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Advances in Laser-Induced Breakdown Spectroscopy analysis for Geology: a critical review

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Abstract

The review focuses on the most relevant advances and is reported in different sections relative to the analyzed objects (identification of rocks/minerals and sourcing ; resources applications ; slurry and drill cores ; rare earth elements ; light elements). Special sections report on the good practices for Laser Induced Breakdown Spectroscopy (LIBS) analysis and the most critical points that should be checked in order to validate any LIBS analysis on most common geological purposes. LIBS gives access to the most relevant elements in geosciences/geology and the typical detection limits fit usual requirements, with the advantage of permitting faster analyses than the other techniques classically used. Whether considering the case of metals of economic interest, that of critical elements, or that of light elements, LIBS has definitely been proved an adequate tool, and there is no need to do more on its evaluation in this field of application. Considering that LIBS measurements require limited sample pre-treatment, and considering also that LIBS is a fast all-optical multi-elemental technique, it is undoubtedly the optimal way to achieve a first quick screening and then provide valuable data prior to any further laboratory analyses. Therefore, the recent development of LIBS imaging should quickly lead to the implementation of LIBS imaging systems in the analytical laboratories worldwide in charge of analyzing geological samples.

1. Introduction

LIBS (Laser-Induced Breakdown Spectroscopy) is a spectroscopic technique based on atomic emission. It uses short duration (nanosecond or less) pulsed laser beam focused onto the sample (solid, liquid, gas) to vaporize it, then atomize and ionize the vapor, and form a plasma in which atoms and ions are driven to excited states (Figure 1). During plasma expansion and cooling, these atoms and ions relax to lower-energy states by emitting specific radiations related to the underlying electronic transitions (Figure 2). The optical spectrum related to the plasma emission is then obtained by the use of a spectrometer in the UV-visible-NIR range. The wavelengths of the detected atomic lines provide qualitative information on the presence of elements within the laser-induced plasma and consequently on the sample. Finally, the lines intensities are related to the element concentrations and the plasma properties. Using calibrated samples, qualitative and quantitative analyses are carried out by monitoring emission line positions and intensities [1–3]. The LIBS technique involves in 2020 about 200 institutions on the five continents plus one extraterrestrial instrument on Mars. The application domains appears to be unlimited as LIBS analysis can be performed with all optical systems, remotely and under various environment conditions. During the last five years, more than 5,000 articles have been published on the LIBS technique, from the fundamental aspects to the applications (these previous bibliometric data, for LIBS analysis, can be found on the Clarivate Analysis website, webofknowledge.com.bases, February 2020).

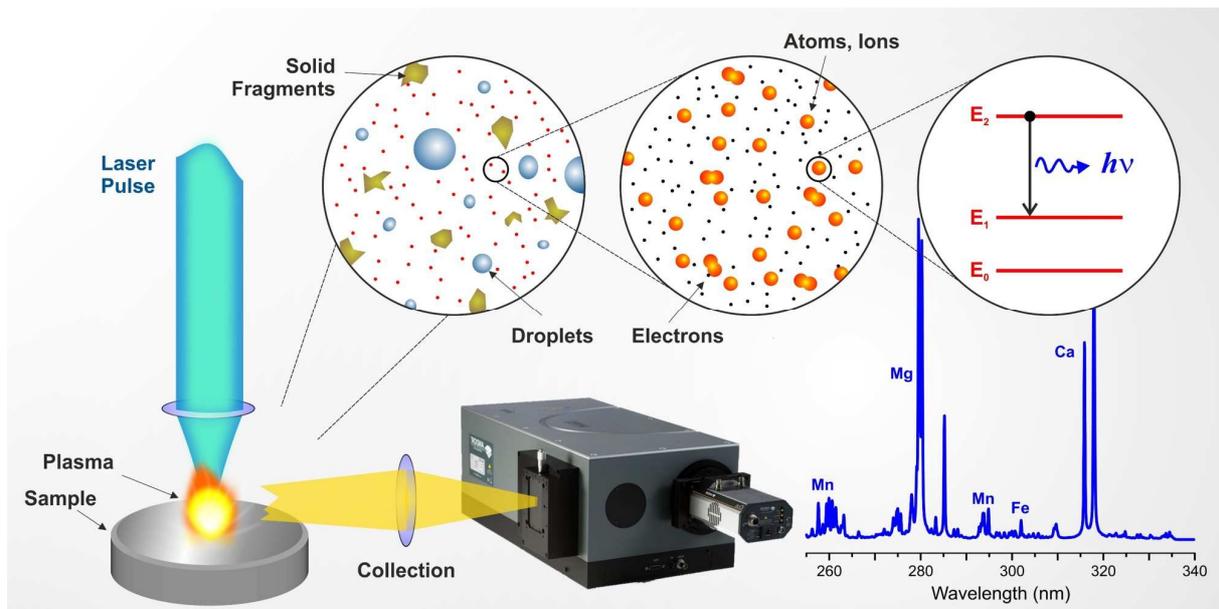


Figure 1 : Schematic physical principle of LIBS technique (V. Motto-Ros, personal contribution with permission)

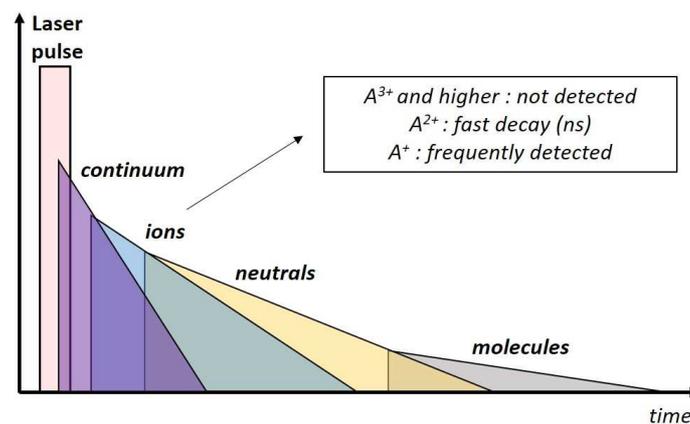


Figure 2 : Schematic observations of ions, atoms and molecules observed on plasma depending on the time delay after laser pulse.

As for the last technical developments that increased the number of applications, one can mention some technological breakthroughs after the detector arrays, with the emergence of ICCD in the 90's, the development of compact CCD on the 2000's - which boosted the development of LIBS imaging - and the new laser sources in the last 2010's [4]. As mentioned by J.D Winefordner and co-authors [5] "...LIBS has dominated the analytical atomic spectroscopy scene in the last decade much like atomic

absorption spectroscopy dominated in the 1960-1970s, ICP atomic emission spectroscopy in the 1970-1980s, and ICP mass spectroscopy in the 1980-1990s". LIBS is a highly attractive technology which is distinguished by its table top, handheld and remote instrumentations, speed of operation, operation in ambient atmosphere, and its ability to produce megapixel multi-elemental images with micrometric resolution (10 μm) and ppm-scale sensitivity (Figure 3).

Even if LIBS has been applied for the last 20 years to a large range of topics such as biology, archeology, industrial applications, plasma investigation, soils, pollution, etc, Earth Sciences is the field that has been the most impacted by this technique. Beyond the relative simplicity of the LIBS set up, the LIBS technique is of first interest for geologists due to its ability to excite multiple sample types with limited sample preparation. The number of publications in geology has stepped from a few articles a decade ago to more than 20 publications for the year 2018 only. Harmon *et al.* in 2013 or Senesi in 2014 [6,7] reported in their papers the most relevant publications about geochemical and geological LIBS applications. One can consider also that the planetary LIBS application, through the ChemCam instrument onboard the Curiosity rover on Mars [8–11], has contributed to enlarge its scientific audience. The present article is a review of selected LIBS studies on Earth Sciences.

LIBS should be considered as any other analytical techniques (i.e, Electronic Micro Probe Analysis, micro X-Rays Fluorescence, X-Rays Diffraction, Laser Ablation - Inductively Coupled Plasma Mass Spectrometry). But, usually the LIBS results, published out of the most technical papers, could not reach a maximum of geologists for allowing the emergence of crossed projects between different scientific teams. In fact, only recently LIBS researchers have published in geological journals e.g., American Mineralogist, J. Geochemical Exploration, The Canadian Mineralogist, Terra Nova, Minerals, even if some of the first applications, Vadillo and Laserna [12] or Fabre *et al.* [13,14] were published in Talanta, Geochimica Cosmochimica Acta and Chemical Geology, respectively.

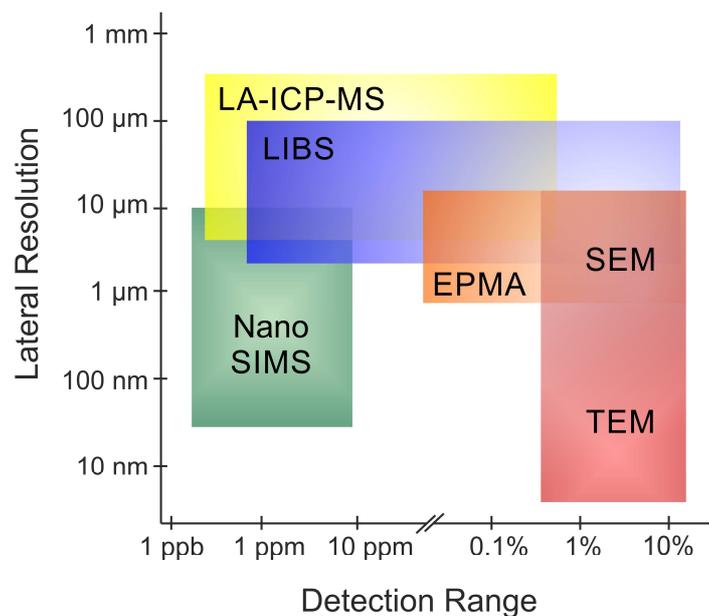


Figure 3 : Diagram of the respective resolutions and levels of detection for the main elemental imaging technologies (space-resolved). LIBS achieves resolution on the micrometer scale with sensitivities in the ppm range. Adapted from [15] with permission. EPMA: Electron Probe Micro-Analysis, SEM: Scanning Electron Microscope, TEM: Transmission Electron Microscope, nano SIMS: nano Secondary Ion Mass Spectrometry, LA ICP-MS: Laser Ablation Inductively Coupled Plasma Mass Spectrometry.

Earth Sciences include a variety of topics: environmental study with pollutants and fertilizers for agriculture topics, paleo-environments, mineral resources from the exploration to production aspects, through the analyses of rocks directly in the mine sites, planetary prospective (in simulated atmosphere or *in situ* analyses), imaging developments using fast acquisition systems, Rare Earth Elements and light element detections, etc. The present review on the geological LIBS purpose has been based on the most relevant publications, to underline the most ‘beautiful’ as well as significant studies and the unique input of the LIBS technique. For classical studies dealing with soils, meteorites and planetology, paleo-environment, archeology or technical characteristics such as multivariate analyses, mapping applications, handheld instrument, the reader is encouraged to refer to existing former well-documented reviews [4,6,7,16–24].

The present critical review aims at pointing out the new developments for the last 10 years in geology, i.e., mineralogy of rocks, mineral resources, gems identification, detection of light and rare earth

elements (REE), via qualitative, quantitative or mapping studies, and the remaining issues for routinely adopting LIBS to characterize such complex materials. In addition, some drawbacks and misuses of LIBS analyses are reported. At the beginning of each section of this review, the main issues that can be observed and discussed are pointed out, e.g., the detection of elements exhibiting very few emission lines, the difficulty of signal extraction in the case of iron or calcareous matrices, small spatial resolution and large sample, paragenesis. For the sake of example, we should avoid studies such as those doing classification of rocks between different end-members with high contrasted compositions (carbonates versus iron oxides or feldspar), adding more complex chemometric tests for a discrimination between iron igneous and carbonate rock compositions, using well-known self-absorption and saturated emission lines for quantification [25], or searching for a potential radioactive elements (U, Th and K which is no longer radioactive) that are hardly detected by LIBS [26]. At any rate, some studies are not pertinent and do not promote LIBS as a high potential analytical technique, due sometimes to lack of expertise of users. As for irrelevant publications, especially for the handheld tools, this negative aspect has also been reported by Steven Shackley [27] in the archeological thematic, in a fine essay on the recent use of portable X-ray fluorescence spectrometry, in terms of “the good, the bad and the ugly”, for a host of applications—volcanic rocks, all other stones, ceramics, and soils. The ugly aspect, also observed in some LIBS geological applications, is the “just shoot a substance, and report the results.” as Shackley has been reporting for several years.

Thus, the main question is *How does LIBS improve characterization of geological samples?* After a remind on the first studies done on the geological aspects since the 90's, as a rigorous basis for the future studies, a second remind is presented on the basis of good practices for LIBS analysis and the critical points that should be checked in order to validate any LIBS analysis on most common geological purposes. Then, a review has been done to select the most relevant advances and reported in different sections relative to the analyzed objects (identification of rocks/minerals and sourcing; resources applications; rare earth elements and light elements).

2. From the birth of LIBS to its geological applications

Los Alamos National Lab contributed a lot to the LIBS technique emergence in the 80's (for more details, see the reviews of history in [1,28]). The first geological LIBS applications are back to the early 90's with Grant *et al.* [29] who pointed out the main interest for LIBS field application and Blacic's study [30] was conducted on sulfide minerals for the licensing and performance of a potential repository at Yucca Mountain. Grant *et al.* [31] used pellets of powdered rocks as standards to obtain quantitative elemental analysis of iron ores using Fe as internal standard for the univariate calibration curve establishments. These authors already underlined the difficulty to obtain good correlation between the actual samples and the pellet standards due to a potential issue with the surface contribution (one aspect of the matrix effect). This conclusion is still of first importance, especially for the geological purpose, for the representativeness of the LIBS analysis and its relation with the sample homogeneity. As mentioned in the Grant's papers [29,31], next technical advances concerning the detector and the laser had permitted to obtain higher sensitivity and fast acquisition according to the pulse ablation. In 1996, in Talanta, Vadillo & Laserna [12] published the first actual geological application for sulfur minerals looking at vanadium. However, pyrite was not the simplest mineral to test due to its high number of emission lines. The authors underlined the necessity to optimize the time delay after the laser pulse to enhance the LIBS signal, reducing the continuum emission. At this time, the analysis was done under atmospheric air without any argon flux, a well-known gas that increases the emission signal.

The particular case of fluid inclusions study can be considered as a good example of why LIBS has emerged in Academic Earth Sciences Departments. Fluid inclusions have been studied from the 1950's as relics of the initial fluid (vapor + gas) [32], trapped during the mineral formation. Studying their chemical composition can help to obtain essential information of the Pressure-Temperature path of the rock. The choice of using a new technique, the so-called LA-OES for laser ablation – optical emission spectroscopy at this moment was drawn by its main advantages: the laser irradiance can drill to reach the fluid inclusion under the surface, then it can vaporize the liquid and the individual fluid inclusion composition can be obtained for the first time (before that, all the crystalline material was

crushed and only bulk analysis or fluid population analysis was possible). The laser spot, down to 10 μm , allowed the access to small fluid inclusion $<30 \mu\text{m}$. In other words, as any other studies in Geosciences, it is the characteristic of the object to be analyzed (its size, composition, location...) that drives the choice of the most appropriate analytical technique. After that, numerous publications demonstrated the use of a LIBS prototype for fluid inclusion purposes from 1999 to 2003 [33–37], in specialized geological journals (Economic Geology, Chemical Geology, Geochimica and Cosmochimica Acta..).

It is interesting to note that a first automatic “LIPS” mapping study of polished manganese nodule and granite polished rock sections was reported by Yoon and co-authors [38] in 1997, published after the 3rd International Conference on the Analysis of Geological and Environmental Materials, Geoanalysis. For this elemental mapping, a motorized X–Y stage was used to move the sample and elemental images of 50X50 mm could be reconstructed in 30 min, then quantification was also performed using univariate calibration curves. Since calibration curves were obtained using pelletized standard rock samples of a similar chemical matrix but displaying different hardness, the actual significance and the physical and chemical properties of the samples remained uncertain values. At this time, LIBS was a good semi quantitative analysis compared to EMPA (Electronic Micro Probe Analysis), with the same need of similar standard as the sample, but LIBS already presented a higher sensitivity in the detection of the most common elements. And LIBS sensitivity has been extensively demonstrated in the last mapping LIBS studies [24]. Several years after Yoon et al., Rosenwasser *et al.* [39], after the 1st International Conference on LIBS (Pisa, 2000), presented an automatic instrument, TRACER™ 2100 sponsored by the US Department of Energy, to develop methods for the real-time analysis. The samples were again prepared as small pressed pellets to obtain high homogeneity, and the calibration curves were provided but the lack of error bars, do not help to estimate the stability of the apparatus. A first LIBS, “point by point” mapping experiment on sponge fossil was reported by Fabre and Lathuiliere [40] with a spatial resolution of 10 μm for a centimetric-scale surface analysis. Then after, automation of the X-Y mapping provided faster LIBS-based imaging analysis in the following years for carbonate rocks related to wet or dry climate periods and marine mollusk shells, respectively

[41,42]. In the early 2000's, the introduction on the market of new detectors, both fast and sensitive, boosted the development of LIBS imaging, allowing the emergence of new applications. Less than ten years later, Novotný *et al.* [43] used low frequency ablation of 1 Hz for the LIBS analysis of a granite sample on a section of 20X20 mm. They compared the cartography to those obtained by LA-ICP MS, with a spatial resolution around 200µm. As no mineral identification can be obtained using only the major element detection, they only compared the surfaces of the element identifications (with a simple association of Ca for feldspar, Fe for hornblende or biotite, Mn not related to any particular minerals) for both techniques, after applying simple image treatment. The resultant compositional maps were quite similar testifying that LIBS can be successfully used for further research in geological purposes [24]. Nowadays, we observe that LIBS-based imaging studies have increased in the last decade and the highly valuable potential of LIBS has been extensively applied to the Earth Sciences field (e.g. megapixel elemental images of large-scale speleothems and coral samples [44,45] revealing laminar structures related to vegetation or climatic variations).

3. Requirements for a correct sample analysis

a. On the necessity of a good sample preparation

These last years, several studies have been published on the optimization of the protocol of sample preparation, more precisely on the effect of the load applied to the powder of samples to make the pellets [46–49], the grain size [46], and also optimization and new concept for sample use or preparation [48,50]. Jantzi *et al.* [50] published a review about the work of researchers who have developed, adapted, and improved upon sample preparation techniques for various specimen types in order to increase the quality of the analytical LIBS data in comparison to EMPA (Electronic Micro Probe Analysis), a non-destructive technique, for which the critical step is to achieve a fine polishing of the geological sample that avoids any surface imperfections which may influence the electron-sample interaction. Using laser ablation based analysis (LA ICP-MS or LIBS), this drawback can be overcome if the surface is plane. Nevertheless, one of the most cited advantages of LIBS is that it does not require sample preparation. However, as reported by Jantzi *et al.* [50] with this very pertinent

sentence: “Sample preparation for LIBS may be the “elephant in the room”; not considering sample preparation for LIBS may be one of the main reasons that LIBS is still not considered a mature technique despite more than 50 years of successful applications.” ‘No sample preparation’ should be replaced by ‘No sample treatment is required’. Thus, some specimen types, and in our case geological samples, require simple but essential preparation techniques (cleaning and polishing at least) to obtain analytical performance (i.e., limits of detection, accuracy, and repeatability) as good as LA ICP-MS or EMPA analyses [50].

The main drawback of the LIBS is the well-known physical matrix effects, caused by changing material properties in terms of hardness, grain cohesion... Optimizing the preparation for sample analysis is thus of first interest, especially for the geological studies, due to potential matrix effect, depending on the minerals (such as oxides, carbonates, sulfurs that display contrasted melt temperatures under the laser irradiance), the different sizes of the grains in porphyritic or sedimentary rocks (from micrometric to millimetric size) [51] and the roughness of the surface when it is not polished [52]. In fact, crystallinity and transmissibility of the minerals, grain size, surface texture, water content, as well as textural and porosity changes, coherence, and indurations, or presence of organic matter, will have a direct effect on the degree of laser energy coupling. To limit this effect for the quantitative studies on minerals or rock, to obtain a mean composition, the sample is usually grinded and powders pressed pellets are used to ensure chemical homogeneity. Synthetic silicate host glasses can be required as standards if the analytical protocol needs hard sample. It is the case for the onboard LIBS standards on the Curiosity rover, where silicate glasses and ceramics were chosen to mimic Martian surface compositions [53–55]. In any case, it is highly recommended to prepare the samples with high level of attention in order to get polished sample, without any surface pollution, fine grinded, pressed pellets etc... and obtain high-quality data.

All of these requirements for a suitable sample preparation can be however difficult to achieve when working with handheld tools. For such geological studies conducted with portable tools, the surface analyzed will not be as flat as expected. However, one can recall that the purpose of a field study is

often only to discriminate between minerals or recognize them, when they cannot be distinguished with the naked eye.

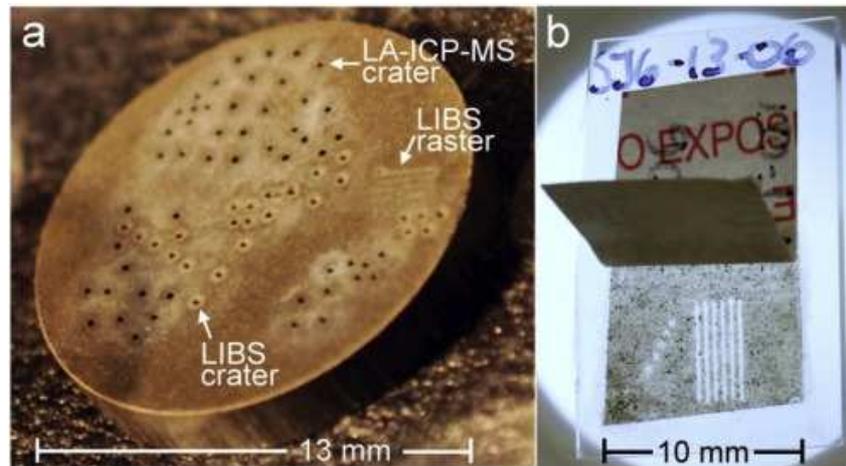


Figure 4 : Modified from Jantzi *et al.* [50] : a) A pressed pellet from milled sediment powder. Ablation craters from multiple laser shots (LIBS and LA-ICP-MS) and rasters can be seen. b) A thin layer of soil mounted onto double-sided tape on a piece of a glass slide. Soil was removed effectively by single laser shots and raster.

b. On the paradigm of the sample homogeneity

Before undertaking any LIBS study, it is appropriate to come back to the fundamental of the attending chemical compositions of mineral or rocks, and to be aware of the possible different phases (minerals and matrix/glass) present in the rock. Rocks and minerals are usually highly heterogeneous, at different scale sizes, and their granulometry and the rock paragenesis are of first importance to unravel their geologic formation or history [56,57]. In this regard, I urge to read a paper published by Diaz Pace *et al.* [58], underlining the possible issues of the LIBS analysis of gems, minerals and rocks. Even if the discrimination between quartz (SiO_2), magnesite (MgCO_3), microcline (KAlSi_3O_8) and so on, could readily be done using the major elements present in the LIBS spectra, they point out the necessity to control the emitted light by optimizing the number of laser shots according to the samples. Thus, while homogeneous samples such as gems, can be shot at a single location, “natural” gems collected in the field must be analyzed by multiple laser shots in various random locations at the sample surface. But the main difficulty is obviously for the analysis of rocks exhibiting a variable

grain size. In Diaz Pace's study [58], the influence of granulometry is detailed and taken into account to optimize the way of collecting LIBS data in the case of tonalite and basalt for igneous rocks, and caliche for sedimentary rock. The use of a grid of measurements, for 25 sampling points for tonalite, the most heterogeneous rock, aims at limiting the relative standard deviation of the peak-intensity ratios of the selected lines.

Another difficulty related to the granulometry aspect may come from the change in the diameter of the ablation crater depending on the laser/matter interaction. The penetration depth varies with the target hardness/density [59]: the softer the target, the deeper the laser ablation (Figure 5). The evolution of the crater volume as a function of the number of shots shows that the ablation rate drastically decreases during a depth profile. Thus, comparing emission lines obtained in different matrices, and then different minerals, it is not as simple as it looks.

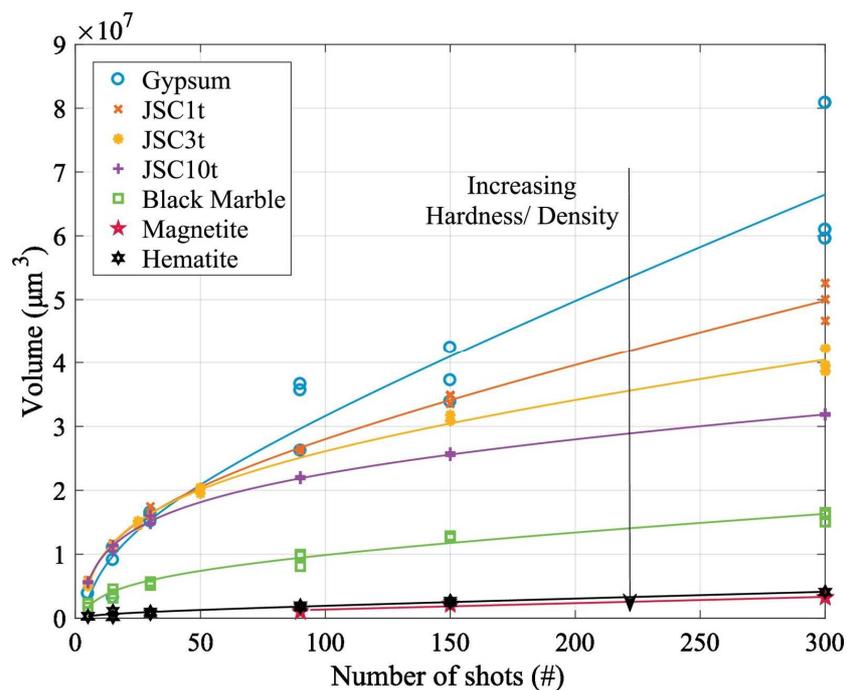


Figure 5 : Evolution of the ablated volume as a function of the number of laser shots deposited in the crater. Modified from Chide et al. [59].

In summary, the LIBS analysis is performed at the size of the laser spot diameter, which is typically from tens to hundreds of micrometers. Consequently, the representativeness of the punctual LIBS spectrum must be accurately considered regarding the actual aim of the study. Indeed, a geological

sample is naturally heterogeneous at a given scale. Heterogeneity can be driven by grain size, or mean size of constituent minerals. In order to overcome any risk of mismatch between the LIBS data and the actual sample composition, it is highly recommended to record a series of LIBS spectra resulting from 1D or 2D raster with a spacing finely tuned to cover any heterogeneity.

c. On the risk of blind data processing

LIBS is one of the most efficient techniques to retrieve chemical information from both atomic emission lines and molecular emission bands. Spectral features from many elements/molecules can be present in the LIBS spectra. It is thus critical to achieve a correct emission lines identification and assess the risk of possible spectral interference. Even if the major part of the LIBS analysts correctly work on the identification of the elements related to the detected emission lines, it is not always the case, especially for some “first LIBS users” researchers. It is thus worth recommending some reviews and critical papers on the good utilization or extraction of the LIBS signals [17,60,61]. Indeed, El Haddad *et al.* [17] have presented a review on the analytical results obtained by LIBS to establish good practices for both classification and concentration measurement, identification of samples and to avoid risk of misclassification and/or wrong interpretation. Both univariate and multivariate approaches are discussed with special emphasis on the methodology, the way of presenting the results and the assessment of the methods. They particularly emphasized the use of several figures of merit to assess the analyses, namely R^2 , Q^2 , RSD (%), RMSE, RE (%), LOD, and LOQ for quantification, and rates of correct, wrong or no classifications, overall accuracy (%), sensitivity and specificity for classification purpose [17]. Moreover, in case of multivariate LIBS analysis involving chemometrics, it is of major importance to interpret and report well-chosen figures of merit. For example, in the study of Panya *et al.* [62], the signification of the PCA loadings is not sufficiently discussed despite it is expected to provide the list of lines/elements responsible from the discrimination between samples. Even if the data seem to be as good as possible, the conclusion can be sometimes insufficiently supported by the results/discussions. In addition, it has been discussed that it is quite complicated to validate results derived from unprocessed data [63].

Following this essential aspect of the optimization of the signal treatment, Motto-Ros *et al.* in 2018 reported a collaborative study [60] on LIBS data processing done on a unique set of LIBS spectra from one single experiment, with the use of the same spectral lines for the analysis. Using several analytical figures of merit, as previously recommended by El Haddad *et al.* [17] such as the determination coefficient, uncertainty, limit of quantification and prediction ability (i.e., trueness), it is interesting to observe that, depending on the type of data extraction, baseline modeling as well as the calibration model, the quantification performance of the technique can be dramatically different. Thus, these two papers [17,60] aim to optimize any LIBS analysis through methodological steps toward a standardization of LIBS. For mapping interpretation Motto-Ros *et al.* [61] recently pointed out the importance of this data processing and in particular signal extraction to provide robust and reliable results. Acquisition of elemental mapping provides thousands to millions of spectra, corresponding to complex LIBS datasets. They proposed a new conditional data extraction procedure relying on the statistical uncertainty associated with the extracted signal. A synthetic spectral dataset is built with controlled spectral features to test the linearity, dynamic range and operating speed of different extraction approaches. This procedure is of particular relevance for the extraction of weak line intensities and in cases where the presence or absence of certain elements is critical (i.e., biomedical applications or trace analysis). In addition, the proposed conditional approach offers new insights into the means of providing LIBS imaging results.

To cope with the very big amount of data recorded by LIBS, preventing manual opening and processing of each single spectrum, it is strategic to build reliable and robust numerical tools for future routine use, as it is the case for the other analytical techniques used in laboratories, such as SEM, EMPA, ICP-MS, and XRF.

4. Sourcing and discrimination of minerals and gems

The number of articles on rocks analysis has increased since 2007 and the major part of these publications is the result of a collaborative work between the US Army Research Office and the Department of Geology, New Mexico State University, Harmon, McMillan and co-authors [64–75].

Here, I would like to focus on one of the first papers of McMillan *et al.* [66] published in the special issue of Spectrochimica Acta B following the 4th international conference on LIBS (Montreal, 2006). It is the first geological paper arguing with a very impressive level of information of the chemical structure and the interest in the LIBS specificities, and not a systematic blind analysis of minerals. McMillan *et al.* underline the subtle chemical difference between close minerals, not always observable by classical analytical techniques. The carbonate and silicate panel of database of composite broadband spectra (52 minerals) represents a very reliable base to test the potential of the LIBS for the identification of minerals. The authors already pointed out the high potential for field application even if “LIBS is yielding compositional and not stoichiometric information” (as previously published by Harmon *et al.* [64,76]). These two departments have published remarkable papers on the classification of minerals and gems to determine their provenance according to their LIBS signatures. This kind of study was already demonstrated through molecular techniques (IR, VNIR, Raman...) or analyzing their fluid inclusions (in terms of gas and liquid). Numerous broadband LIBS spectra of beryls [65], garnets [67], conflicts minerals [77] sapphires and rubis [70], diamonds [71], tourmalines [72,78], are undertaken to obtain a database and compare their LIBS signatures. Because of social political or human rights abuses concerns, the provenance of gems is now essential for the systematic controls in legal laboratories. All of these studies are supported by robust chemometric tools, from correlation coefficient resulting from the regression of the intensities of pairs of LIBS spectra, principal component analysis, partial least squares regression, etc... In 2008, McManus *et al.* [65] proposed an instructive study on the provenance of gem stones and in this specific case, beryl gem using PCA investigation. This paper can be also used as a very good reference for the use of chemometric technique, for geological/mineral purpose, reminding the readers to take into account of the PCA loading meanings for interpretation. Some papers deal with the identification of different laboratory grown gemstones by trace elements amount [79], and the possibility to perform a complete standardless chemical characterization of minerals with a non-complex chemical composition like for red beryl [80].

For readers interested in PLSR approach in geology, there is a paper published in *American Mineralogist* in 2015 [70] on the study of 569 sapphire and ruby specimens from 21 localities. The use of ratios of many elements (Ca, Zr, Fe, Ba, Mn, Ti, ...) allowed to obtain the unique compositional signature of each deposit from 11 countries (Figure 6). All of these selected papers, dealing with the gem provenance, have seen the number of samples largely increase, from several dozens, to several hundreds, to reach more than 2300 spectra to be tested in statistics, with 300 samples of diamonds to be analyzed [71]. Regarding to all of their conclusions, the high potential for LIBS in the gemology is obvious, as the laser spot can be very small. This technique can be considered as quasi non-destructive, and all the chemical information that is relevant to the provenance of the gems is provided in a unique LIBS spectrum, thus LIBS tool is here considered as robust, relatively inexpensive, rugged and simple to use. However, the cited sentence as “the analyst needs no rigorous training in spectroscopy or gemology” should be taken with carefulness. For this aspect, it validates the development of a new software in 2018, so-called Quantagenetics® [75]. In this last studied case, more than 768 million data points have been investigated, regarding the entire library that is composed of 19 200 spectra. As their studies demonstrated that chemometric analysis of LIBS spectra makes accurate, rapid provenance determination possible with a success rate higher than 95%, two US patents have been deposited (US Patents 9,063,085 and 8,699,022) about the use of multivariate statistical method based on Bayesian statistics using the Euclidian distance between LIBS spectra.

Finally, mineral/rock discrimination through LIBS strongly depends in the first place on the measurement itself, in particular in the case of field measurements for which the sample surface may exhibit significant roughness and a lack of planarity and secondly, on the lack of reliable and robust algorithms to make the decision univocally, directly from raw data.

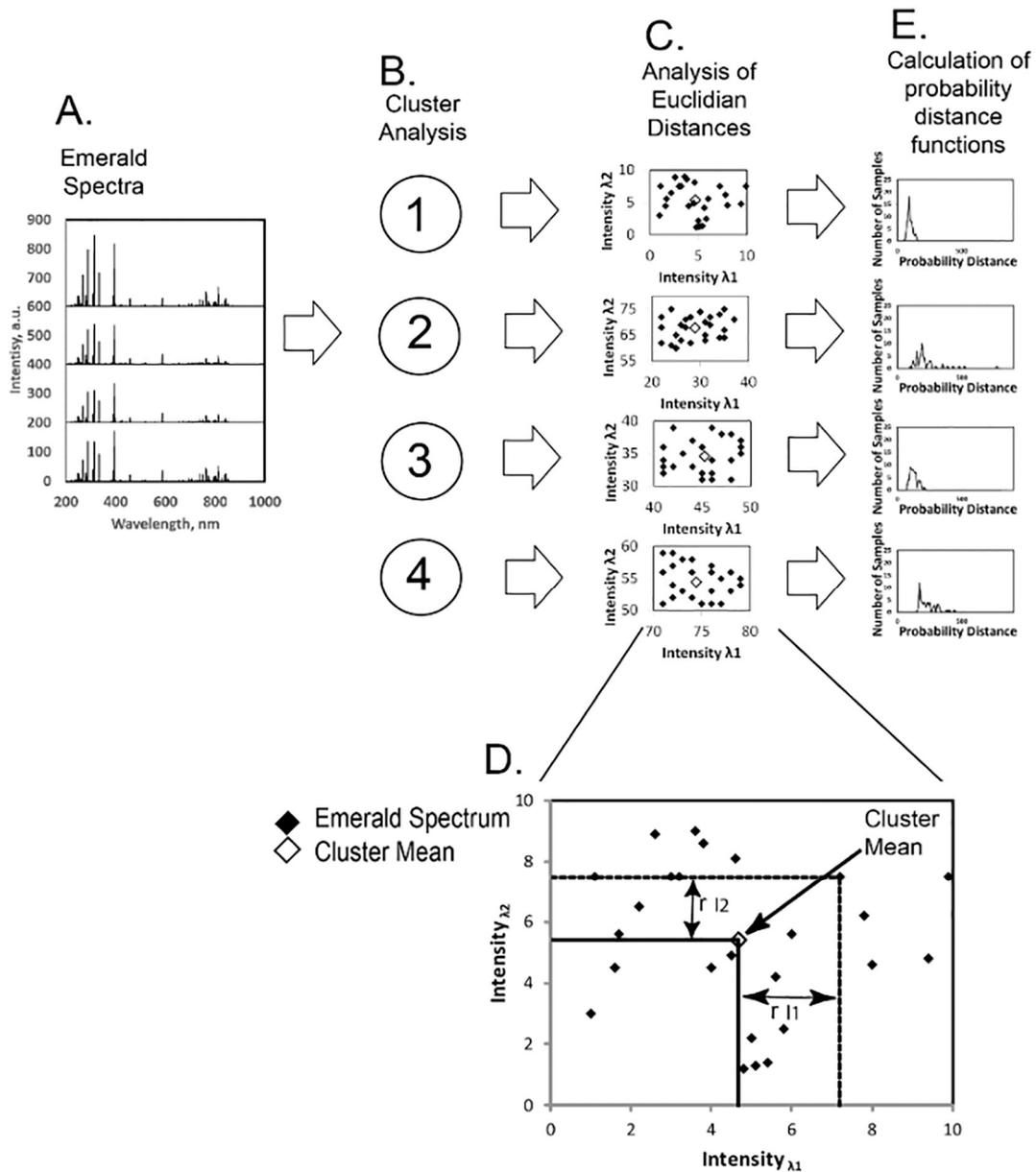


Figure 6 : *Quantagenetics®* method for training a dataset for classification purposes. Modified from Mac Manus et al. [75]

5. Applications for resources

Resources thematic deals with large aspects from the exploration for mining companies, with access to the tailings that comprise the crushed rocks from drillings. The drill cores allow the characterization of the major mineral phases after the interpretation done by a geologist/mineralogist on the site. Thus, resource estimation for metals in mine tailings and ore deposits requires many samples, usually in the form of drill cores. However, depending on the minerals that are prospected, chemical information can

be essential to recognize the minerals, to access not eye-visible minor elements or in substitution in the mineral phase. The chemical characterization can be a very helpful step to optimize the future drillings, or to limit the surface of exploration in the field. After exploration, the aims of exploitation of the rocks through mineral processes are to separate and extract the different investigated elements. The detection and the quantification online are the main objectives for exploitation companies, usually using portable tools. Mineral flotation processes must be controlled by monitoring the grade of the present minerals. If assaying of the minerals in the slurry flows can be provided, it will greatly optimize the performance of the flotation process. The main difficulty is the access, in a very short time, to on-the-spot and quantitative mineral or elemental identification of the slurries. Numerous publications attest that LIBS can lead to many benefits such as rapid control of concentrate quality [46], enhanced recovery and savings in money, time, energy and manpower [81,82]. Thus, a blind classification of rocks can be investigated for on line analyses (in exploitation mine, drilling, or in rock treatment), where a fast acquisition is required without any human contribution.

Some works have been done using LIBS systems, which can be operated on the field as portable ones [16,64,83,84], and some of these studies have been supported by national or international programs, which are not systematically valued in the LIBS community through scientific publications. If we look at the portable-XRF handheld instrument, largely used for the detection and quantification of elements by junior or major exploration companies for more than 20 years, only few data are published in the open literature. This is also the same thing for the LIBS handheld instruments. Even if numerous LIBS systems are nowadays operating in the field, mainly in the North America and China, almost no data have been published on their actual capabilities. Thus, the major part of the applications is only displayed by the manufacturers for compact handheld instruments (e.g. from SciAps, Brucker) or benchtop tools (e.g. from ELEMISSION, HoneyBeeRobotics, National Research of Canada -NRC). However, when looking at new and pertinent LIBS studies in the Earth Sciences, it is essential to consider conferences that reach a wide audience, far from the most technical, scientific or spectroscopic LIBS aspects. Thus, from the most technical conferences, such as EMSLIBS, LIBS, SciX, EWLA, and COLA, for instance, numerous LIBS applications are now presented in specific

geological conferences (i.e. AGU, Goldschmidt, GACMAC, LPSC conferences...). In this review, industrial works have been also reported for the developments or optimization of specific LIBS prototype or software and, more largely, academic teams in university or national research laboratories.

a. Slurry and drillcores studies

In 2000, Bolger [85] made the first investigation of time-resolved LIBS for mineral assaying applications in drill core. Tentative calibration curves have been done for Cu, Cr, Fe, Mn and Ni, showing good correlation between LIBS and bulk analysis, but neither Relative Standard Deviation nor root-mean-square error were reported. To optimize the signal variations, the emission lines were corrected by the total plasma emission intensity: Ag was also detected for a “concentration” estimated to be <83 ppm in the assay.

Drill core and then tailing slurries have been investigated using LIBS by a scientific team in Finland under the OUTOTEC expertise [86,81,82,87]. These industrial studies led to the development of an accurate and reliable analyzer, the Outotec Courier ® 8 SL analyzer, for on-line measurement of the elemental concentrations of plant feed, tailing, and concentrate slurries. A new concept of data fusion is also reported to combine different analyses, such as LIBS, reflectance spectroscopy and XRF measurement. Khajehzadeh *et al.* [87] validated the use of PLS regression for data fusion, that can provide direct quantification of the important minerals in the flotation plant [87]. This accomplishment provides quantitative knowledge about mineral contents from the nearly real-time assay data, without any modification on the measurement setup or further instrumentation. In geology, different minerals can present similar element contents, such as hematite and magnetite, or silicon-bearing minerals like quartz and other mixed silicates that display different flotation properties. LIBS technique cannot then distinguish between such minerals, so that other techniques must be undertaken on the same slurry samples. This difficulty, reported for tailing slurries, is also an essential aspect for any geological purposes, as the signature of LIBS spectra does not give any information about the molecular structure of the minerals. Then, the information for the anions are also hard to interpret as C and O can be related to the atmospheric air, and S is hardly detectable.

In mineralogical study, the elemental information (cations and anions) is related to the mineral composition of the sample. New publications in the mining industry field, published over the last decade, report LIBS applications to characterize the spatial distribution of elements in ores, providing key information about their sources and depositional processes. These data assist the decision makers for further prospects in the field and in the evaluation of economic viability for extraction and refining. Fifteen years after the first studies reported by Bolger *et al.* and Fabre *et al.* [85,88] huge development has been done due to a new interest of mine companies and constructors, reporting high potential for elemental or mineral mapping with industrial or academic LIBS set up [89–94]. These set ups provide elemental mapping of several cm² of surface for numerous elements, revealing rather complex elemental distributions in less than 3 hours. This acquisition is faster than conventional techniques such as EPMA or SEM.

Complexity of rock structures may impose the use of multivariate analysis for processing the spectral data set, as explored by Trichard *et al.* [90], especially to have access to contents of hardly detectable elements such as S, B, and As. This ore sample is from the richest gold deposit from the Val-d'Or in eastern Canada and is composed of several mineral phases needing a combined multivariate analysis extraction. More than 15 elements including P, As, C, Ca, Si, Mo, B, and Zn have also been detected, and elemental images were recorded, covering sample surfaces in the range of cm² with a micrometric spatial resolution (10 μm). However, one can notice that direct interpretation about the presence of complex minerals, such as renierite ((Cu, Zn)₁₁(Ge, As)₂Fe₄S₁₆) from the correlation of the emission lines intensities of S, As, Zn and Cu, is risky since this mineral is very rare. Actually, Arsenic is more probably present as trace element in a Zn-sulfur, or with the Cu in substitution. It is hard to compare the element intensities in different minerals, and the relative ratio between two elements are tricky to establish. As Moncayo *et al.* [95] reminded, the points that limit the development of the LIBS technique are undeniably the expertise and the time required to extract a relevant signal from the dataset. The complexity of the emission spectra (e.g., elemental responses, structure of the baseline), the high dynamic range of measurement (i.e., possibility to image major elements and trace elements), and the large number of spectra to process require new data analysis strategies. In this work, a

turquoise sample (an hydrated copper-phosphate $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$) was analyzed to determine the elemental distribution of Al, Fe, P, Cu and Si (see [95] and Figure 7). Then, using PCA classification, discrimination between the minerals present is possible and the mineral mapping mimic the paragenesis of the sample (pyrite, turquoise, silicate).

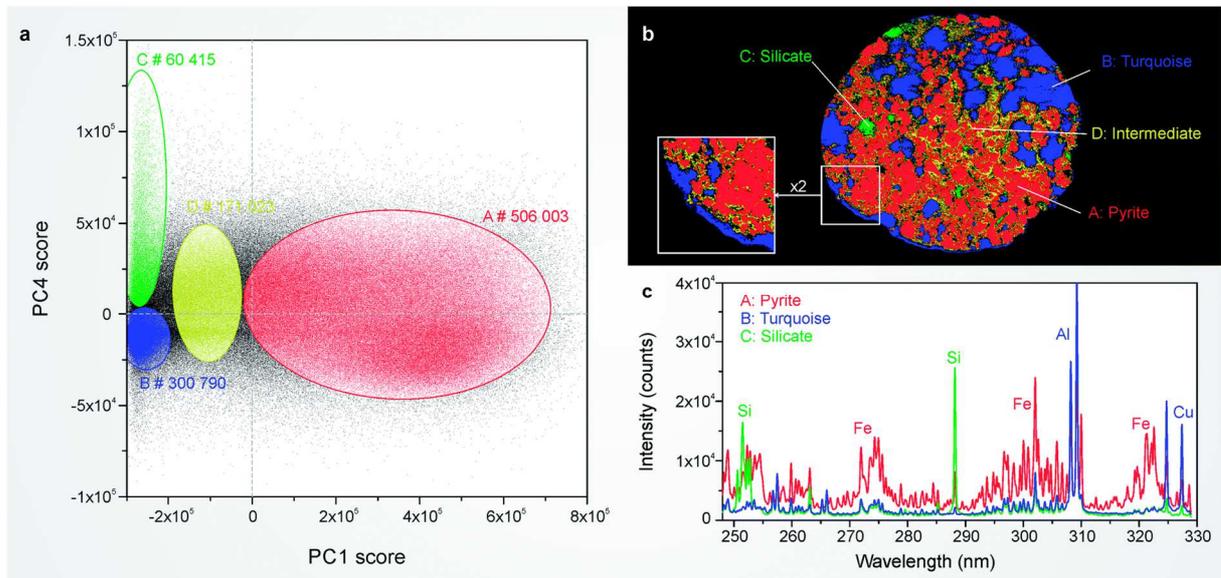


Figure 7 : Example of advanced data manipulation using PCA analysis for megapixel imaging.
Modified from Moncayo *et al.* [95]

Arguing that multivariate is the best approach to examine LIBS images of minerals, El Haddad and collaborators from NRC [93] also used MCR (multivariate curve resolution) on rock tiles, even in the presence of mixed mineral phases (sulfurs, molybdenite, quartz, chlorite, feldspars, fluorite and calcite) within the laser spot area. Using a single laser shot, a root-mean-square-error below 10% was achieved for the main minerals with absolute errors below 3.5% for the major minerals and below 1% for the minor minerals. This study could be scalable to automated mineralogy measurements for coarse rocks.

In any case, identifying and quantifying minerals is a key for plutonic rock classification and plutonic rock nomenclature, which is based on mineralogical composition (specific minerals in the rock sample). Nikonow *et al.* in 2019, [96] from the German Federal Institute for Geosciences and Natural

Resources, present novel advances in instrumentations. For instance, energy dispersive x-ray fluorescence mapping (μ -EDXRF) or hyperspectral imaging (HSI) provide now fast and non-destructively spatially resolved and large-scale chemical information. The authors combined chemical, mineralogical and textural information from μ -EDXRF, LIBS and HSI for petrographic analysis of plutonic rocks. The LIBS technique provides very low detection limit for lithium and obviously enables the identification of Li-enrichment in biotites or plagioclases. Thus, using supervised classification of spectral information, mineral distribution maps are obtained for image analysis including geometrical data of each grain, such as grain size, grain orientation and grain location for subsequent targeted analysis. The authors obtained the modal mineralogy for plutonic rock classification for 20 rock slabs but only 4 slabs were scanned by LIBS.

b. Economic and strategic elements

Mineralogical investigations applied for exploration of mineral deposits and mining residues require a good database regarding mineralogy, geochemistry, as well as the access of the rock texture for the evaluation of the economic potential of a deposit. Current standard procedures accepted by the industry are time consuming, expensive and personnel intensive. Due to the current crisis hitting the mining industry, an elevated demand exists for new exploration strategies and methods. They are aimed at providing a reference database in shorter time, at comparable accuracy and information level, but at definitely lower costs.

As already mentioned, it is sometimes hard to find the actual data obtained on a mining area. Some nice in situ studies are not published as scientific paper, but they are more largely published as notes in the company's websites or only presented in specific mining meetings or even as internal documents. For example, the last achievements based on the use of the handheld instrument Z300 by SciAps© for mining purposes about gold and lithium prospection have been reported as application notes on the website of the company and only a few applications of this instrument are reported in scientific publications [84]. For studies undertaken by the LIBS instrument providers, some applications are listed by Applied Spectra© on geochemical fingerprinting of "coltan" minerals, the Colombite-

Tantalite minerals enriched in niobium-tantalum elements [77], after elemental mapping of Marcellus shale core samples. They are predominantly composed of black shales as those analyzed by Jain *et al.* [97,98] and Washburn [99]. This company also reported some studies on ruby-in-zoisite gem rock using the J200 LIBS instrument, but without any related publication.

Hyperspectral LIBS imaging

Geological studies increasingly require highly sensitive elemental techniques able to image the distribution of elements in minerals with microscopic-scale resolution. Meanwhile, very fast high-resolution multi-elemental LIBS technique for the mapping of geological samples has been developed. The repetition rate is up to 1 kHz and the spatial resolution from 15 μm to 50 μm [44,92]. A new methodology of data treatment was adapted to a multi-phase material. This megapixel LIBS imaging, done on a sample surface of 5 cm^2 by Fabre *et al.* [100], is based on mask spectra according to each mineral phases. The study is conducted on a hydrothermal ore sample with a complex mineral structure involving five different mineral phases (different sulfur phases, quartz and carbonate). Minor and trace substituent elements were mapped with a spatial resolution of 15 μm using more than 2 million spectra. The authors demonstrate the potential for LIBS-imaging to both detect and image the substituents present at the ppm-scale level in various mineral phases (Cd in sphalerite; Bi, Ag and Sb in galena; Be and Al in quartz; and Sn in chalcopyrite).

As resource estimation for metals in mine tailings and ore deposits requires many samples, usually in the form of drill cores, the LIBS technique can provide rapid answers on the metal enrichment or depletion. In a very complex rock sample, Kuhne *et al.* [89] used two different core scanning methods to obtain chemical information. The samples are three drill core meters from tailings of a former Pb–Zn mine. Elemental mapping of the drill core sections was performed by a prototype LIBS core scanner manufactured by LTB Berlin (Figure 8). The amounts of major elements (Si, Al, Mg, relative to sand/clay alternation) and strategic elements (Pb, Zn, Co) provide an objective basis for further sub-sampling of the drill cores and help reduce the amount of samples and therefore the costs for further investigations.

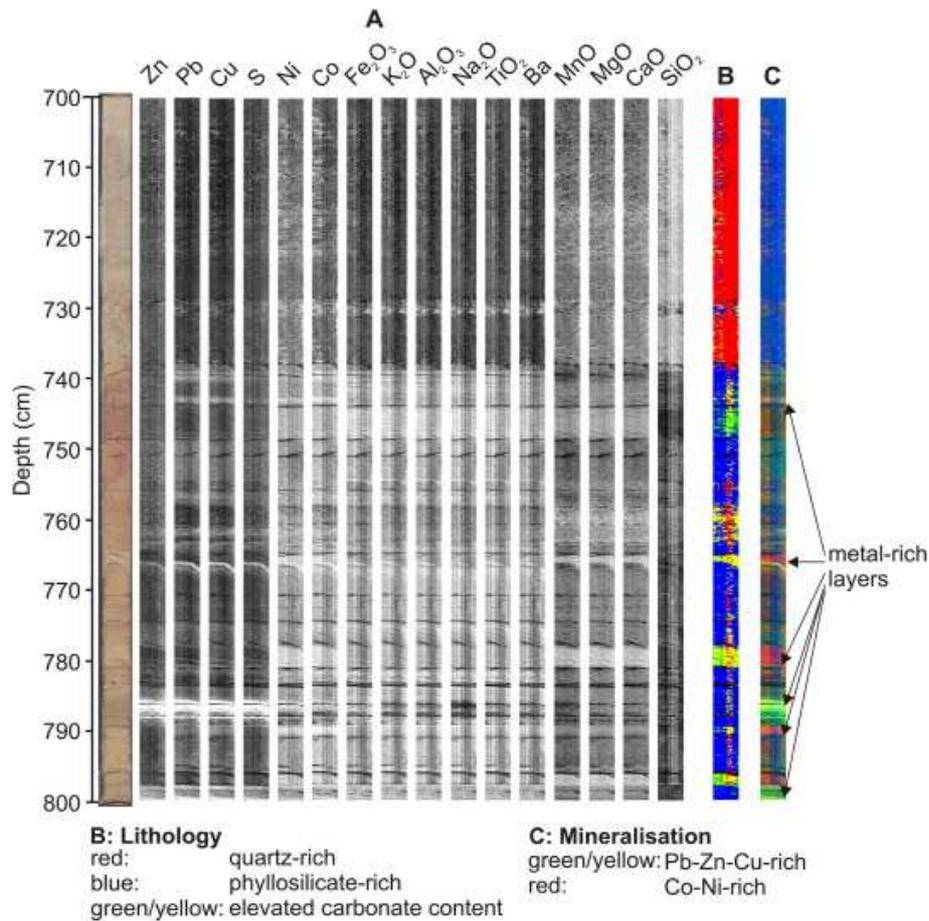


Figure 8 : A: Spatially resolved element maps of one drill core meter measured with the LIBS core scanner. The predicted concentrations after PLS regression were transformed into grey value pictures. Bright colors reflect high and dark colors low concentrations. B: Lithological classification image generated by SAM and majority analyses on basis of the LIBS maps. C: RGB image reflecting the distribution of Pb+Zn+Cu-rich layers and Ni+Co-rich layers. Modified from Kuhne et al. [89]

Looking for silver and gold

There is a need in the mining industry for determining quickly and in the field the concentration of gold in mineral ore samples. Currently, portable analyzers can detect gold but cannot determine its content at the ppm range, but geologists are also very interested to obtain the simple elemental gold detection in raw sampled rocks for exploration targeting. Developing a functional LIBS analyzer involves several challenges to be addressed prior to its use in the field. In fact, the analysis should be representative of the entire sampling and thus of the surface of the mineral samples. This aspect can be answered multiplying the number of analysis points on the sample. As in all geological samples,

matrix effect is the most potential effect when analysis is done on several mineralogical compositions or, on different minerals.

Connors *et al.* [84] from SciAps© performed on-site analyses of sulfide minerals in different rocks enriched in gold, using the SciAps Z-500 handheld LIBS instrument. Several assayed geochemical sample sets, including igneous rocks and soils, were investigated, allowing the acquisition of elemental mappings in heterogeneous samples. Then, they built calibration models for the elements of interest. Comparing to laboratory LIBS set up, such rapid raw element mapping obtained on field, on rock phases more or less flat and unpolished, is of first interest for the optimization of the sampling to reduce the amount/weight of the rocks to be analyzed in the lab. This methodology allows the detection and the location of some strategic elements in different mineral phases at millimetric scale. For junior companies involved in resources prospection, this elemental imaging at mineral scale (typically 1 cm²), can become a strategic step before any time-consuming and expensive gold.

Thus, the National Research Council Canada (NRC) and Laval University published several papers on the recent on-going work using LIBS for gold mining, from the determination of gold-bearing rock composition to direct detection of gold and system prototyping [3,91,93]. In any case, the analyzer has to probe a representative sampling of the surface of the mineral samples and has to tackle the matrix effect resulting from the mineralogical mixture of the samples. In order to answer the question of the direct quantification of Au in different geological samples for Si-rich and Fe-rich matrices, a specific prototype LIBS system has been built by NRC, the so-called CoreLIBS, with a core sampler.

Recently, quantification of silver and gold has been attempted by Diaz *et al.* [101]. Ores from a gold-producing mine and samples were doped with Au and Ag solutions. They reported that in ore samples, silver detection and intensity measurement were possible for concentrations from 0.4 to 43 µg/g but Au was not detected for 9.5 µg/g Au-ore sample, and gold detection limit of about 0.8 µg/g was determined for surrogate samples. They concluded that, regarding the number of spectra 'positive' for gold detection to the number of laser shots, the detection of gold is enhanced with the number of analyses. For some samples that withstood 5,000 shots, gold quantification in ores was successfully

achieved at mean concentrations as low as 1 µg/g. Even if the results are encouraging and illustrate the applicability of LIBS to gold and silver in field semi-quantitative analysis, we can point out that Ag (or Au) usually occurs in high-concentration accumulations or as native metal ore deposits. Thus, it seems to be difficult to accurately compare the LIBS surface measurement and in the same time, to focus on the detection limits of the technique for gold purpose. The results obtained on surrogate samples with “a dilute” concentration is hardly comparable to the Clarke concentration that represents the mean concentration in the continental crust or to the mean concentration in the rock. In fact, such dilute concentration is not representative to the actual gold amount on any positive point that is to say, when LIBS spectra displays Au or Ag emission peaks. This difference is one of the most important things to remind when searching for economic elements, using any localized analytical technique. The value of the standard references does not reflect the actual amount of gold that could be sampled by LIBS on the sample surface. In fact it is the number of laser shots and thus the surface investigated, that are the limiting characteristics for LIBS analysis, as underlined by Diaz *et al.* [101]. Therefore, LIBS imaging seems to be the ideal tool to overcome this issue for disseminated element on rocks (as native gold or electrum).

In the same topic for gold detection, validation of the use of LIBS imaging for gold investigation has been done by Rifai *et al.* [91,92] from ELEMISSION ©. Elemental compositions of drill cores were investigated using a LIBS imaging system operating at kHz repetition rate. This system allows real-time in-field geochemical application, given access to gold content. When it is possible to combine LIBS maps obtained on rock samples, the resource companies may then be able to determine volumetric chemical variations at the microscale. Recently, following these works, Gervais *et al.* reported [102] LIBS “tomography” of gold-bearing sample using the MISSION:CORIOSITY benchtop from ELEMISSION ©. In fact, this paper is not the first result of compositional tomography of a geological sample. Five years ago Chirinos *et al.* [103] already provided simultaneous LIBS and LA-ICP-MS 3D imaging using commercial set up provided by Applied Spectra ©. The major interest of Gervais’s paper [94] is the comparison of the two chemical imaging maps obtained from LIBS and SEM-SDD techniques on a 6x8 mm² surface on an ultramafic schist. One may regret that no LIBS

spectra was provided to appreciate the signal of the Au emission line which is usually largely weaker than the Ag lines also detected in this sample. To obtain this tomography, a z-stack of 63 images was considered, representing around 1 mm depth, and recorded in 21 min. Even if the results of the tomography of the gold structure seem to be interesting, it is hard to interpret such gold volume on the 3D representation. As during the ablation process, some ablated material can be deposited on the bottom of crater and on its rims, the final volume of the gold can be complex to interpret in a 3D configuration. However, the limit of detection of 100-500 ppm for Au makes possible the detection of visible native gold or as electrum (Ag and Au) in such ultramafic schist environment.

c. Detection of light elements

In geology, light elements refer to those elements with atomic number (Z) less than 11, even if there is no official cutoff as to what is a light element, but few analytical techniques can provide detection and quantification of light elements. These elements are largely used for battery or electronic devices and thus offer a highest economic interest. For X-Rays instruments, light elements are the subject of a unique treatment because the induced X-rays fluorescence they generate can be very difficult to measure quantitatively and even be simply detected. In LIBS, some issues also exist for the analysis of such light elements. Indeed, one can observe a limited number of electronic transitions and thus very few emission lines compared to those detected for the transition elements. In addition, spectral interferences have been observed for the emission lines related to H and C, as it is reported in the recent studies for Martian applications [52]. Technically-speaking, one can also notice that the most intense emission line of carbon at 193.1 nm is hardly detectable for common spectrometer. Nowadays, it is well established that the detection limits one can expect from LIBS for fluorine is very high if the spectral analysis is based only on its atomic emission lines. Therefore, the use of molecular bands (CaF) is a very efficient strategy to quantify fluorine with much lower detection limit.

Lithium analysis

Lithium is an important geochemical tracer for fluids or solids. However, variations of Li abundance at the micrometric scale are rarely imaged/observed through conventional techniques and their amount are most often estimated from bulk analyses. Nowadays, detection and analysis of Li using the Scanning Electronic Microprobe has become possible thanks to a newly developed Soft X-ray Emission Spectrometer (SXES). But LIBS remains one of the best analytical techniques for the detection of lithium, acknowledged as a highly emissive element. It is expected to give access to very low detection limits, and to be helpful for either qualitative or semi-quantitative analysis. The first quantification of lithium for geological materials was done by Fabre *et al.* in 2002 [14], using a home-made LIBS set-up. Univariate calibration curve was built from synthetic glasses and natural minerals, giving a limit of detection of 5 ppm Li for a micrometric spatial resolution (6 to 8 μm), using the major emission line at 670.7 nm. For spodumene ($\text{LiAlSi}_2\text{O}_6$) and petalite, the Li_2O concentrations are obtained 7.6 \pm 1.6 wt% and 6.3 \pm 1.3 wt%, respectively, in agreement with those obtained using ion microprobe analyses or bulk analyses. For eucryptite crystals, the Li concentrations were scattered because grain size was smaller than the laser spot size. Lithium concentration on silicate glasses on melt inclusions were found to range between 90 and 400 ppm, with concentration values up to 6.2 wt% for the Li-rich daughter minerals. More than 10 years after that, Sweetapple *et al.* [104] measured Li, Be and B on altered spodumenes and other Li-rich minerals. They estimated that the limit of detection was approximately 240 ppm for Li (with a 125- μm laser spot diameter). In their study, LIBS mapping was applied to petrographically characterized samples of hydrothermally altered spodumene from the Neoarchean Mt. Cattlin lithium pegmatite. Mapping was carried out using a grid of analysis on a sample surface cut by a diamond saw blade without further preparation. The Li-mapping discriminates between spodumene, its alteration mineralogy and silicate minerals of the matrix. The quantification of LIBS results using lithium-doped borosilicate glass as standards were limited due to issues with the sensitivity of matrix matching standards and the self-absorption effects at high Li_2O values. However, the emission line at 812.644 nm they selected for this study is not expected to

exhibit self-absorption compared to the strong lines usually considered. It should be noticed that the ablated mass was found to be lower for the glass samples than for pellets. In addition, the risk of possible loss of lithium during the melting process of the synthetic glass is present. Thus, different ablation rates and potential loss of lithium during melting could explain the poor predictive ability of the calibration model in this case. At least, the calibration model has been built from raw LIBS spectra without any normalization. This may explain the difference observed among the two matrices. However, the relative standard deviation (RSD) calculated on the emission intensity could have been provided to better approximate the variation on the standards. Despite these limited performances, the results of this study testify to the effectiveness of LIBS as a mapping tool for light elements, which may be used as a complement to other analytical techniques.

Rossi *et al.* [105] proposed a pioneering study using CF-LIBS (calibration-free LIBS) on gem-quality alexandrite, hiddenite and kunzite, elbaite and topaz minerals. Due to the presence of chromophore elements at minor levels and/or as traces, light lithophile elements (Li, Be and B) and differences in their crystal chemistry, these minerals were studied through a multi-methodological investigation based on EMPA-WDS, LA-ICP-MS, and CF-LIBS. For the first time in a real geological purpose, the authors demonstrated that the results from calibration-free LIBS were in a good line with EMPA, and LA-ICP-MS data for major elements such as Si, Al, Be and B. Very promising results were also obtained for chromophore elements such as Fe, Cr, V, and Mn. However, due to probable self-absorption of the emission lines of the lightest elements (namely Na and Li) the concentrations found by LIBS were not in good agreement with those found via other conventional analysis methods. Nevertheless, with this work, Rossi *et al.* [105] demonstrated that LIBS technique can be employed in mineralogical studies for the identification and characterization of minerals, and as a fast screening method to determine their chemical composition. Verlaquet *et al.* [106] have done a microstructural study and chemical LIBS profiles across host-rocks between successive cookeite veins (Li-Al-rich chlorite), in Alpine metabauxites that were preferentially transferred to veins at blueschist peak P-T conditions. The constant value of Li observed on the Li-profiles show that about half of the initial cookeite remains homogeneously distributed in host-rocks, which suggests a diffusion distance of 2-4

cm for this element. Lithium, which is a strategic element, was observed to preferentially migrate or segregate into veins during the metamorphic processes, which may be of importance for further Li-exploration purposes.

Shale and carbon, hydrogen, azote analyses

Current standard techniques for bitumen determination in oil sands ore suffer either from their time-consuming labor intensive method of sample preparations or from requiring a high number of samples to obtain a good calibration. LIBS application on shales for the detection of carbon, hydrogen and azote could be very promising for the industrial applications if the information for the presence of “bitumen” can be done directly on a drill core. This information may improve drastically the reactivity during the drilling project. Access to a surface imaging for C-H can also inform on the porosity of the rocks and then petrographic characteristics of the reservoir rocks. Thus, evaluation of bitumen content directly in oil sands feedstock is essential to control the extraction process and improve the recovery efficiency. Comparing to any other resources samples previously presented (solid rock without any water content), here the analysis of bitumen ore samples is very challenging due to the presence of several phases of wet or dry particles and heterogeneous mixture of clay, bitumen, water, and solid contents. Regarding to this complex topic, Harhira *et al.* [107] present a new enabling method using LIBS technique to determine rapidly and without sample preparation the bitumen content in oil sands ores. Using PCA and PLS methods on LIBS data for quantitative purpose, they assess bitumen content and its properties. They obtained a good correlation between LIBS spectra and bitumen content and a prediction averaged absolute error around 0.7 wt % is obtained. This statistical method demonstrates that LIBS is a real tool for rapidly assessing oil sands ore grades either in the lab, at-line, or online.

In 2018, after AGU Fall meeting (Washington), Jain *et al.* [98,97] proposed LIBS-based imaging for the analysis of hydrocarbon-bearing shale samples from the so-called Marcellus gas well [97]. The data collected from these experiments were used to construct 2D elemental maps including hydrocarbon-forming elements, such as C and H elements. Shale samples were analyzed by LIBS using an 81 × 81 grid pattern covering an 8 × 8 mm² area. Spatially resolved elemental composition

for H (0-0.7 wt%), C (0-13 wt%) and H/C are obtained reflecting the probable differences between the matrices of the samples and the depth of their sampling along the log. A larger number of reference standards would have much improved the validation of the univariate calibration curve for C and H estimates. In this study, only three points/standards were used and no RSD value was given for each of them, but these results are satisfying and intensity maps are very instructive for the geologists.

Fluorine detection using either elemental emission lines or molecular bands

Fluorine and chlorine in geological samples do not produce atomic and ionic emission lines of sufficient intensity to permit their detection by most of the conventional LIBS tools. However, these elements do combine with alkali-earths and other elements (Ca, Mg...) to form molecules whose related spectral features can easily be identified, enabling their detection in ambient conditions with much higher sensitivity than using the atomic lines. Nevertheless, using the 685.6 nm atomic emission line (F I), fluorine has also been identified and detected in rock with an LOD of 135 ppm on a millimetric chemical map [108], allowing the access to the best calibration method for quantifying the amount of fluorine in a set of prepared phosphate rock standards. However, this atomic emission line remains very weak. To lower the limit of detection, when some specific elements are present on the matrix (Ca, Mg...), LIBS analysts commonly use molecular bands of CaF, as reported on the Figure 9 . After previous works using luminescence, M. Gaft is one of the first researchers looking at Fluorine and REE (Rare Earth Elements) using LIBS technique but searching for the molecular bands of recombination elements on the plasma, after several microseconds [109,110]. This specific recombination has been noticed on Mars surface, on Martian soils for mineral identification by ChemCam and for some lab experiments during tests under simulated Martian atmospheric conditions [111–113], and recently for on line quantification of Fluorine during flotation processes [46]. Here, Foucaud *et al.* used MVR (minimum variance reduction) models to demonstrate that an accurate quantification of fluorine is possible using a calibrated portable LIBS instrument (Z300 SciAps®) on powder pellets, considering peak areas of the normalized CaF molecular bands. Calibration provides an on-line estimation of the separation processes efficiency and a possible real-time adaptation. This

fluorine quantification can be applied to the mineral processing field as in-situ quantification apparatus with the only one prerequisite of having a roughly constant particle size in the samples.

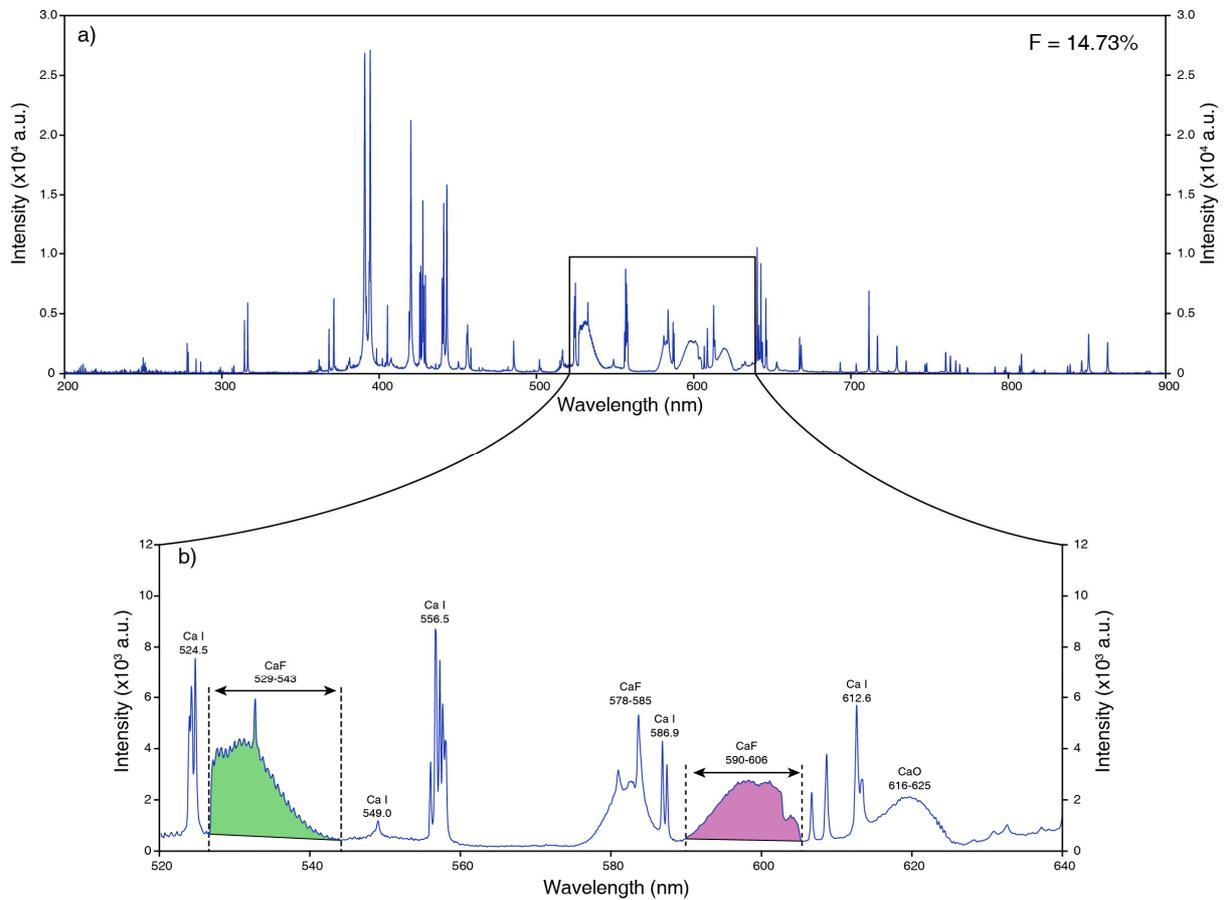


Figure 9 : LIBS spectra displaying ionic and molecular bands on pellets, from Foucaud et al. (2019) with permission.

d. Detection of Rare Earth Elements

European commission has classified rare earth elements (REE) as critical material due to high supply risk as well as economic importance [114]. Thus their detection in ores and their quantification are a serious issue. REEs have been divided into two groups, heavy rare earth elements (HREEs) and light rare earth elements (LREEs) with also scandium. Yttrium belongs to HREEs and its demand has been predicted to increase in the future, which could lead to possible shortage of supply in 2020. In geological environments, yttrium can be found in a lot of minerals in various concentrations, but currently it is mainly supplied by China. Searching for these elements is not an easy task for the geologist. Usually, their analysis is done via bulk analysis only (ICP OES) or using EMPA, as they

cannot be directly recognized by optical observation. These techniques generally take several days to weeks and a prior check for REE element presence, using LIBS analysis, is of first interest for a large range of metallogenists.

In 2011, Abedin *et al.* [115] collected some raw monazite sands from the beaches in southern Bangladesh. After the selection of the darkest grains, monazites, a number of lanthanides (Ce, La, Pr, Nd, Y, Yb, Ga, Dy, Er) have been simultaneously detected by LIBS in the sample previously pressed as pellets. Recently Bhatt *et al.* [116] used multivariate analysis (PLS-R) models for the quantification of Ce, La, and Nd in geological samples. Analysis of unknown samples indicated that the predicted contents of these samples were found comparable to those obtained by global ICP-MS analysis. Relevant emission spectra are provided in this study, with the selected emission lines, without any interference. The calibration curves undertaken for the REE elements also display figures of merit (slope, Offset, RMSE, R-square) allowing the readers to better evaluate the quality of the calibration. Those data support that LIBS has potential to quantify REEs in geological minerals/ores.

The powerfulness of the LIBS technique for the detection of REE has also been validated in a complete study for the geological formation of the Norra Kärr Alkaline Complex in southern Sweden [117] in an elemental mapping. Yttrium was detected as trace elements in eudialyte ($\text{Na}_{15}\text{Ca}_6(\text{Fe},\text{Mn})_3\text{Zr}_3\text{Si}(\text{Si}_{25}\text{O}_{73})(\text{O},\text{OH}\cdot\text{H}_2\text{O})_3(\text{OH},\text{Cl})_2$) and catapleiite ($\text{Ca}/\text{Na}_2\text{ZrSi}_3\text{O}_9\cdot 2\text{H}_2\text{O}$) minerals. Singular value decomposition (SVD) was used for the classification of the mineral rock samples based on their mineralogy. Based on the SVD classification, the percentage of yttrium-bearing ore minerals was calculated for the fine-grained rock samples. Following this very exciting first study, Romppanen *et al.* [118] combined time-gated Raman and LIBS study on the same kind of REE-bearing rock. The combination of these two complementary laser-based spectroscopic methods offers valuable elemental and mineralogical information.

On the same kind of geological samples, Chirinos *et al.* [103] published a nice paper on a 3D geological imaging involving REE. The authors presented 2D layer-by-layer mapping, 2D cross-sectional imaging and 3D volume rendering of elements and isotopes in a Bastnäsite matrix. This rock is a rare earth ore sample due to its heterogeneity and wide elementary content including most of the

lanthanides and some actinides. Even if LIBS is an inherently faster technique than LA-ICP-MS, the acquisitions of the signals were synchronously done over the same location and for the same plasma. However, chemical LIBS mapping was only done for the most conventional elements (Al, Ca, Si) as they were poorly determined using LA-ICP-MS.

In a metallogenetic exploration from hydrothermal ore deposit involving five different mineral phases (sulfurs as galena, sphalerite or chalcopyrite, quartz and ankerite as carbonate phase) Fabre *et al.* [100] detected and imaged unexpected rare earth elements (La and Y) in carbonate phases. They also detected unexpected substituents present at the ppm-scale level in various mineral phases, such as cadmium in sphalerite, bismuth, silver and antimony in galena, beryllium and aluminum in quartz and tin in chalcopyrite. Due to potential emission lines interference and matrix effect, the different detection limits observed here are thus drastically dependent of the mineral phases. This parameter underlines the not-easy way to interpret hyperspectral imaging and to do quantitative maps from elemental imaging, as the efficiency of the element emission is directly related to the matrix bearing the measured element. Using the same set up developed in [95], the last study of Gaft *et al.* [119] presents mega-pixel imaging of rare earth elements (REEs) obtained by combining molecular emission (LaO and YO), atomic LIBS analyses, and plasma-induced luminescence (PIL) using an unique set up on the same plasma source. Thus, both molecular emission and PIL are characterized by a long plasma lifetime, from tens to hundreds of microseconds, when nearly all interfered emissions do not practically exist. As result, imaging of REEs becomes more sensitive.

In the previous sections, I have pointed out that LIBS gives access to the most relevant elements in geosciences/geology. The typical detection limits that have been reported are in perfect agreement with most of the requirements, with the advantage of permitting faster analyses than the other techniques classically exploited. Whether considering the case of metals of economic interest such as gold or silver, that of critical elements such as rare earths, or that of light elements such as lithium or fluorine, LIBS has demonstrated satisfying. Let's just use it routinely and get advantages of its performance to push further both the research and industrial projects in geosciences.

6. Perspectives and conclusion

According to all of these publications, we can conclude that LIBS is now a well-known technique for geologists due to its main advantages in the field: fast decision making, preventing processing gangue, enabling reduction of dilution by upgrading ore, reducing analysis delay and cost, fast screening sampling, discrimination and sourcing of rocks or minerals. One issue that may remain in resources studies is the rapid comparison between the LIBS analyses done on the sample surface (as a small series of single points or micro cartography) and any other bulk analysis obtained on a larger portion of the same sample. Conducting a geological study, we should be aware that if a “homogeneous” sample cannot be achieved, then we should consider this sample as different geological parts in a more global sampling. For geological study, the relationship between the location of the laser spot and the mineral/rock association is the most critical stage before any good interpretation. The acquisition of an image of the laser spot related to any analysis is always relevant to answer the following question: “Is it a mixing between several minerals or a homogeneous phase?”

Anyway, if all technical parameters are well fixed and all the steps of the LIBS analysis are right followed, the figures of merit validated and compared, then a good analysis protocol makes LIBS a reference analysis for geological purpose. For the classification purposes, if the loadings and the scores of a PCA are well provided to validate the sample identification then LIBS enables good classification of rocks and minerals and even the determination of their extraction mine. The most recent papers published on LIBS mappings (2D visualization) underline that a fast discrimination or a qualitative screening need to increase the number of sampling points and then to work using high to very high frequencies for the laser and the spectra recordings. Thus, more than a simple identification or quantification of elements in punctual analysis, LIBS mapping now provides important information about the elemental distribution in samples through thousands to millions of LIBS spectra, permitting the characterization of heterogeneous mineral phases or the detection of major to trace elements down to the ppm level. For economic targets, variations in the elemental compositions or in pertinent element ratios such as substitution of elements in specific phases have also been investigated. Thus, concerning the industrial megapixel LIBS imaging for the geological characterization of minerals,

most of these publications appear extremely promising for the geological domain and should pave the way for innumerable LIBS applications.

Here, it is important to add a comment on the general processing of data, both for spectrum analysis and for processing large amounts of data generated in the case of imaging or sourcing. Publications rarely report the software or at least algorithm used for the treatment of the LIBS spectra. This first part of the study which can be time consuming due to the high number of emission lines, their identification and their treatment can be made by two different softwares, one for the detection/identification and one for the quantification/signal treatment. Nevertheless, the multivariate analyses are commonly done using software such as R or OsiRis, but we can report for these geological purposes the use of PYMCA®, SpectraGryph®, or some specific development like the software Quantagenetics®. Indeed, we can underline the necessity to obtain reliable results from user-friendly software. Commercial ones, provided with the detector, are usually developed for the acquisition of the signal and not allow to accomplish expert spectral treatment, and large part of the LIBS instruments can be considered as 'home made' ones.

Obviously, the portable LIBS instruments are now of first importance and it can be an essential part of the geologist toolkit. But geologists should use them properly and the manufacturers should produce instruments that can be internally calibrated to provide results that can be shared and understood on a high scientific level. We can encourage teachers in universities to develop specific LIBS classes for the future young researchers/user as for any other classical analytical techniques, for plasma applications, laser/matter interactions, or field applications... The teaching thematic seems to be an essential point for the scientific acceptance of LIBS and its future development in more laboratories academic and industrial. For example, EUROCORE (European Core) Sample Collection is a Master Training project, between France (Lorraine University and CREGU), Fraunhofer-Gesellschaft, Geological Survey of Finland, Tallinn University of Technology and the Technical University of Madrid. It is funded by EIT Raw Materials to assist the mining industry in the formation of students and mining company personnel on the use of innovative in situ technologies for exploration (LIBS, Raman, XRF and IR handheld tools). Considering handheld LIBS as any other techniques dedicated to

mineral characterization is the way that should be now taken. As economic activities increase the last years, number of junior companies will require portable spectroscopic tools and the LIBS technique can be an essential tool for the detection of minor and trace in rock or drill cores or drill tailings.

Thus, one can say that now all-field LIBS applications can be done in any place, for dangerous rocks or liquids, and now some new horizons have even been opened for the underwater analysis for resources of future hydrothermal resources [120]. Thus, due to the potential of alkaline quantification on small minerals, the last ten years a new approach of LIBS applications have been developed to investigate the feasibility of in-situ K-Ar dating [121–125], for the estimates of K amount, as the ^{40}Ar is obtained through a mass spectrometer. In this thematic of extreme conditions, we can underline the proposals for future spatial missions involving LIBS apparatus [121,126,127].

Finally, considering that LIBS measurements only require very little sample pre-treatment, meaning no metallization, no vacuuming and no addition of hazardous substances as acid, or gas, and considering also that LIBS is a fast all-optical multi-elemental technique, easy to set up even out of the laboratory, it is undoubtedly the ideal technique to achieve a first quick screening and then provide valuable data (smart sampling) prior to further laboratory analyses when needed. Moreover, the recent development of LIBS imaging should drive very soon to the implementation of LIBS imaging systems in the analytical laboratories worldwide in charge of analyzing geological samples, as it is already the case in the field of biomedical applications. Indeed, based on the very first articles illustrating the interest of LIBS imaging in geosciences, there is no doubt that LIBS imaging will be the source of major future advances in geosciences.

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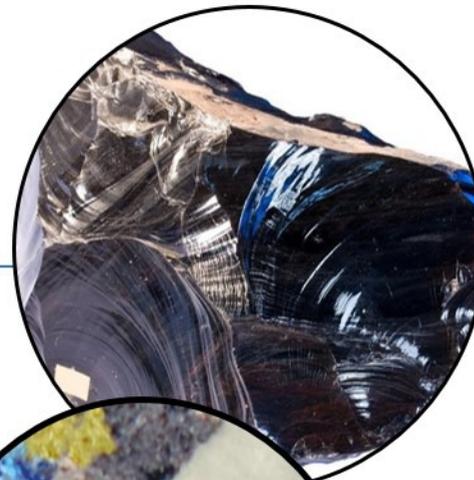
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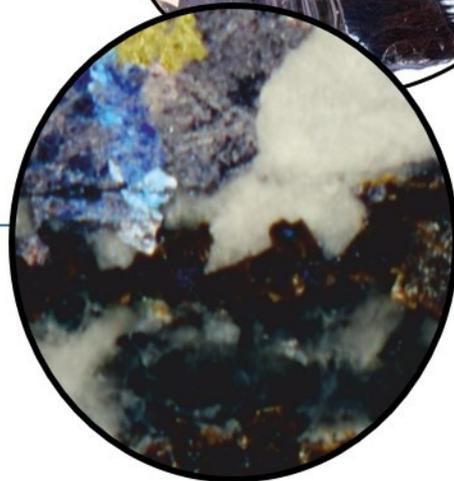
Atomic Number →	1	← Symbol
Name →	H	← Atomic Weight
	Hydrogen	1.008

5	6	7
B	C	N
Boron 10.81	Carbon 12.011	Nitrogen 14.007
13	14	15
Al	Si	P
Aluminium 26.9815385	Silicon 28.085	Phosphorus 30.973761998

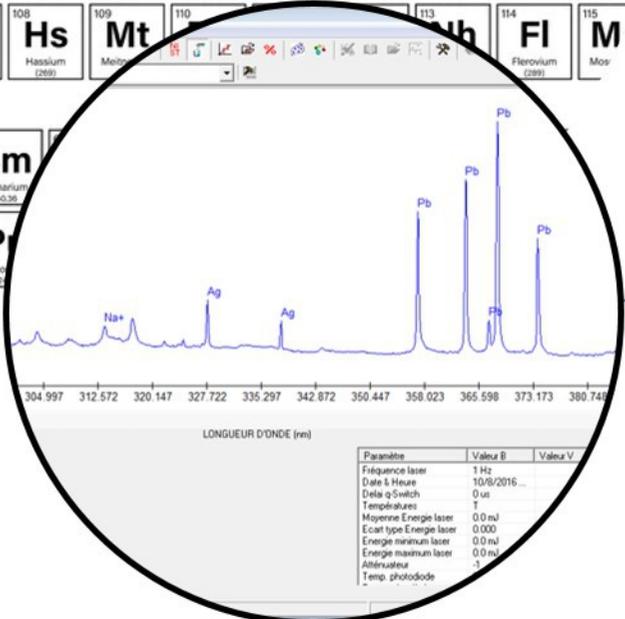
22	23	24	25	26	27	28	29	30	31	32	33
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
Titanium 47.867	Vanadium 50.9415	Chromium 51.9961	Manganese 54.938044	Iron 55.845	Cobalt 58.933194	Nickel 58.6934	Copper 63.546	Zinc 65.38	Gallium 69.723	Germanium 72.630	Arsenic 74.921595
40	41	42	43	44	45	46	47	48	49	50	51
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
Zirconium 91.224	Niobium 92.90637	Molybdenum 95.95	Technetium (98)	Ruthenium 101.07	Rhodium 102.90550	Palladium 106.42	Silver 107.8682	Cadmium 112.414	Indium 114.818	Tin 118.710	Antimony 121.760
72	73	74	75	76	77	78	79	80	81	82	83
Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi
Hafnium 178.49	Tantalum 180.94788	Tungsten 183.84	Rhenium 186.207	Osmium 190.23	Iridium 192.227	Platinum 195.084	Gold 196.966569	Mercury 200.592	Thallium 204.38	Lead 207.2	Bismuth 208.98040
105	106	107	108	109	110	111	112	113	114	115	
Rf	Db	Sg	Bh	Hs	Mt	Nh	Fl	M			
Rutherfordium (261)	Dubnium (268)	Seaborgium (269)	Bohrium (270)	Hassium (269)	Moscovium (288)	Nihonium (286)	Flerovium (289)	Moscovium (288)			



Rock sourcing



Mineral identification



....using LIBS analysis