Professional Development Workshop on

Critical Raw Materials Content in Thermal Waters: Analysis and Assessment

30th March 2023
University of Miskolc, Hungary

Remote, standoff and laboratory-based applications of laser induced breakdown spectroscopy

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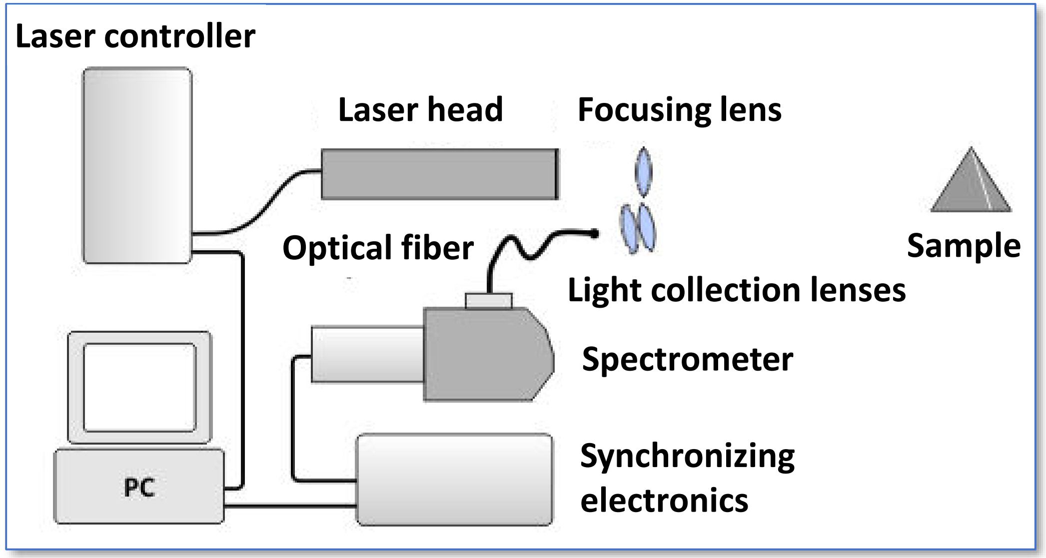
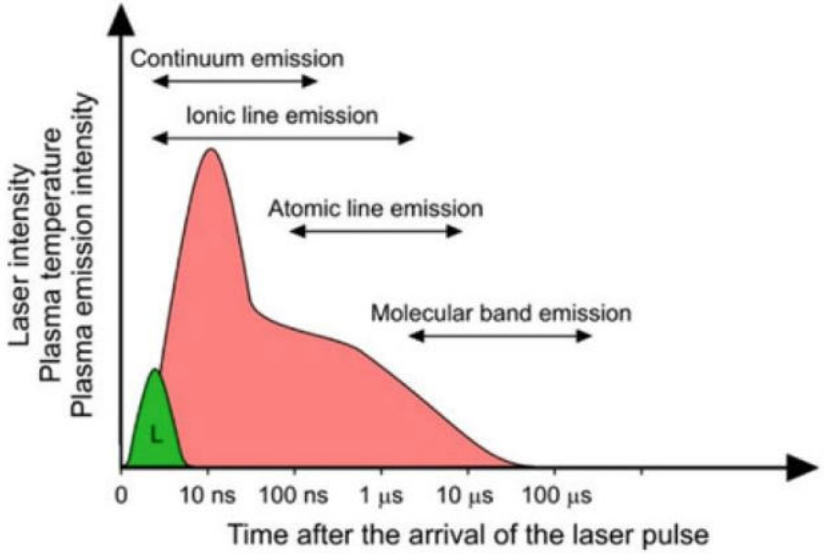
LIBS: Principle of operation

Laser induced breakdown spectroscopy (LIBS) is based on the observation of the light emission from a microplasma generated on the sample surface (or inside it) by a high intensity (GW-TW/cm^2) pulsed laser beam.

The sample material absorbs laser light and hence becomes evaporated/ablated in the focal spot. The temperature of the microplasma can be as high as 10-20 000 K, thus sample material gets atomized and ionized and thermally excited.

The spectrometer that detects the plasma emission is tightly synchronized with the laser (gate delay: 1-3 µs, gate width: 1 µs to 1 ms).

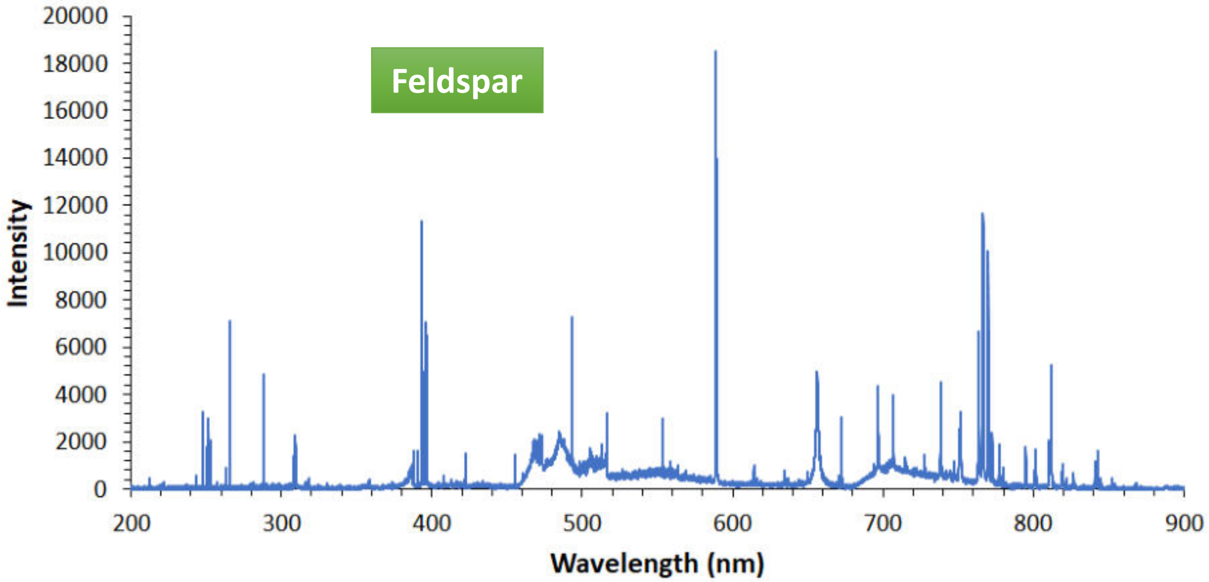


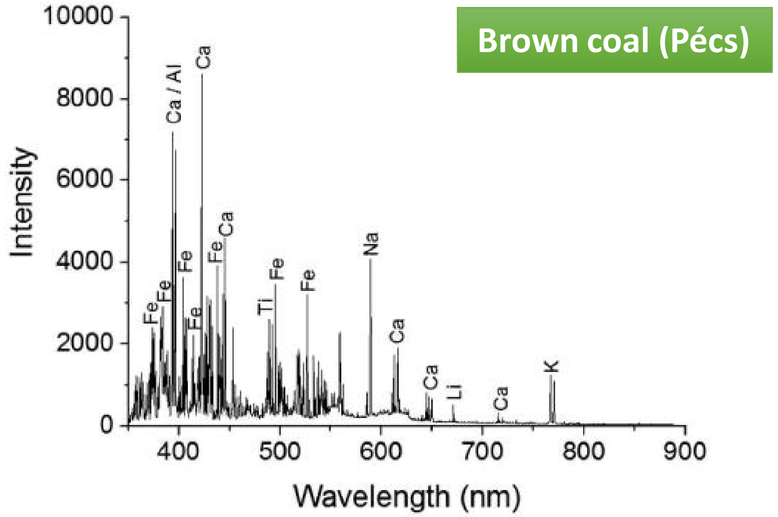


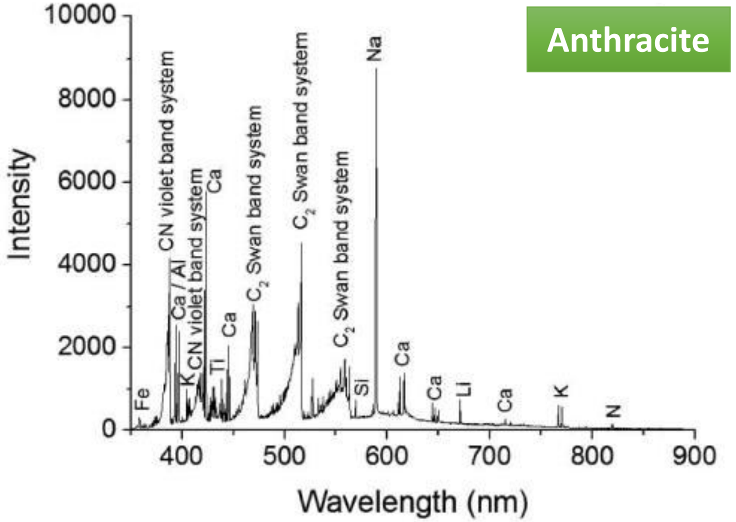
LIBS: Principle of operation

The dynamic LIBS spectrum contains many (10s of thousands) spectral lines, therefore are highly characteristic of the sample's qualitative and quantitative composition („fingerprints”).

The spectra contain atomic and molecular spectral features, but only provide information about the elemental composition.







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Comparison of analytical performance: LIBS, XRF, LA-ICP-MS

	LIBS	XRF	LA-ICP-MS
sample phases	solid, liquid, gas	solid	solid, liquid
sample size/shape	unlimited	some limitation	strong limitation
measureable elements	all	most, except light ones	most, except light ones
limit of detection	trace (ppm)	trace (ppm)	trace (sub-ppm)
isotope information	some	none	yes
info content of specta	very high	high	medium
destructiveness	micro	none	micro
speed of analysis	very fast (seconds)	fast (< minutes)	fast (< minutes)
remote/standoff analysis	yes	no	no
robust	yes	yes	no
field-portable	yes (even handheld)	yes (even handheld)	no (lab-based)
spatial resolution	yes (microns)	yes (microns)	yes (microns)
depth-resolved analysis	yes	no	yes
easy-to-use	yes	yes	no
cost of instrumentation	low to medium	low to medium	high

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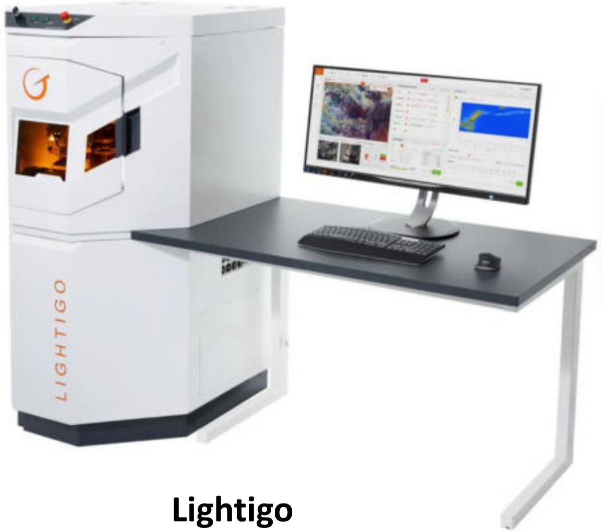
What can LIBS offer for geology?

- spatially and depth-resolved measurements (e.g. zoning, inclusions)
- quantitative measurements for all elements (e.g. prospection)
- sample recognition (qualitative discrimination)
- ultra portable instrumentation (e.g. UAV, rover, handheld, backpack)
- remote measurement capabilities (e.g. via fiber optics)
- standoff measurement capabilities (up to hundreds of meters)

Applied Photonics

Atomtrace

Applied Spectra



Lightigo

Bruker EOS-500

BW & Tek NanoLIBS

Hitachi Vulcan

Vela Instruments

Rigaku KT-100S

SciAps Z-200

Thermo Fisher Scie. Niton Apollo

TSI ChemLite

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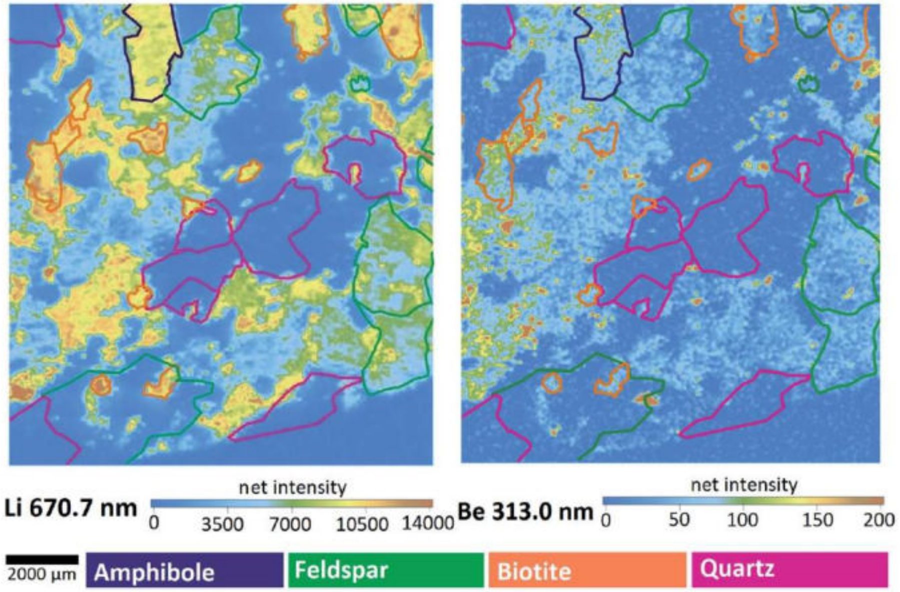
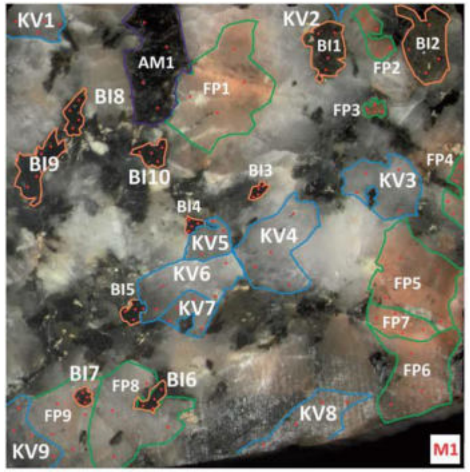
Selected applications of LIBS to geological samples

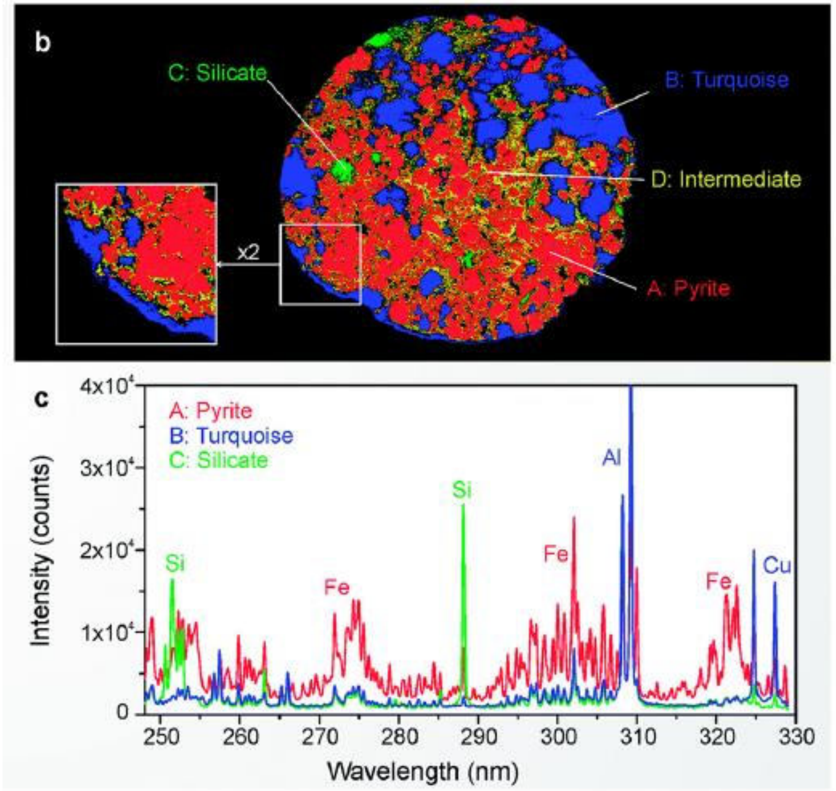
Lab-based: Mineral grain identification and prospection

- chemometric evaluation of the LIBS hyperspectral data set obtained from rock mapping can be used to
  - automatically identify and localize the occurring mineral grains
  - assess the elemental content of the rock





Minerals in Mórágy granite rock, identified with 92% accuracy by RF method



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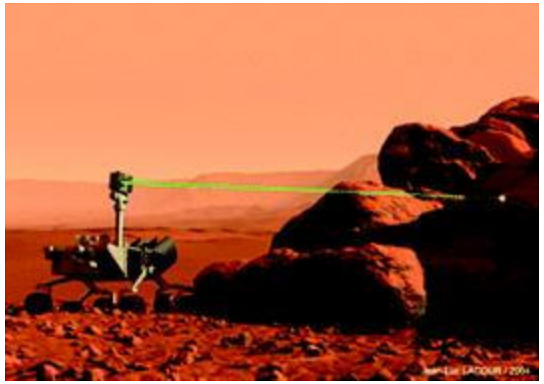
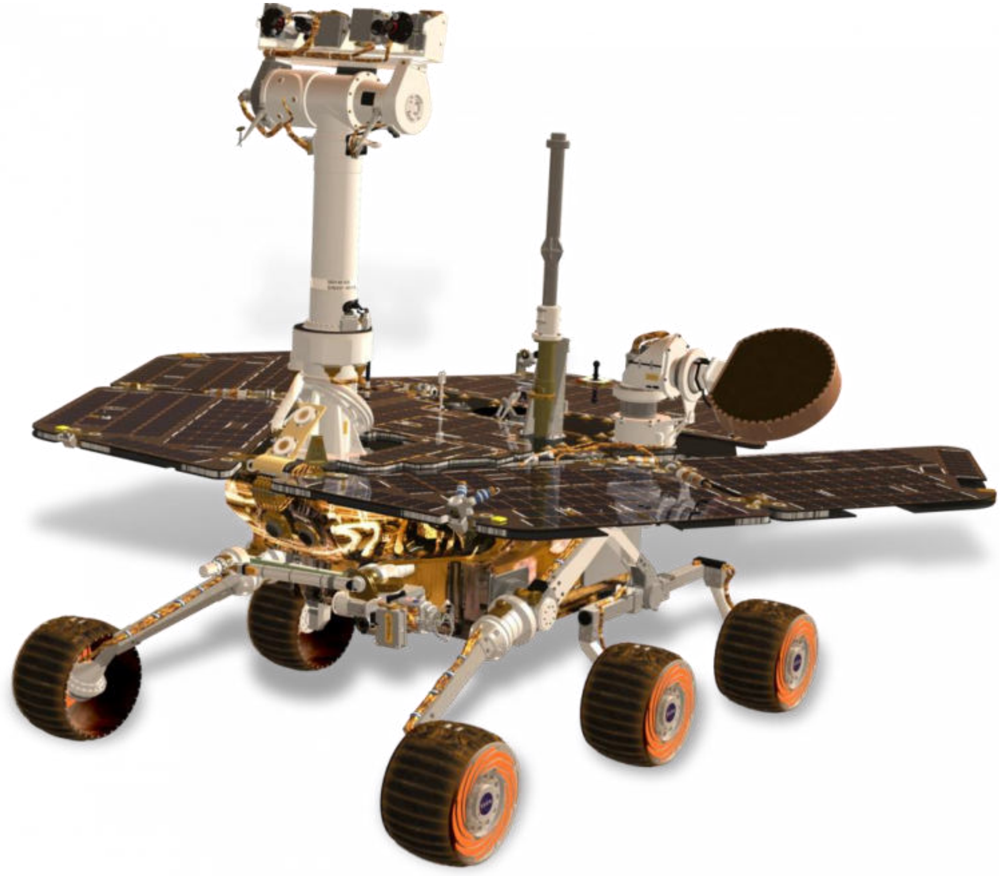
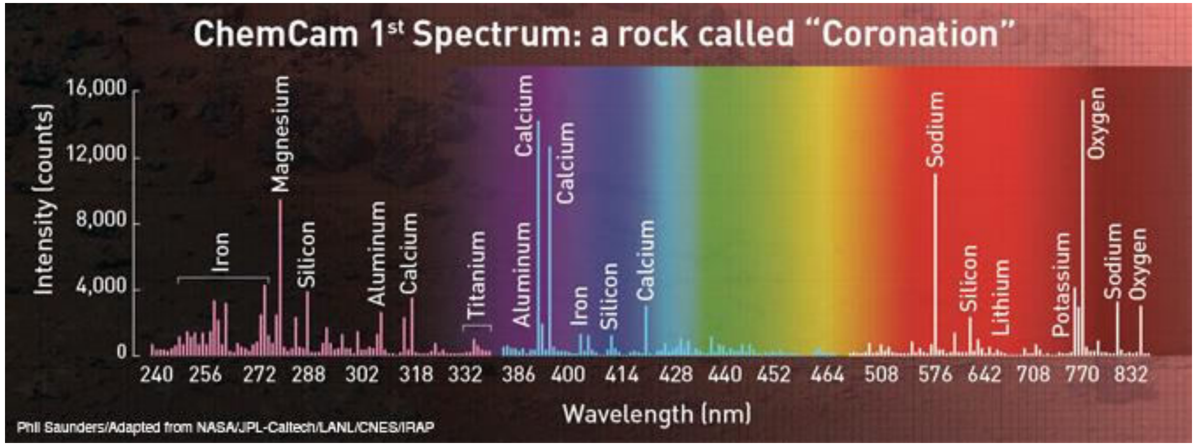
S. Moncayo, L. Duponchel, N. Mousavipak, G. Panczer, F. Trichard, et al., *J. Anal. At. Spectrom.* 33 (2018) 210–220.

Standoff: Space explorations

- multiple Mars rovers are/have been equipped with LIBS instruments
  - NASA Curiosity, 2012
  - NASA Perseverance, 2020
  - Zhurong, 2021
  - ESA Exomars/Rosalind Franklin, 2028?







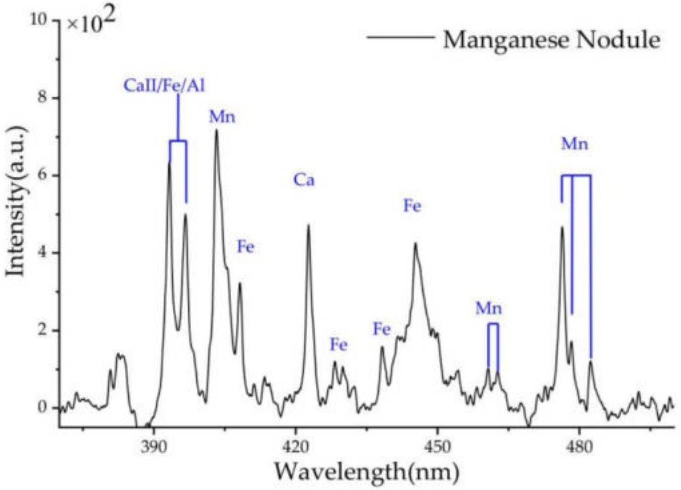
https://youtu.be/fEZ5dEi4oPo

Standoff/remote: Hydrothermal vents/deep sea deposits

- deep sea deployable (> 3000 m) LIBS instruments were constructed for the analysis of
    - sea water
    - sediments and rocks at the sea floor
    - polymetallic nodules at the sea floor

Table 3
Composition of sediment and rock samples obtained from the seafloor in the NW Pacific. Elements with concentrations > 1% are shown in bold.

Sample	Depth m	Zn %wt	Cu %	Pb %	Fe %	Mn %	Co %	Ni %	Mg %	Al %	Ca %	Ti %	Ag ppm	Sb ppm
Jade chimney	1340	**19.80**	**4.39**	**12.20**	**10.20**	0.08	< 0.01	–	0.02	0.01	0.02	< 0.01	182	215
Hatoma chimney	1485	**12.00**	**5.25**	**10.30**	**3.50**	0.46	< 0.01	–	0.05	0.51	0.06	–	486	5940
Yoron chimney	569	0.64	0.10	0.76	**2.52**	< 0.01	< 0.01	–	< 0.01	0.04	0.11	–	532	3330
Manganese crust	1390	0.10	0.06	0.21	**9.50**	**16.20**	0.57	0.46	**1.03**	0.98	**6.32**	0.34	< 100	< 100
Basalt	1418	0.02	0.02	0.02	**8.66**	0.20	< 0.01	0.02	**4.99**	**6.79**	**9.96**	**1.45**	–	–
Limestone	1147	< 0.01	0.01	< 0.01	0.38	0.47	< 0.01	0.03	0.09	0.25	**25.20**	0.04	–	–



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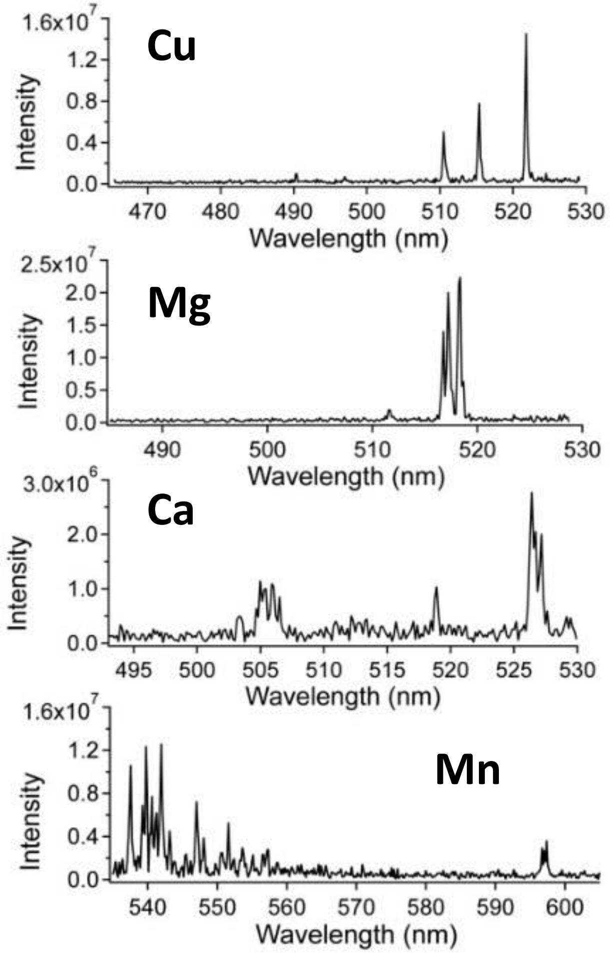
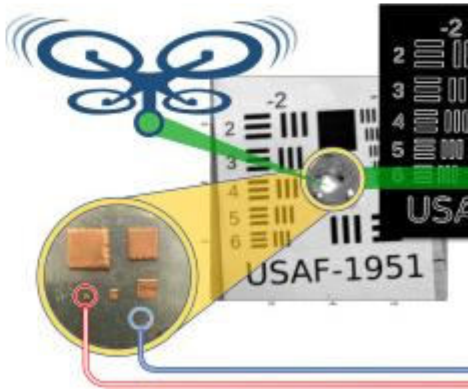
C. Liu, J. Guo, Y. Tian, C. Zhang, K. Cheng, W. Ye, R. Zheng, *Sensors* 20 (2020) 7341.

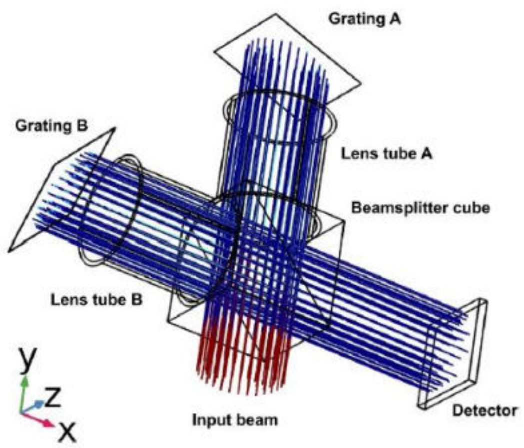
Standoff: Airborne LIBS

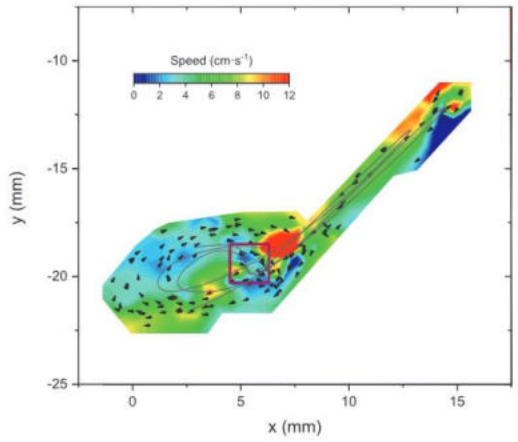
- ultra compact standoff LIBS instruments were designed for UAV deployment. Some of the challenges and their handling:
  - sensitivity boost with innovative spectrometer designs (e.g. spatially heterodyne spectrometer)
  - signal scatter (caused by vibrations and motion) reduction using a camera
  - safety issues

20 m standoff SHS-LIBS
(1° solid angle, 127 mm telescope)









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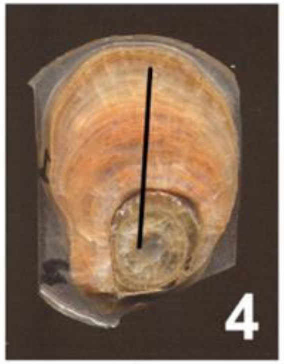
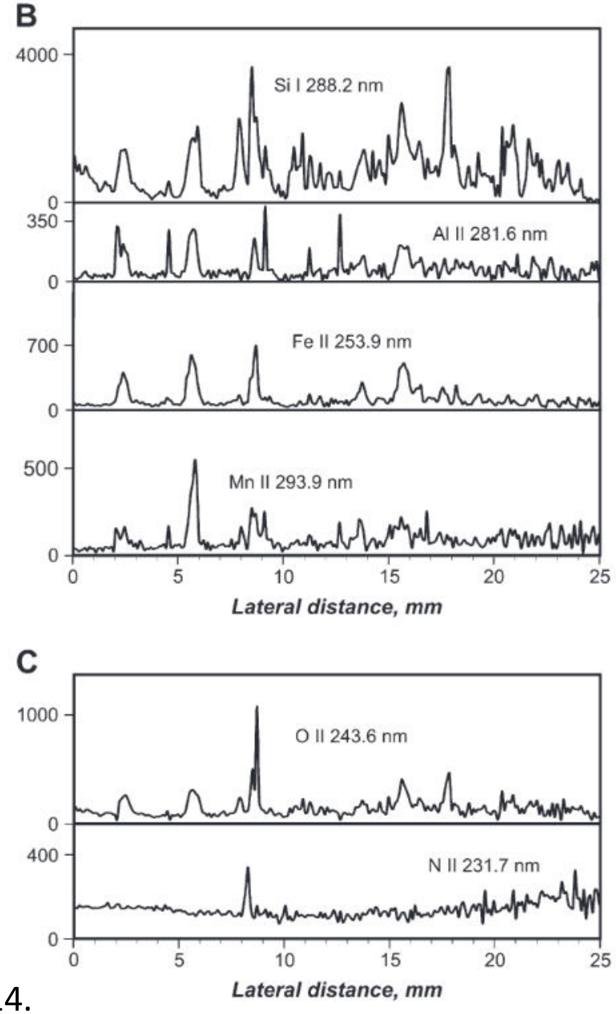
Lab/field-based: Speleothem (stalagmite/stalactite) analysis

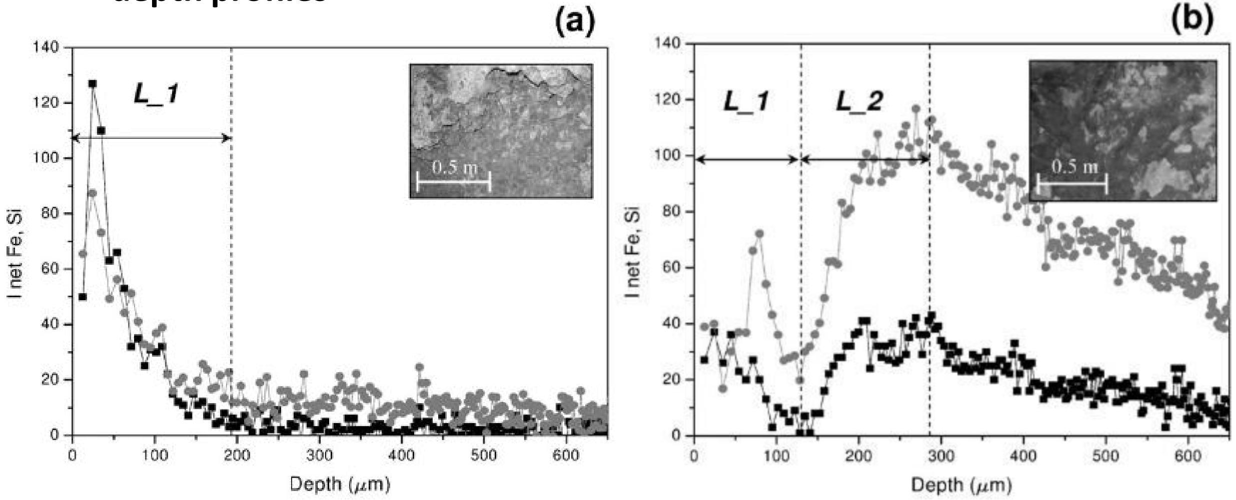
- compositional analysis is possible with high spatial/depth resolution, also for trace elements or light elements, partially *in-situ*.
  This can facilitate
  - degradation studies
  - contamination studies

Baradla Cave (Hungary) lateral profiles





Nerja Cave (Spain) depth profiles



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J. Cunat, S. Palanco, F. Carrasco, M.D. Simón, J. J. Laserna, *J. Anal. At. Spectrom.*, 20 (2005) 295-300.

Field-based soil analysis

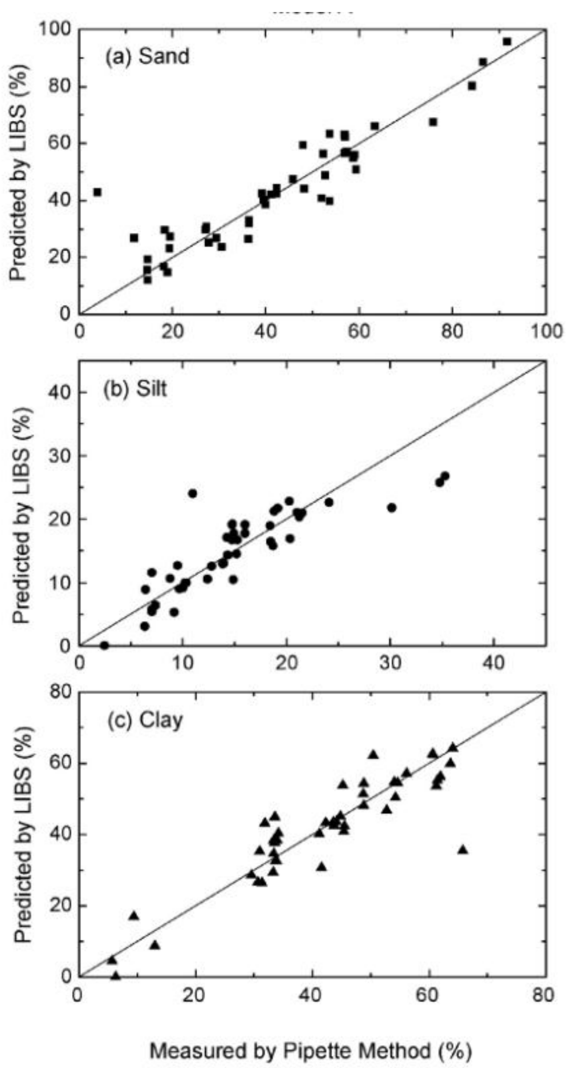
- soil texture (relative proportion of sand, silt and clay in soil) directly affects critical properties, such as susceptibility to erosion, water holding capacity, organic matter content, etc. → PLSR LIBS model based on 51 spectral lines of 12 elements

- soil pH → PLSR LIBS model based on Ca, Al, O, H spectral lines (associated with alkalinity)

Table 1
Reference and predicted pH values, and absolute errors of prediction, for ten samples of the validation set.

pH reference value	pH predicted value	Absolute error*
6.2	4.9	1.3
5.4	5.0	0.6
4.5	4.4	0.1
5.4	5.3	0.1
5.0	5.1	0.1
4.5	4.5	0.0
5.6	5.6	0.0
4.1	4.4	0.3
4.8	4.7	0.1
5.9	5.7	0.2

* Mean absolute error (MAE) = 0.3



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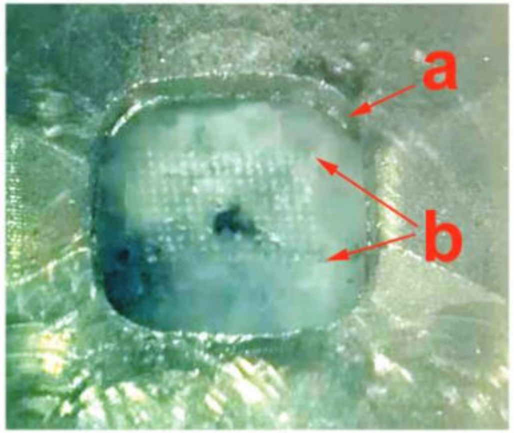
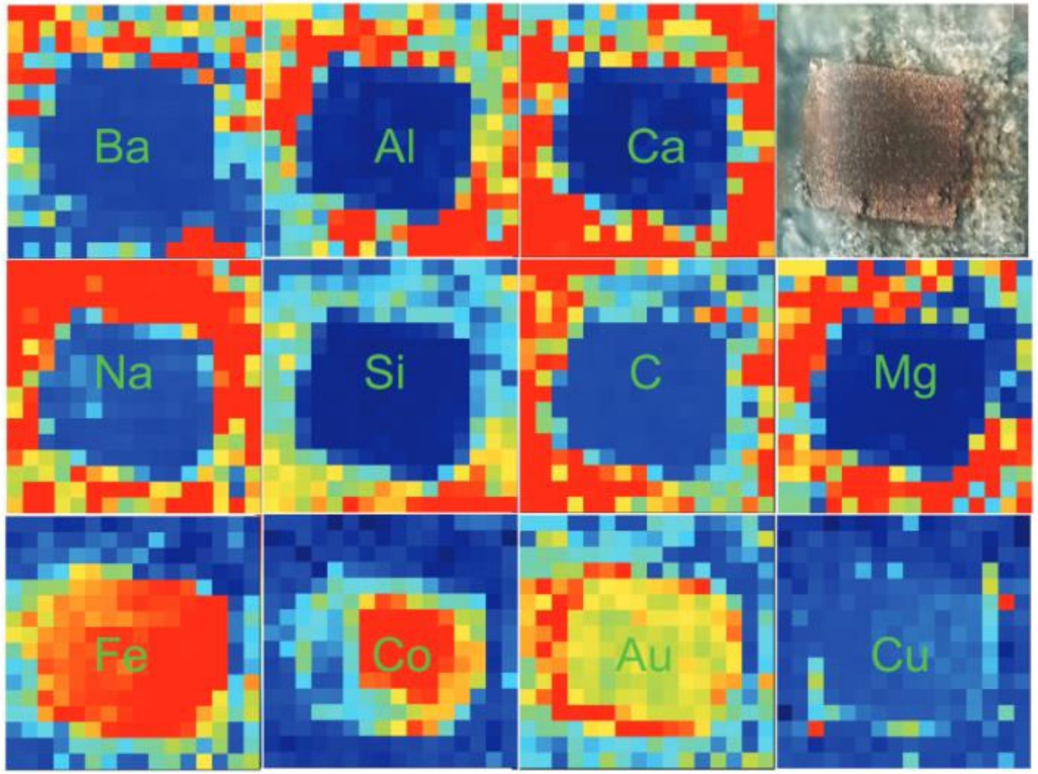
E.C. Ferreira, J.A. Gomes Neto, D.M.B.P. Milori, E.J. Ferreira, J.M. Anzano, *Spectrochimica Acta B* 110 (2015) 96-99.

Field-based prospection

- newer portable LIBS instruments are capable of small rastering, thereby allowing for quick and more reliable assessment of rock composition

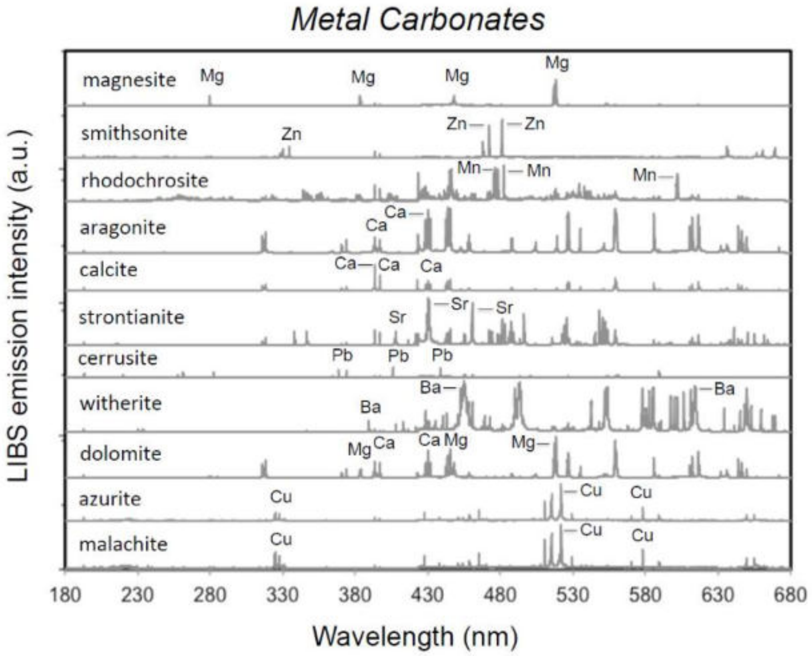




B. Connors, A. Somers, D. Day, *Applied Spectroscopy* 70 (2016) 810-815.

Field-based geochemical fingerprinting

- differentiation of minerals from different locations is possible in the field



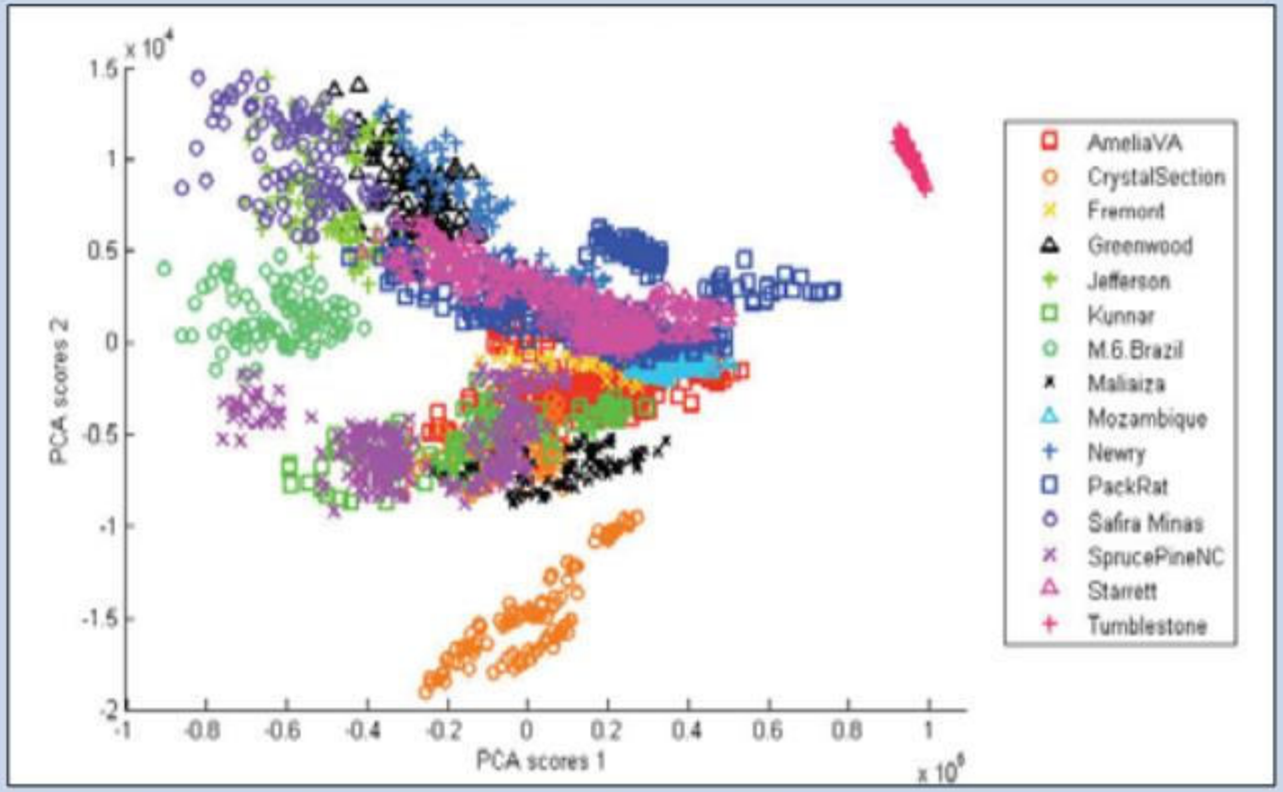


Figure 6: Principal Component Analysis result for 7,560 LIBS spectra of 24 columbite-tantalite samples from 17 locations.

R.S. Harmon, C.J.M. Lawley, J. Watts et al. *Minerals*. 9 (2019) 718.
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