



list

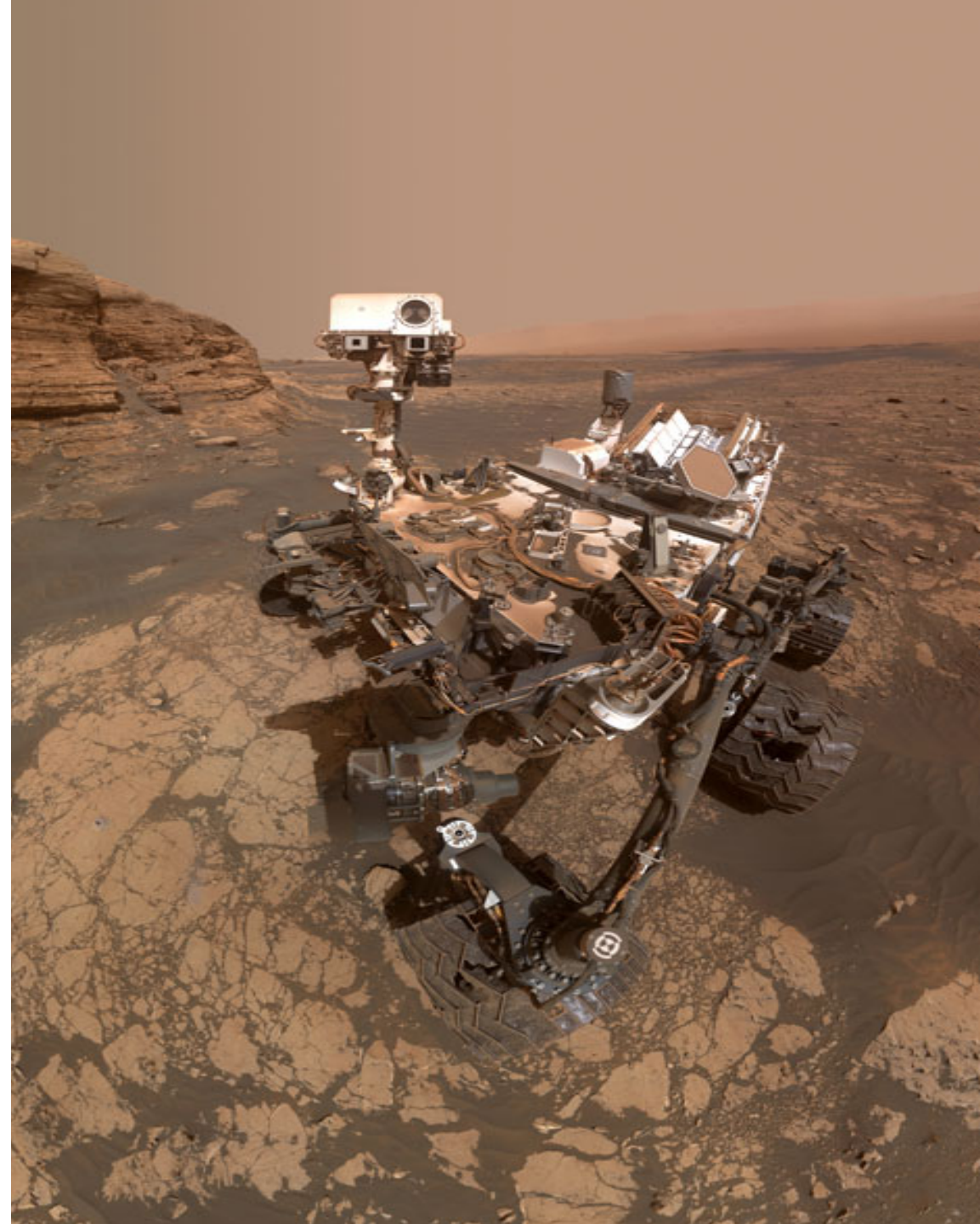
HyperPCA

At the Interface of Random Matrix Theory and
Laser-Induced Breakdown Spectroscopy

Riccardo Finotello *CEA Paris-Saclay (DIASI/SIALV/LVML)*

(loosely) based on Spectrochim. Acta B, 192 (2022), 106418

8e colloque de la SFPT-GH – Paris, 5–6 July 2023

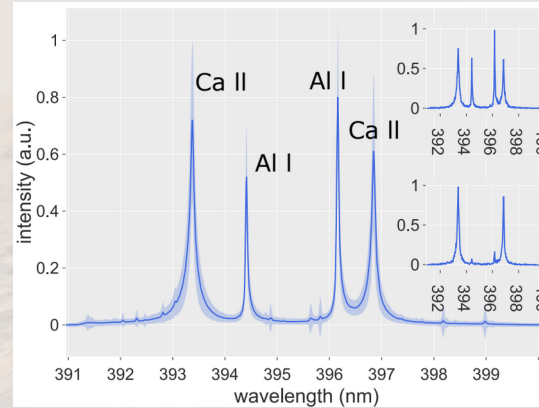
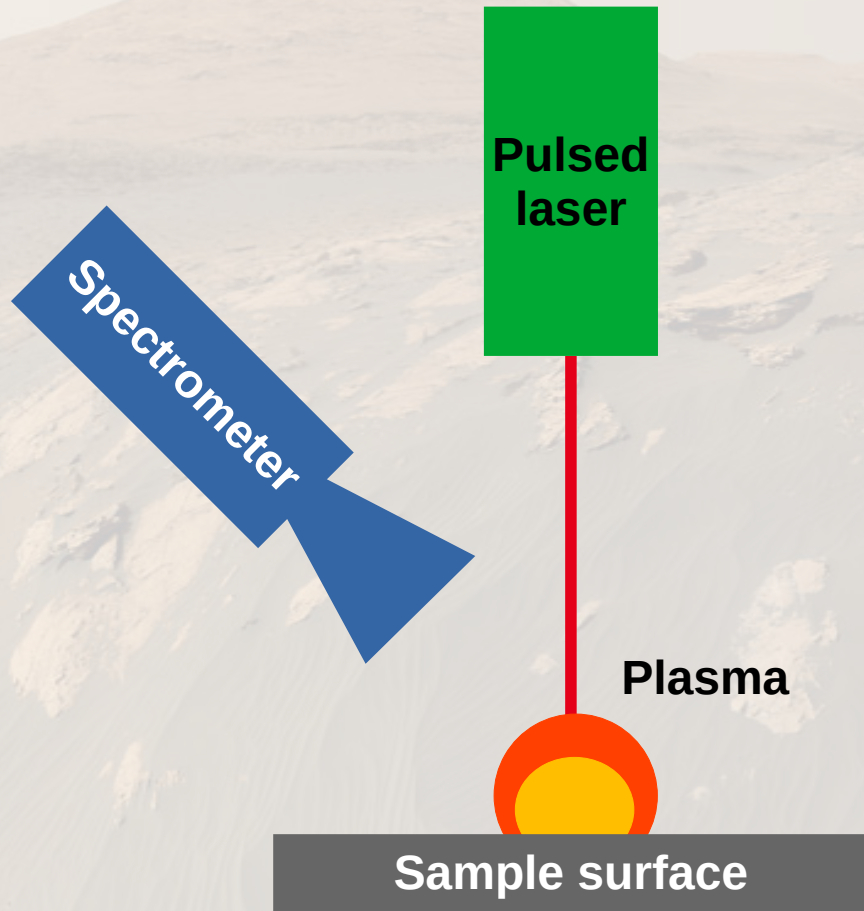




1 ■ Laser-Induced Breakdown Spectroscopy

The principle and a simple analysis

Laser-Induced Breakdown Spectroscopy

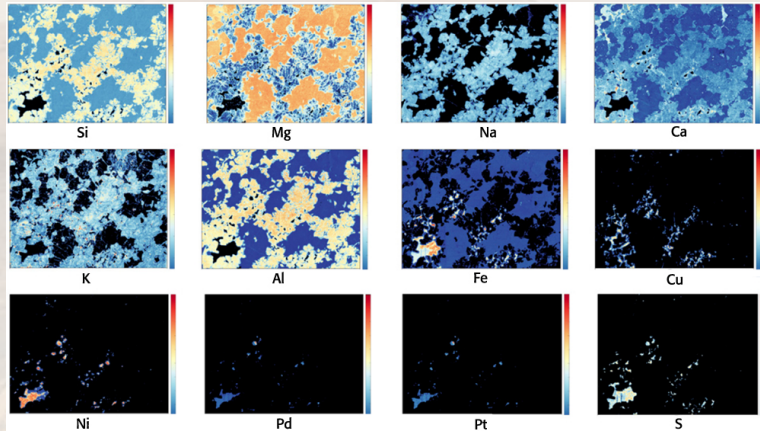


Advantages of **LIBS**:

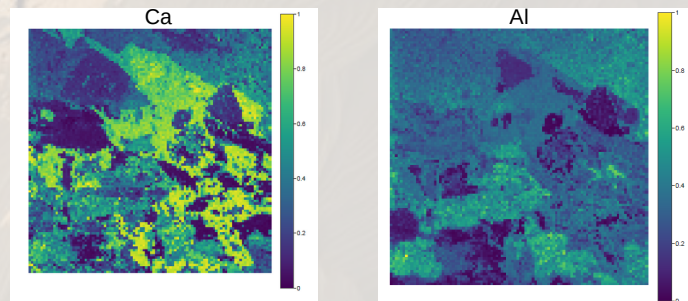
- **Fast** measurements
- **Ambient** air
- **Light** elements (up to H)
- **High** resolution



LIBS Mapping



Senesi and Harmon. *Spectroscopy Europe/World Vol. 33 Issue 4* (2021)



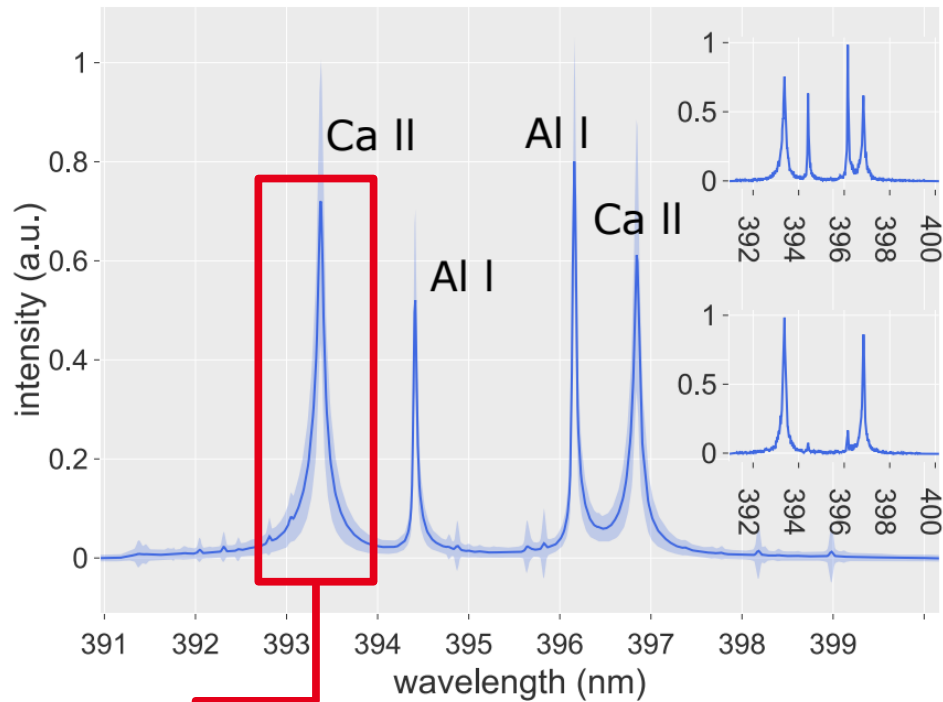
Finotello et al. *Spectrochim. Acta B: At. Spectrosc.*, 192 (2022), 106418

LIBS mapping:

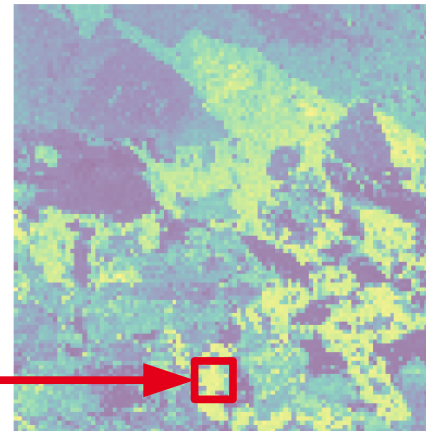
- **Resolution** $< 10 \mu\text{m}$
- Ability to cover **large surfaces** (very recent: 4K images with 1 kHz laser, see Harrel et al. (2023))
- **Elemental** chemical maps
- **Minimal** sample preparation
- **Qualitative** and **quantitative** analyses
- Applications to geology, space sciences, biology, etc.



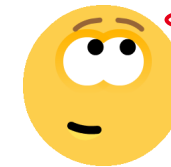
Standard Line Intensity Analysis



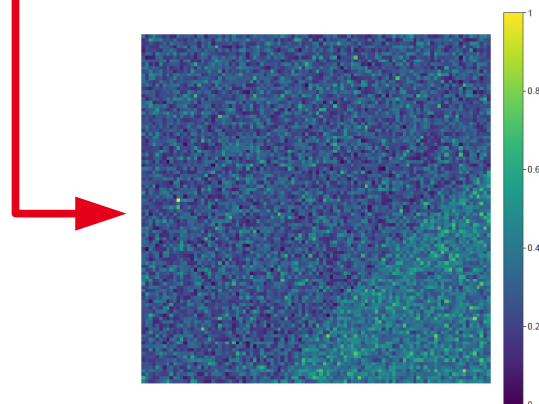
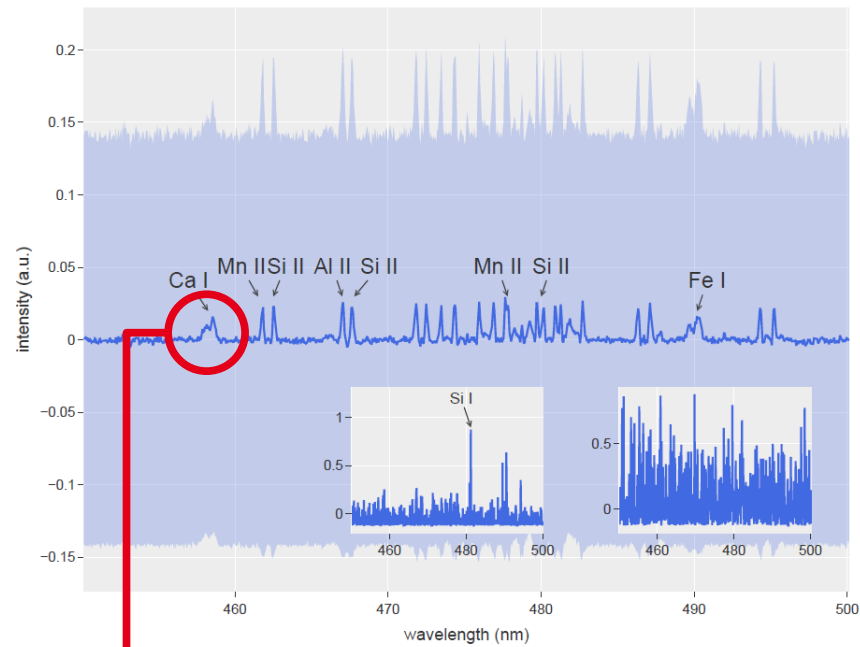
- Plasma radiation **characteristic** of **elements** in the sample
- Laser shot emission **spectrum** characterizing elements in a **pixel**
- Known **emission lines** (at given wavelengths) 2D **elemental maps**



MAPPINGS ARE ASSOCIATED TO WAVELENGTHS!



Standard Line Intensity Analysis



analytical
chemistry

Spectral Interference Elimination in Soil Analysis Using Laser-Induced Breakdown Spectroscopy Assisted by Laser-Induced Fluorescence

Rongxing Yi, Jiaming Xiaoyan Zeng, an



Optics and Lasers in Engineering
journal homepage: www.elsevier.com/locate/optilaseng

Spectral interference elimination and self-absorption reduction in laser-induced breakdown spectroscopy assisted with laser-stimulated absorption

Yun Tang^{a,c,*}, Shixiang Ma^b, Rui Yuan^b, Yuyang Ma^b, Wei Sheng^a, Shiping Zhan^a, Junnan Wang^b, Lianbo Guo^{b,*}

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Article
pubs.acs.org/ac

ROYAL SOCIETY OF CHEMISTRY

Carbon quantification in soils with different textures using laser-induced breakdown spectroscopy: spectral interference correction and use of a 3D plane model†

Keyelson Stenio^{a,*}, Alfredo Augusto Pereira Xavier^c, Carla Pereira De Moraes^b and Debora Marcondes Bastos Pereira Milori^{a*}

June 2022, 14

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View Journal | View Issue

for updates

Anal. At. Spectrom., 2017.

Optics and Lasers in Engineering 134 (2020) 106254

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Optics and Lasers in Engineering

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Spectral interference elimination and self-absorption reduction in laser-induced breakdown spectroscopy assisted with laser-stimulated absorption

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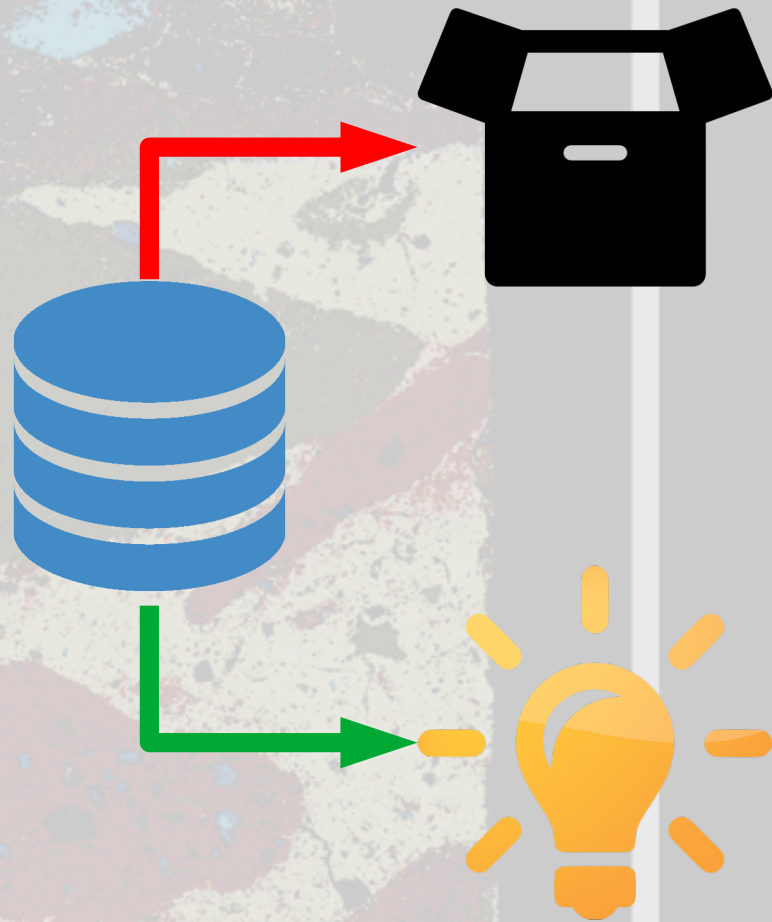
- **Spectral interference** is a longstanding problem in elemental spectral
- Element discovery can be difficult due to the specific **expertise required**



2 ■ Multivariate Analysis and Random Matrices

Towards an advanced Principal Components
Analysis

Extracting LIBS Information



*Black box approaches
(CNNs, ViTs, etc.)*

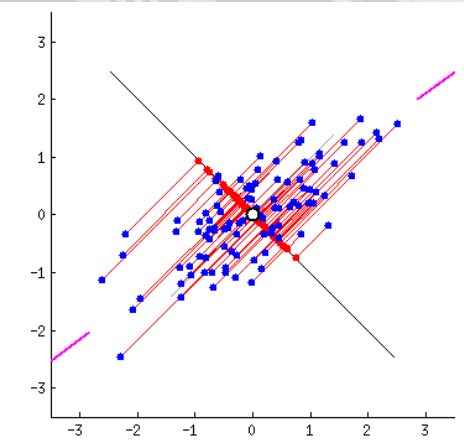
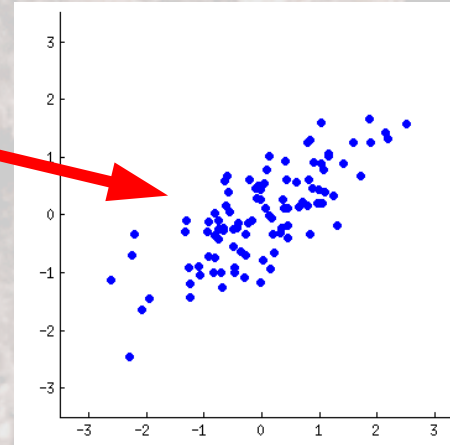
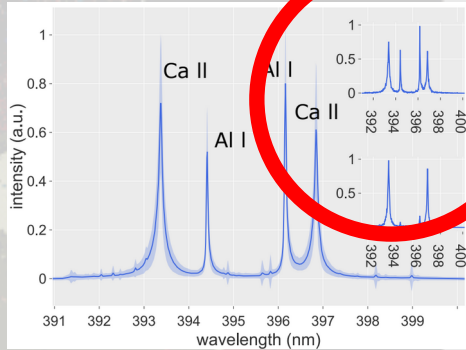
*Interpretable statistical
model*

M3

- Use **more information** contained in spectra
- Consider data as **compact structure** (image) rather than single pixel
- Avoid complicated models: **streamline** complexity and computation
- **Reduce expertise** required to interpret the results

Background: Herreyre et al. *J. Anal. At. Spectrom.*, 2023, 38, 730-741

Principal Components Analysis



- Find **new representation**
- **Minimize** reconstruction error

$$W_{PCA} = \arg \min_{W^T W = \mathbb{I}} \left\{ \|X' - X W\|_2^2 \right\}$$

$$PCA : \mathbb{R}^{n \times p} \rightarrow \mathbb{R}^{n \times p}$$

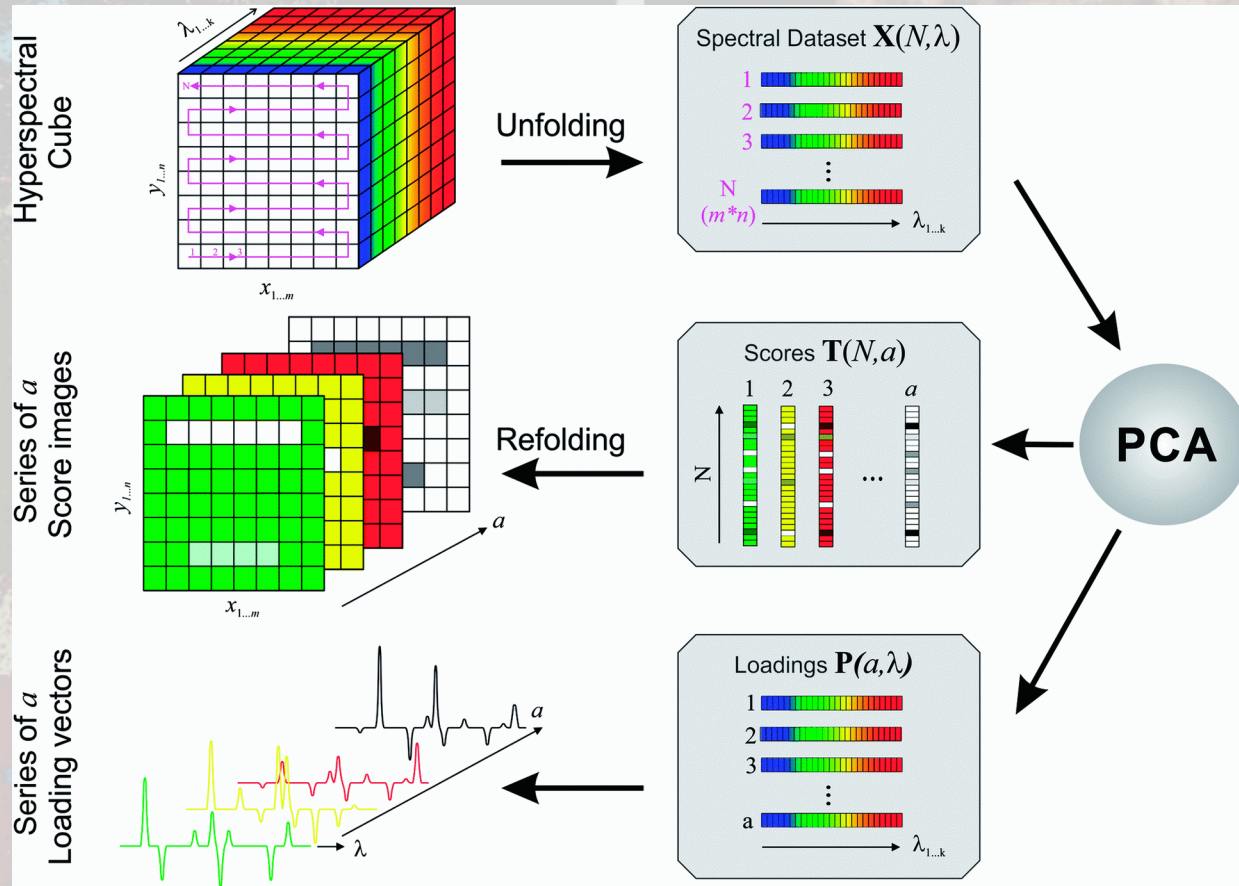
- **Maximize** variance \rightarrow find signal

$$w_{(1)} = \arg \max_{w^T w = 1} \left\{ \sum_{i=1}^n (x_{(i)} \cdot w)^2 \right\}$$

$$X \mapsto X' = X W$$

Background: Herreyre et al. *J. Anal. At. Spectrom.*, 2023, 38, 730-741

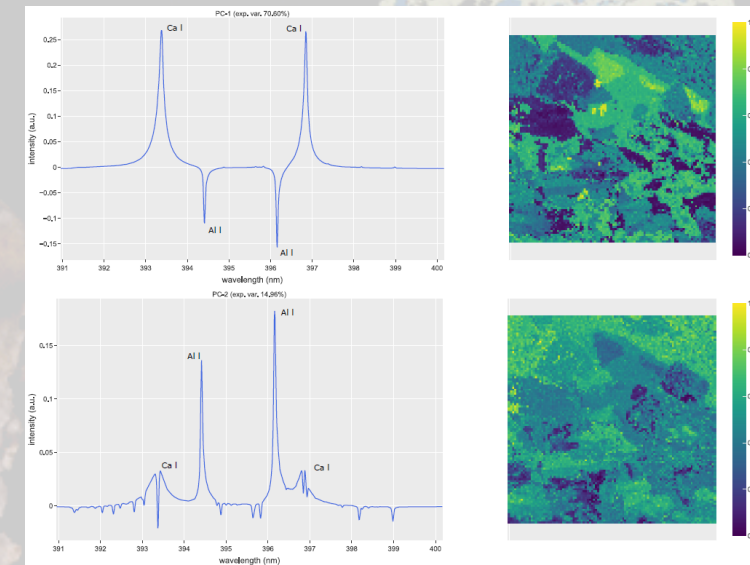
Principal Components Analysis in LIBS



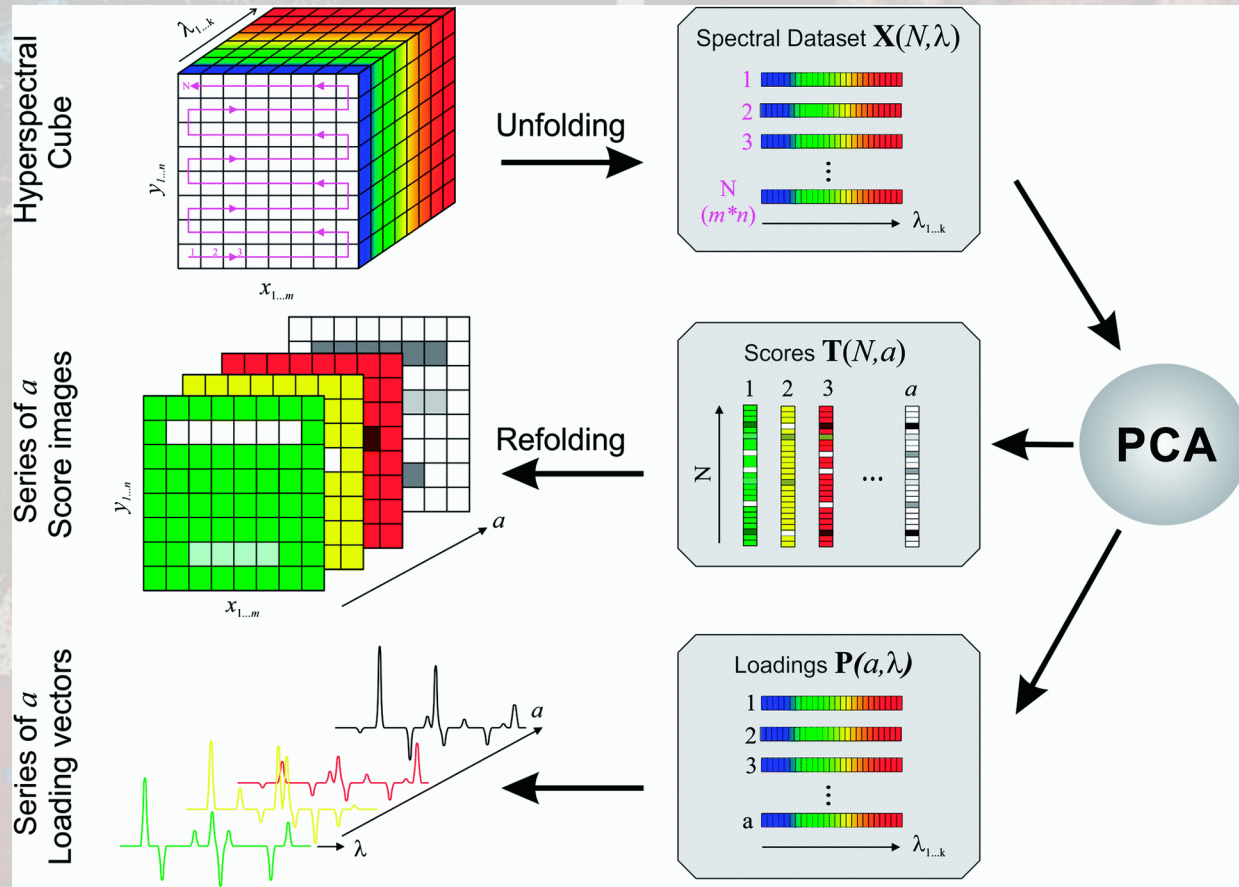
Moncayo et al. *J. Anal. At. Spectrom.*, 2018,33, 210-220

Background: Herreyre et al. *J. Anal. At. Spectrom.*, 2023, 38, 730-741

- **Scores** can be refolded to **images** after projection on the same subspace of all subpixels
- **Loadings** are **fingerprints** of the associated 2D map, representing the coefficients of the "rotation" of the components



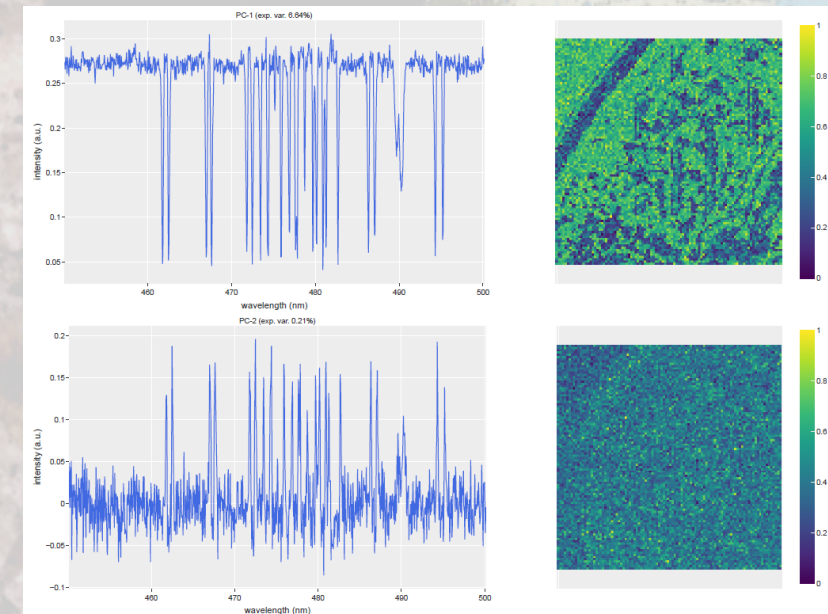
Principal Components Analysis in LIBS



Moncayo et al. *J. Anal. At. Spectrom.*, 2018,33, 210-220

Background: Herreyre et al. *J. Anal. At. Spectrom.*, 2023, 38, 730-741

- Highly sensitive to **noise** and spectral **interference**
- Loadings may have a **difficult interpretation**



A Random Matrix Approach

$$Y = \Sigma^{1/2} Z = (\mathbb{I} + X)^{1/2} Z = \overbrace{\left(\mathbb{I} + \sum_{i=1}^k \beta_k u_i u_i^T \right)^{1/2}}^{\text{signal}} \underbrace{Z}_{\text{noise}}$$

$$\text{PCA: } Y^T Y \longrightarrow f(Y^T Y) \simeq f(\Sigma) + R(\Sigma, Z)$$

A particular case $\rightarrow \Sigma$ is **sparse**  $R(\Sigma, Z) = \mathcal{O}(n^{-\alpha})$
 $f(0) = f'(0) = f''(0) = 0$

We can **asymptotically** work with the **sparse** signal!

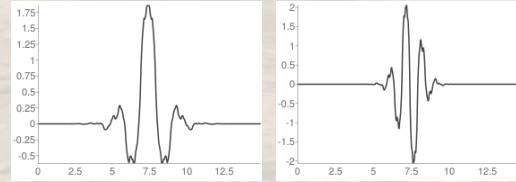
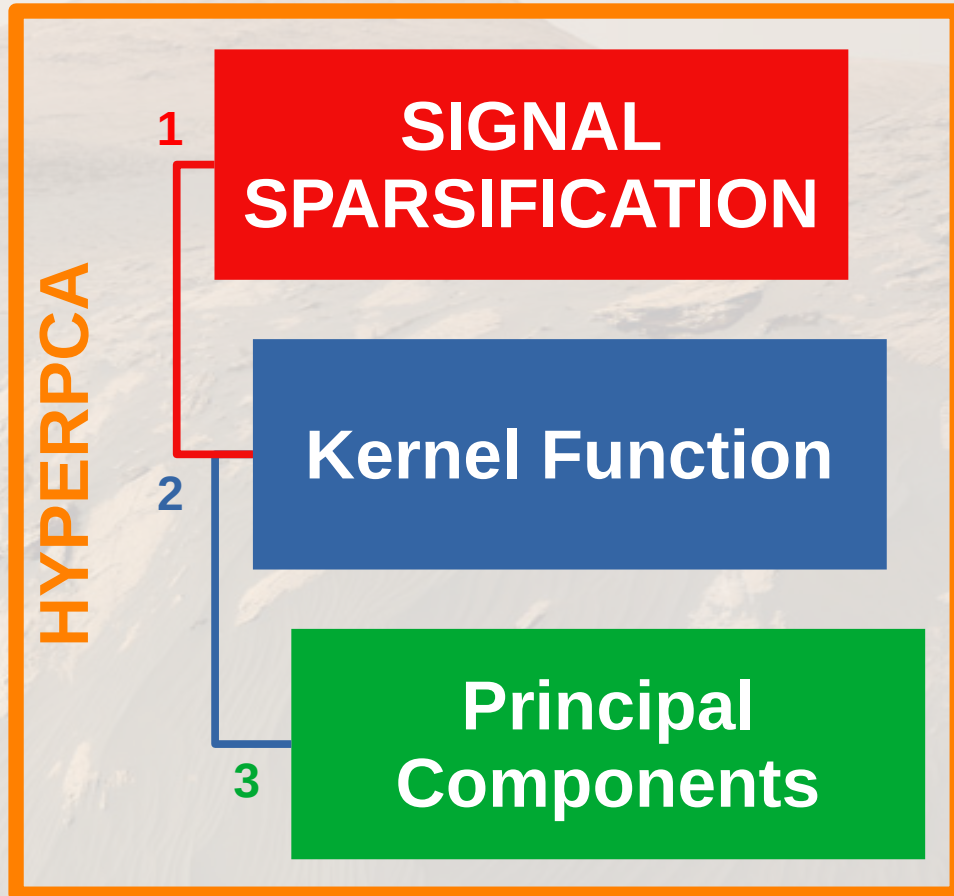
Seddik et al. ICLR 2019



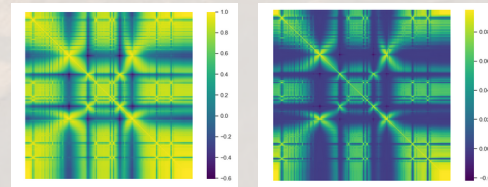
3 ■ Back to LIBS

Working with (hyper)spectral images

HyperPCA for LIBS



Wavelet decomposition



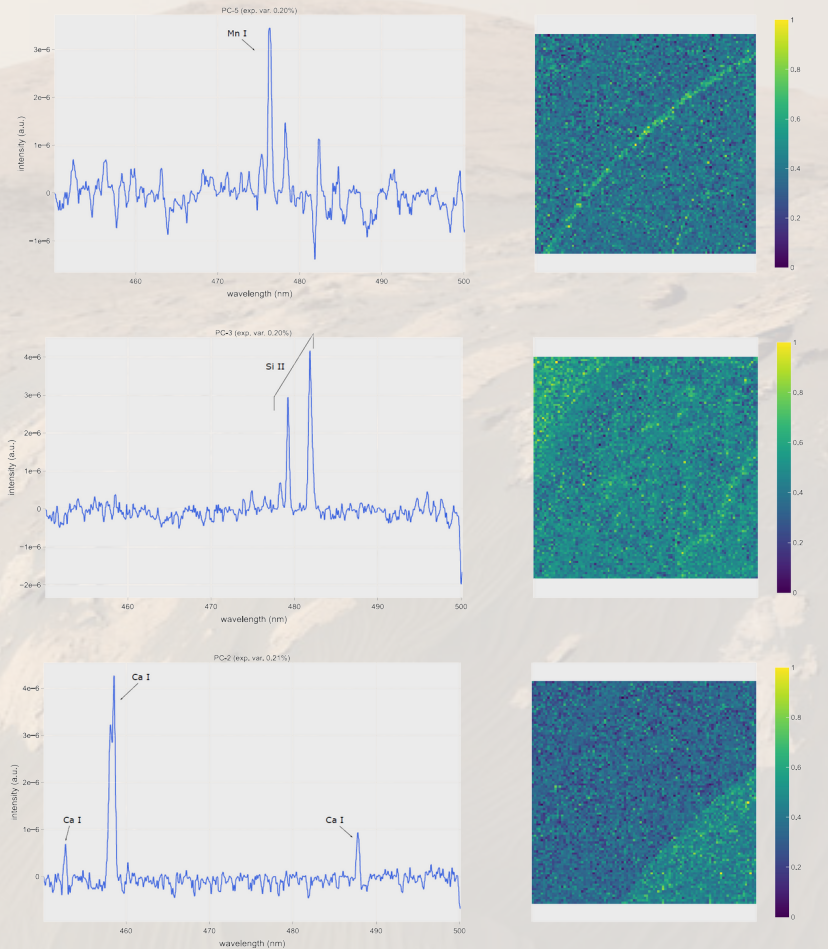
$$f_a(t) = t \left(1 - e^{-at^2} \right)$$

A traditional PCA with the newly defined covariance matrix

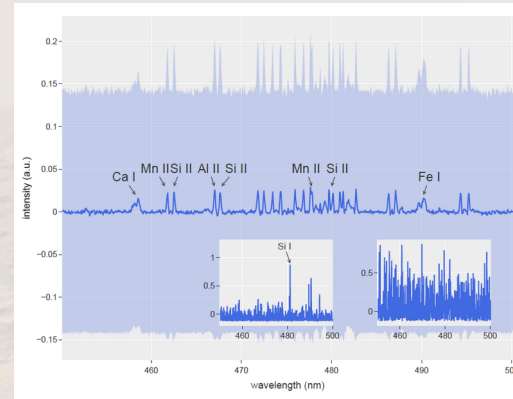
Finotello et al. *Spectrochim. Acta B: At. Spectrosc.*, 192 (2022), 106418



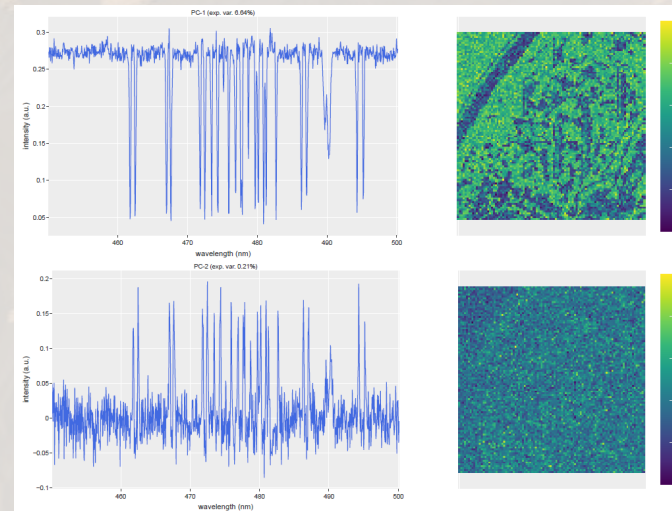
HyperPCA for LIBS



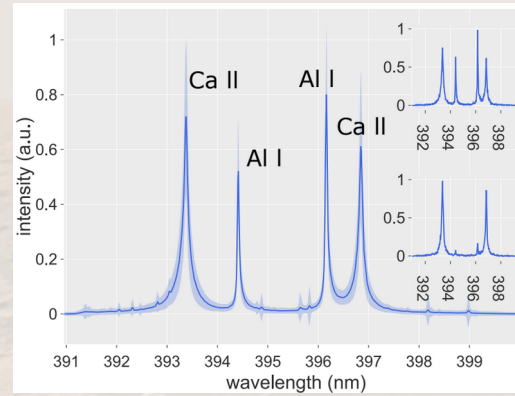
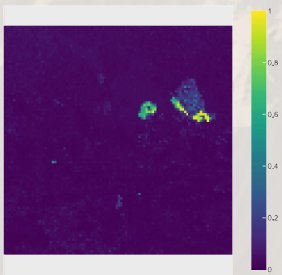
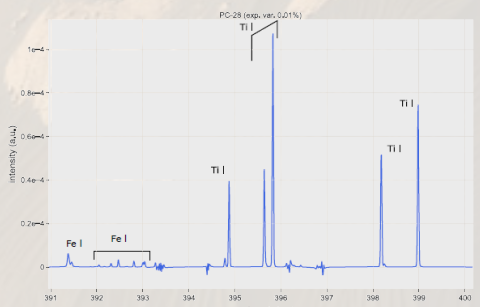
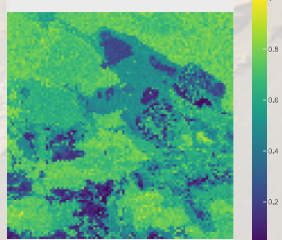
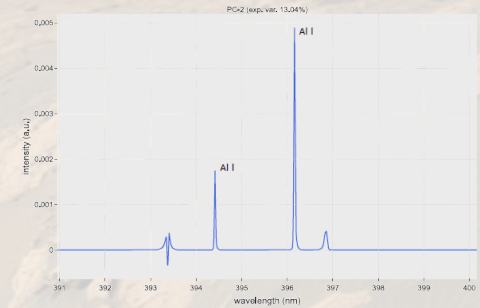
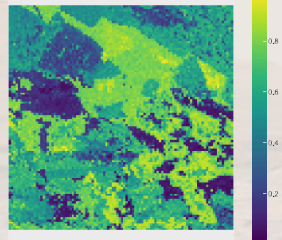
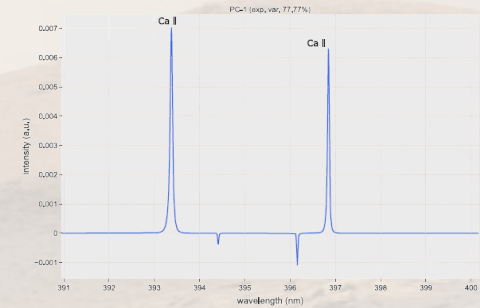
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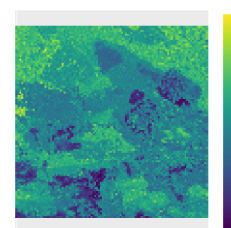
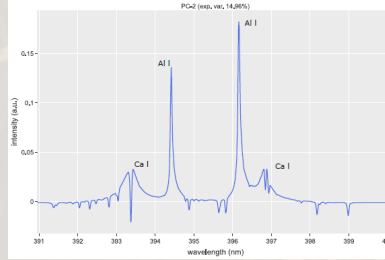
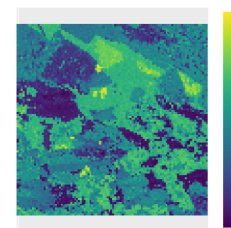
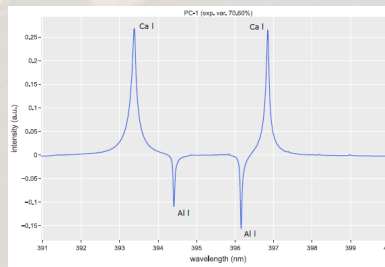
Standard PCA



HyperPCA for LIBS



Standard PCA



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In the end...

- Provided a sparse signal, it is **asymptotically** possible to neglect the noise **distribution** in a **spiked** model
- Spectroscopic data are not necessarily perfect spiked models, but to some **approximation** they can be treated as such
- **LIBS mapping** data represent a perfect use case
 - *High dimensionality*
 - *Strong spectral interference*
 - *Low signal-to-noise ratio*
- **HyperPCA** is a *plug-and-play* tool which enables **tuning** the traditional **PCA**





list

HyperPCA

At the Interface of Random Matrix Theory and Laser-Induced Breakdown Spectroscopy

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