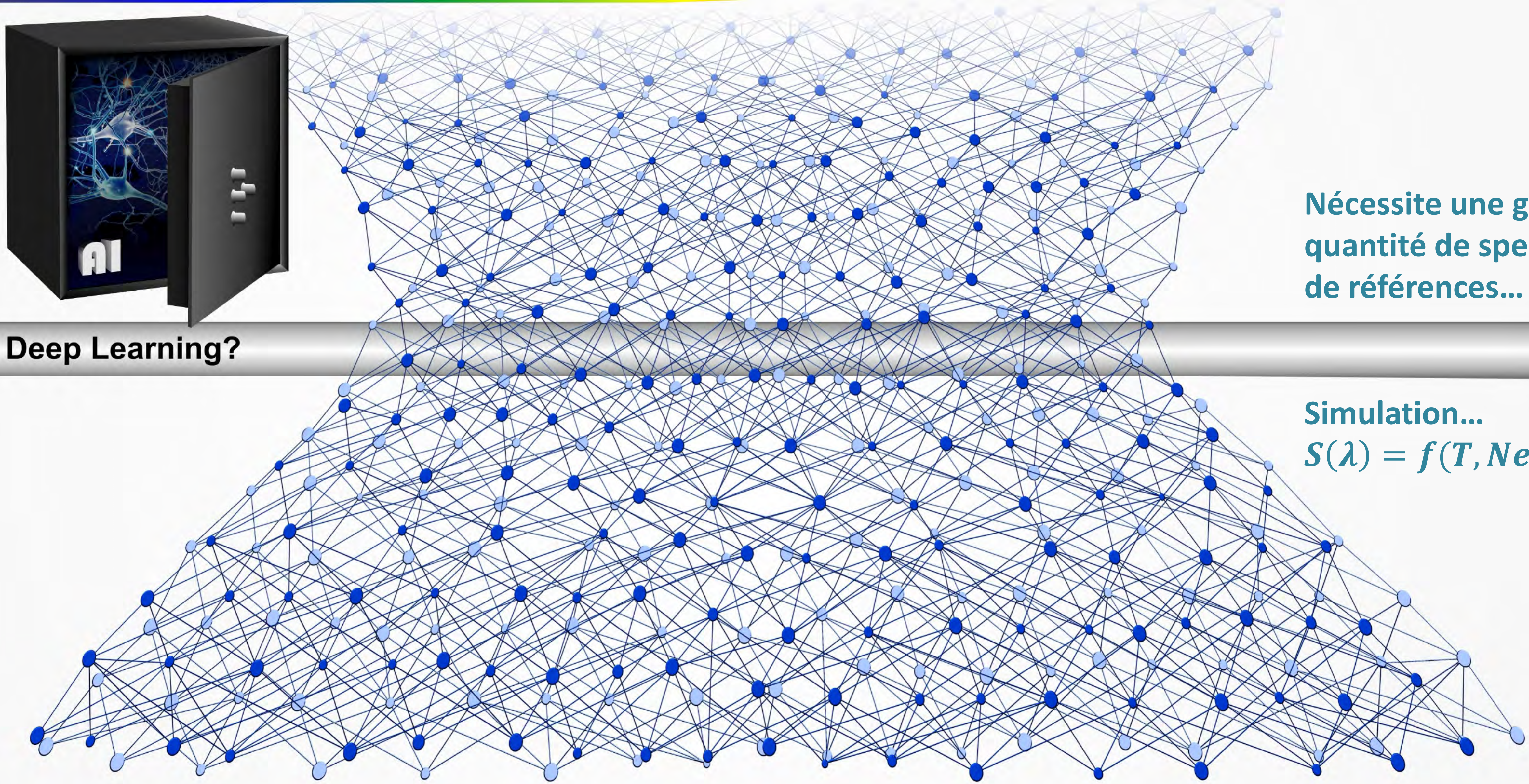
Deep learning in LIBS imaging

A dream?



Deep Learning?

Nécessite une grande quantité de spectres de références…

Simulation…

$S(\lambda) = f(T, Ne, C_x)$

Deep learning in LIBS imaging

Spectra simulation

Collaborations
Jörg Hermann
Ludovic Duponchel

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)

Simulation of pure elemental emissions for various T and Ne

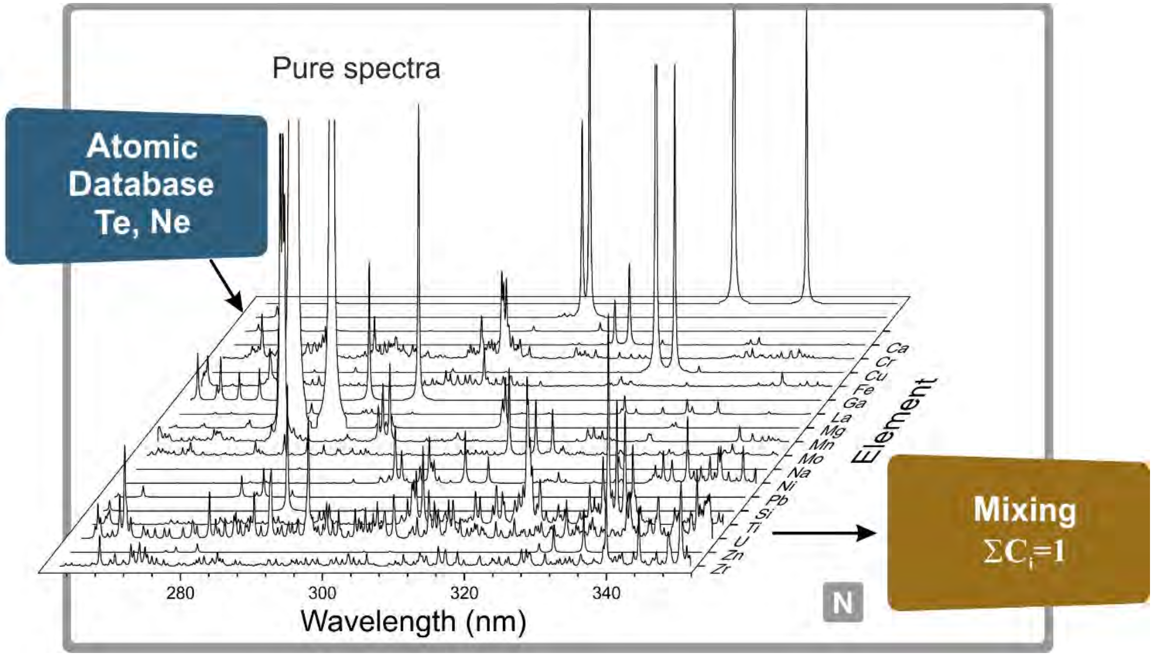
Saha equation: Ionization states

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

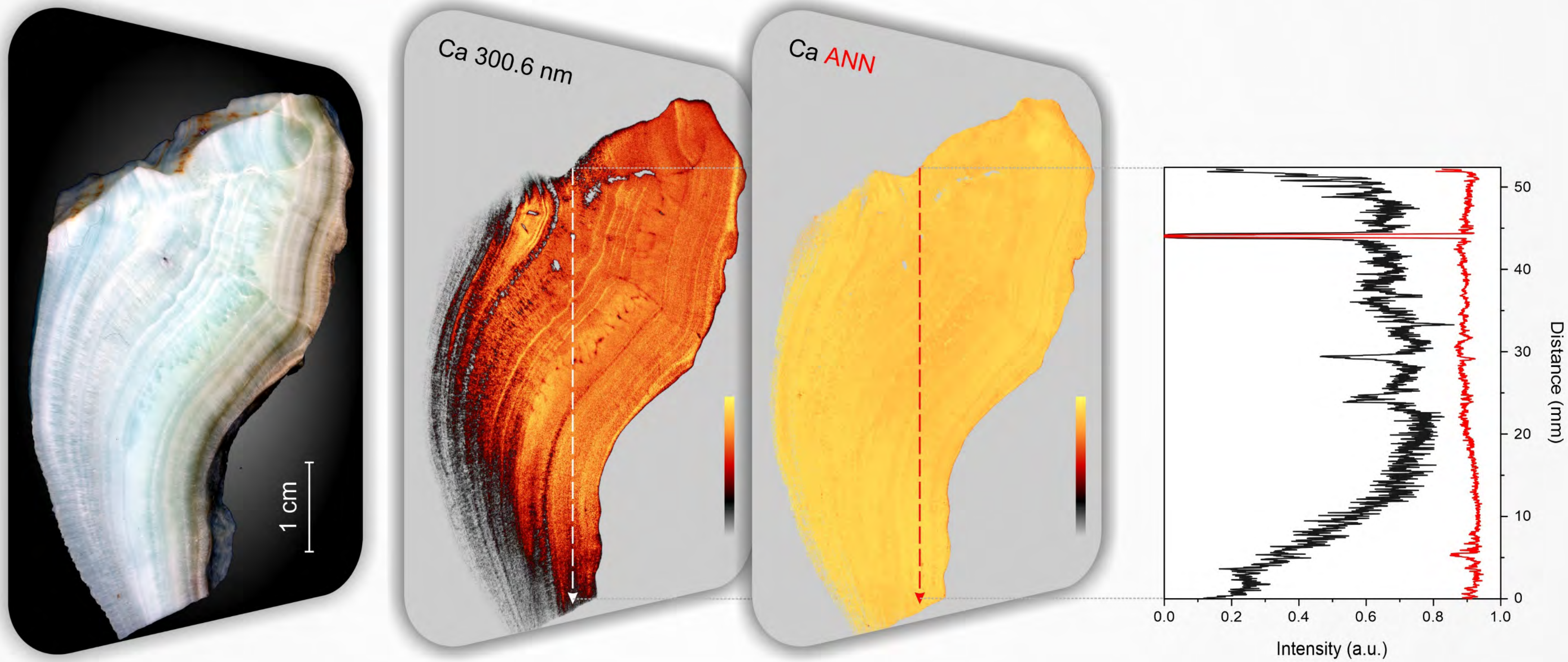
Spectral radiance (self-absorption)

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

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

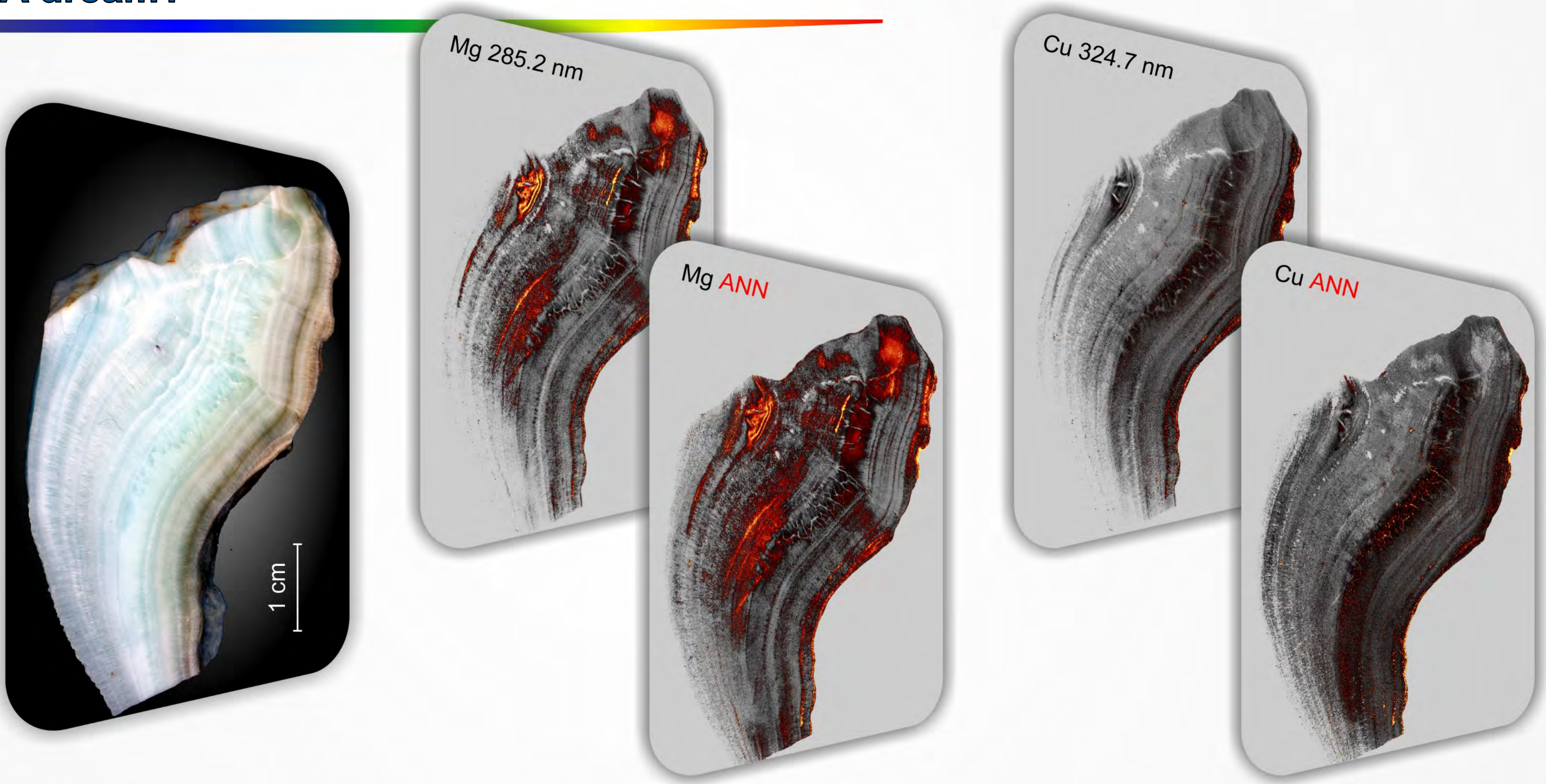


Deep learning in LIBS imaging
A dream?



Deep learning in LIBS imaging

A dream?

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L. Sancey


F. Pelascini

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L. Duponchel


C Fabre

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Thanks for your attention!