Laser-Induced Breakdown Spectroscopy (LIBS) applied to geomaterials
A multi-wavelength approach

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Jean-Marc BAELE, Séverine PAPIER and Corentin COBERT*

Department of Geology and Applied Geology, Faculty of Engineering, University of Mons

* *jean-marc.baele@umons.ac.be, 9 Rue de Houdain, 7000 Mons*

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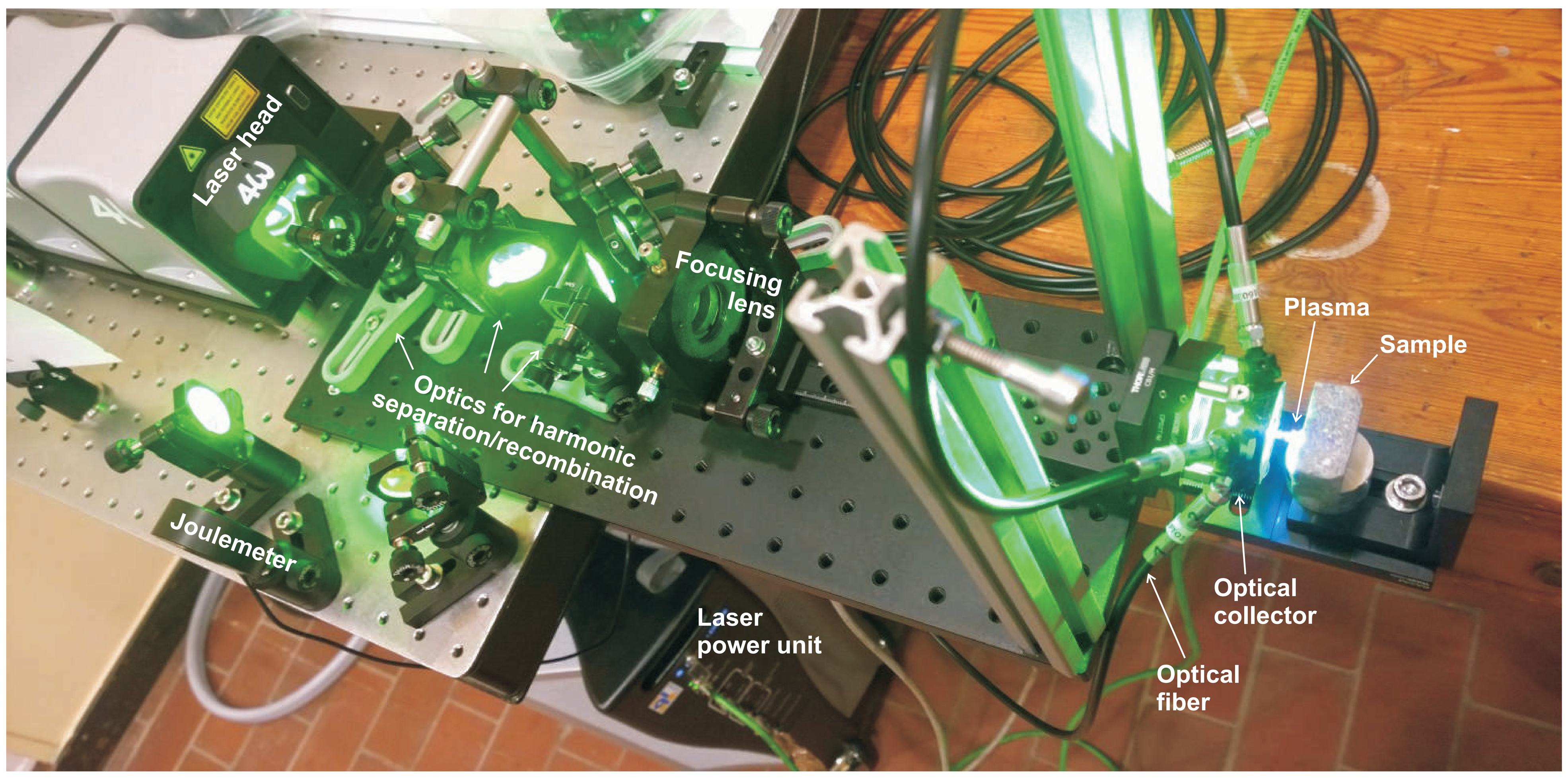
Introduction

Laser-Induced Breakdown Spectroscopy has gained much interest over the past decade for fast elemental analysis in various solids, liquids and gases (Musazzi and Perini, 2014).
In this technique, a high-energy laser pulse is focused on the sample to create a plasma on its surface. As the plasma cools, de-excitation of ions, atoms and molecular radicals results in the emission a characteristic spectrum, which can be recorded with an optical spectrometer.
The main advantages of LIBS are fast analysis capability (< 1s to a few s), no or few sample preparation and the ability to detect all elements, including the lightest (H, Li, B, Be, etc.) In addition, LIBS setups are rather simple, affordable and can be portable for measurement on the field. However, detection limits are higher compared to well-established techniques such as ICP-AES and ICP-MS and quantitative analysis is still at its infancy.
Here we report preliminary qualitative results on signal enhancement obtained when using different laser wavelengths on two common phases in geomaterials : quartz and organic matter (coal). A iron sulphide (pyrite) was also tested.

Experimental setup

A flashlamp-pumped Q-switched Nd:YAG laser was used for our LIBS experiments (Quantel model Q-smart 450)(fig. 1). This laser delivers 20 pulses per second with 5 ns duration and 450 mJ energy each. The fundamental wavelength is 1064 nm but harmonic generators equipped with frequency-doubling crystals convert part of the laser energy into 532 nm and 266 nm harmonics.
Harmonic separators allow separation and recombination of the different laser wavelengths. Beam traps are used to block or transmit the wavelengths in order to perform LIBS experiments in single- or multi-wavelength mode. Beam sampling with a fused-silica window and a pyroelectric joulemeter allowed monitoring the laser energy. Typical shot-to-shot energy stability is <15%.
The laser beam is focused ca. 10 mm below the sample surface using a fused silica lens with 250 mm focal length, which produces ablation craters of about 750 µm in diameter.
A in-house multi-port optical collector then captures the light which is emitted by the laser-induced plasma and injects it in up to four all-silica optical fiber bundles. The fibers then feed a 8-channel CCD-based optical spectrometer (Avantes ULS2048), with 194-907 nm spectral range and 0.05 to 0.20 nm resolution from the UV to NIR regions, respectively. The delay between laser shots and trigger for spectrometer integration can be adjusted with the spectrometer or with a digital pulse/delay generator (Stanford Research Systems model 535).



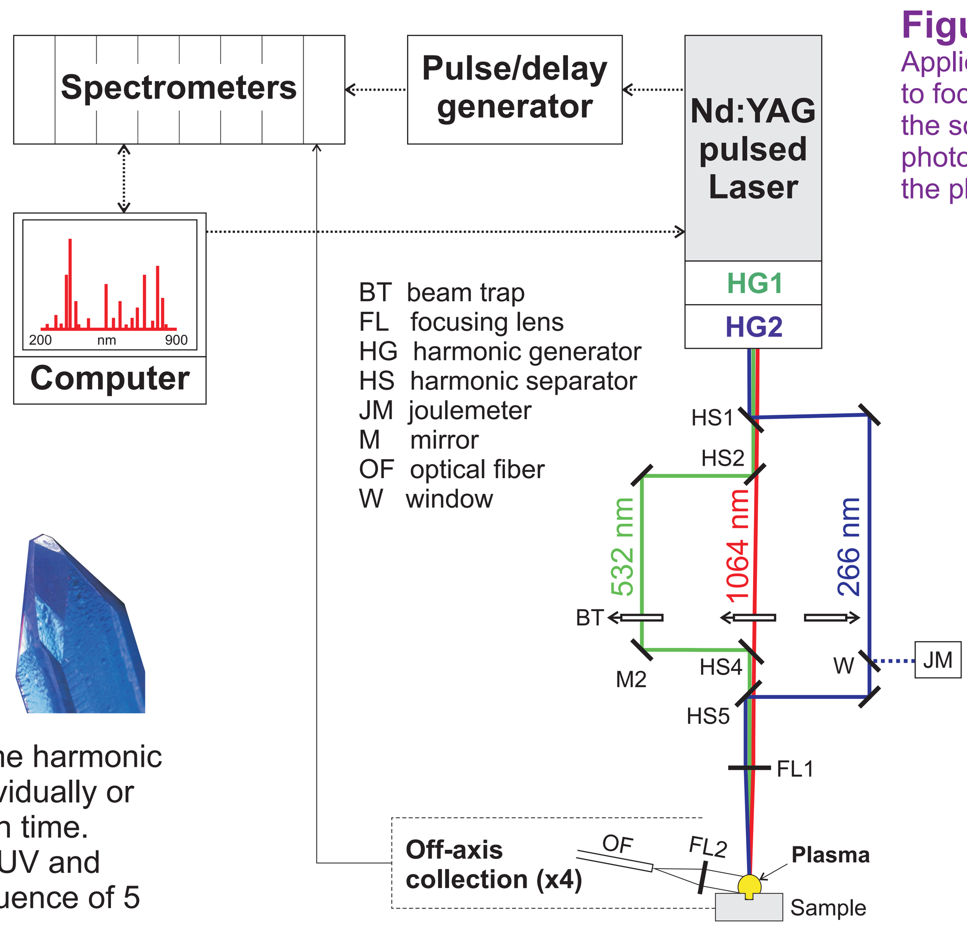


Figure 1. The multi-wavelength LIBS experimental setup at Geology and Applied Geology Dept. In the photograph, all three laser wavelengths were allowed to focus on the sample (all beam traps were removed). In the situation depicted in the schematic below, only the UV component reaches the sample. In the photograph, the sample was intentionally offset from the optical collector to make the plasma visible.

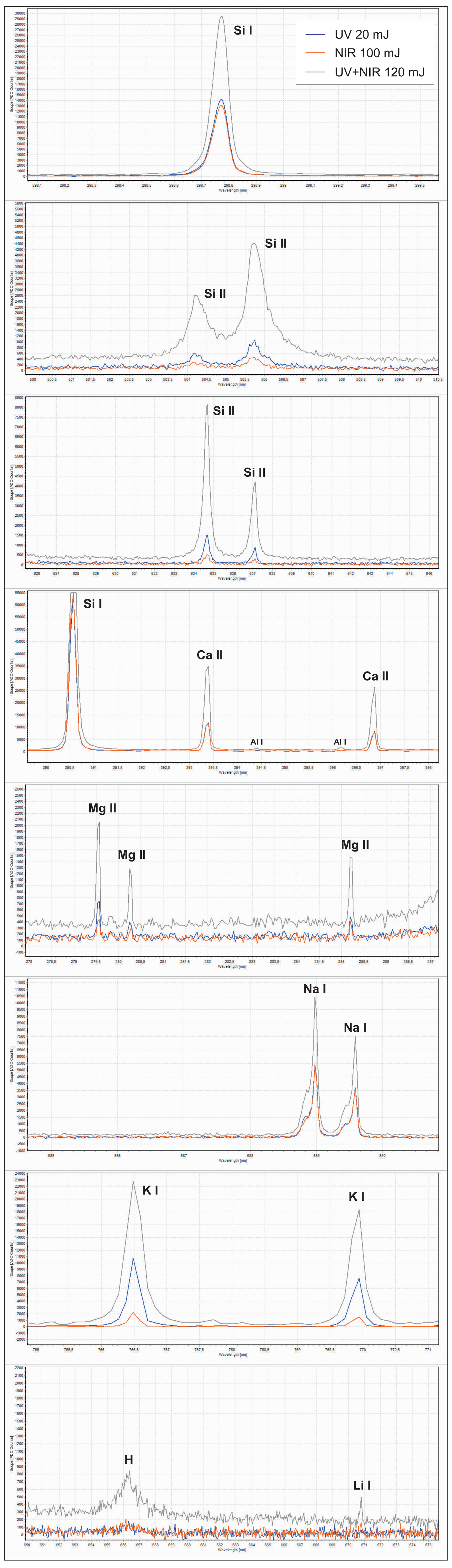


Figure 2. LIBS spectra of natural quartz crystal recorded with a single UV (blue), a single NIR (red) and a mixed UV-NIR laser pulse (grey). Single laser shot per spectrum with 20 mJ UV and 100 mJ NIR.

LIBS analysis of quartz

For our preliminary experiments, the two extreme harmonic wavelengths (UV and NIR) were used both individually or mixed, with 1.4 µs delay and 1.05 ms integration time. Pulse energy was about 20 mJ and 100 mJ for UV and NIR, respectively, which yielded an estimated fluence of 5 to 25 J.cm^{-2} (1 to 5 GW.cm^{-2} irradiance).
Quartz was chosen as it is the most common rock-forming mineral in geomaterials and its trace-element content is commonly used for ore exploration, reconstructing fluid migration in sedimentary basins and for sourcing raw materials. The sample studied here is a nearly-pure natural quartz crystal from central Asia. No chemical composition is available yet but the detected elements are most likely in the 1-100 ppm range as artificial high-purity synthetic quartz for opto-electronic industry yielded comparable spectra.

Single-wavelength pulses

Despite they have less energy than NIR pulses, UV pulses produce a similar (Si I, Na I, H, Li I and Mg II) or stronger LIBS signal (Si II)(fig. 2). The enhancement can be explained by a better coupling between UV pulses and the quartz matrix and a reduced plasma shielding (St-Onge et al., 2002). Therefore, more energy of a UV pulse is used for ablation, producing more analyte atoms in the plasma. With NIR pulses, the greatest part of the laser pulse is absorbed by the early-formed plasma, which is then strongly excitated but becomes increasingly opaque to the laser and prevents further ablation (plasma shielding).

Multi-wavelength pulses

Mixing UV and NIR laser pulses results in signal enhancement, with a two- to five-fold increase in line intensity. A two-fold increase in signal intensity might be expected based on the results with single-wavelength, suggesting the effects of single-pulse excitation are simply adding together. The stronger enhancement, which is observed for ionic lines, could be interpreted as a higher plasma temperature probably associated with a bigger plasma volume when UV and NIR pulses are fired simultaneously. Thus the multi-wavelength approach in LIBS really improves the detection capability. Some elements, for example Li, were not detected using single-wavelength pulses but with multi-wavelength. However, for all lines, the background level is raised in multi-wavelength LIBS. Then, less improvement is achieved on the signal/noise ratio, which is an important figure-of-merit in spectroscopy.

LIBS analysis of coal

Organic matter is a common accessory component in sedimentary and metamorphic rocks. Both the abundance and composition of organic matter in rocks are widely used in a number of studies including hydrocarbon exploration. Here we have tested the LIBS setup with natural coal from the Hainaut basin.

Single-wavelength pulses

Most emission lines are 2- to 3 times stronger with NIR pulses compared with UV pulses, which is contrasting to quartz (fig. 3). As a temptative explanation, the carbon matrix of the coal would couple better with NIR than UV, producing more ablation and a resulting bigger plasma.

Multi-wavelength pulses

Mixing UV and NIR laser pulses also results in signal enhancement of all the emission lines, especially for the carbon line at 247.5 nm, with an 4- to 17-fold increase in intensity relative to the NIR or UV pulse, respectively. Other lines, yet unidentified also exhibit a strong enhancement. Contrarily to quartz, in coal there is no clear difference between neutral and ionic lines. Then a simple explanation based on plasma temperature alone is no longer valid.

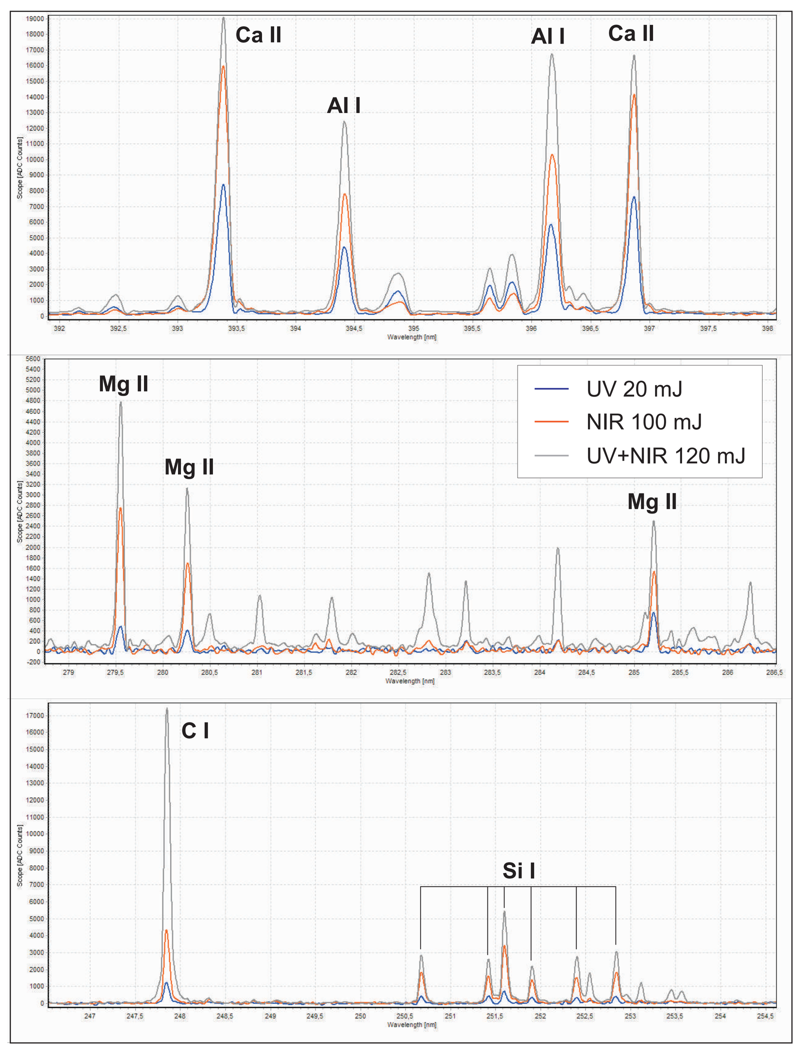
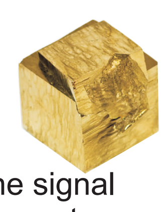


Figure 3. LIBS spectra of natural coal from the Hainaut Basin recorded with a single UV (blue), a single NIR (red) and a mixed UV-NIR laser pulse (grey). Single laser shot per spectrum with 20 mJ UV and 100 mJ NIR. The lines showing the strongest enhancement with UV+NIR pulses in the Mg II region and right to the Si I region are not identified yet.



LIBS analysis of pyrite

Iron disulphide (pyrite) was analyzed to check the signal enhancement in a matrix with a more metallic character. LIBS spectra of transition metals are very complex, with many emission lines (fig. 4). Single UV and NIR pulses yielded similar line intensities but when mixed, UV and NIR pulses produce a clear enhancement, which, however, includes the background. Surprisingly the enhancement is increased towards higher wavelengths.

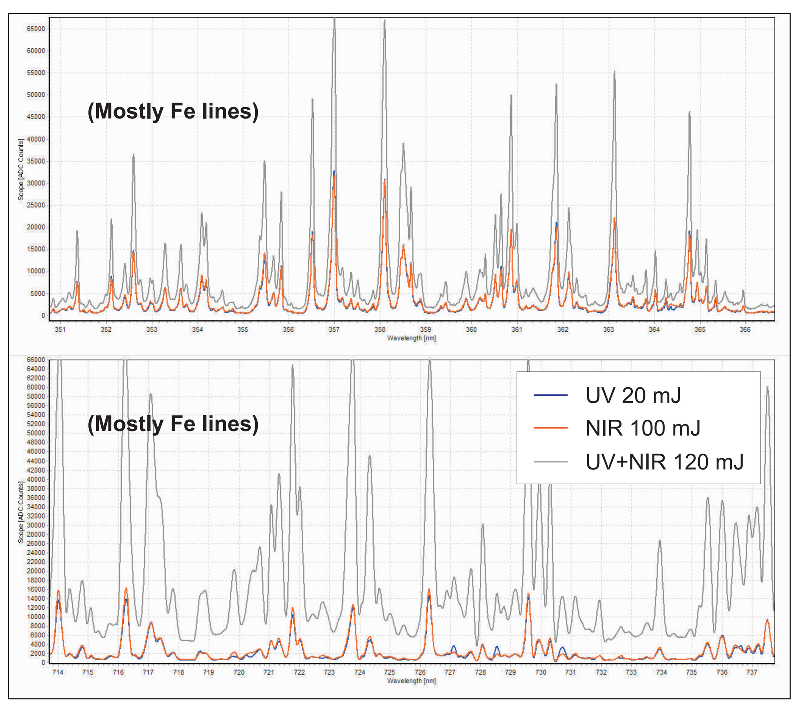


Figure 4. LIBS spectra of pyrite from Peru recorded with a single UV (blue), a single NIR (red) and a mixed UV-NIR laser pulse (grey). Single laser shot per spectrum with 20 mJ UV and 100 mJ NIR. A stronger enhancement of the Fe lines is observed at larger emission wavelengths.

Conclusions and future development

Although our results are preliminary, LIBS appears as an effective technique for the analysis of geomaterials as it can quickly detect major but also trace-elements with no or few sample preparation. As pointed out by St-Onge et al. (2002), using a combination of different wavelengths is a promising method for signal enhancement, which can be implemented with a single laser, as opposed to other more popular methods that need two lasers (e.g. dual-pulse LIBS).

Future development includes the investigation of :
- a wider spectrum of geomaterials, for studying matrix effects in more details ;
- the influence of the focusing geometry (focal length of the lens and the lens-to-sample distance) ;
- the influence of NIR energy and delay, to seek for optimal settings ;
- the influence of ambiant gas (He, Ar, N_2, etc.) instead of air.

Much attention will be paied to the NIR pulse delay, as more enhancement is expected. To our knowledge, this parameter was not studied yet in the very short range (<10 ns). The results could also provide an insight into the balance between ablation and excitation processes. A technique for measuring ablation rate should also be used, such as crater profilometry.
Quantitative analysis is a more long-term development project as it first requires a comprehensive collection of solid calibration standards with good homogeneity at a scale below mm.

References

Musazzi, S., And Perini, U. (2014) - Laser-Induced Breakdown Spectroscopy. Theory and Applications. Springer-Verlag, Berlin Heidelberg, 565 p.

St-Onge, L., Detalle, V., And Sabsabi, M. (2002) - Enhanced laser-induced breakdown spectroscopy using the combination of fourth-harmonic and fundamental Nd:YAG laser pulses. Spectrochimica Acta, B57, 121-135.

Acknowledgements

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