LIBS core imaging at kHz speed: Paving the way for real-time geochemical applications

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A B S T R A C T

This paper demonstrates the new capabilities of laser-induced breakdown spectroscopy (LIBS) to perform fast high-resolution multi-elemental mappings of geological samples. A rock sample with a 5-mm surface roughness and one with a plane surface were laser scanned at a repetition rate of 1 kHz with a spatial resolution of 50 μm, using the Mission: Coriosity platform from ELEMISSION Inc. The elemental mappings of the few cm^2 surfaces for 6 elements were obtained, revealing high levels of detail and complexity in the element distribution. In addition, the distributions of 9 elements along linear segments on the rock surfaces reveal correlations between the elements which allow inferring the mineralogical content of the samples. The platform provides a novel approach for fast simultaneous mapping of several elements as it can acquire and process 1000 spectra per second, which was not technically possible with traditional LIBS instrumentation. In addition, the platform is coupled with advanced graphical algorithms allowing the direct visualization of the distribution of several elements on the same image.

1. Introduction

According to the Canadian Council on Mining Innovation and the Mining Association of Canada, characterization, and analysis of an orebody in real-time and on-site during exploration and different mining production stages would be a major breakthrough in term of modernization of this sector [1]. Such a disruptive technology would bring significant exploration and production cost reductions. Some technologies, allowing almost real-time analysis on solid samples, have already been evaluated for the characterization and the analysis of an orebody. These are near-infrared spectroscopy (NIR), X-ray diffraction (XRD), X-ray fluorescence (XRF), energy dispersive X-ray (EDX), back-scattered electron (BSE) and hyperspectral imaging. All these techniques allow identification by surface mapping of the ore and, except for XRF, quantification of its mineralogy directly or indirectly. These technologies present, however, some limitations regarding spectral range, spectral selectivity, and surface quality requirements (such as roughness, and the presence of dust and water, which can affect the absorbance of the sample). They also cannot provide information on the elemental composition. On the other hand, XRF, which provides elemental analysis, has already been used successfully for the quantitation of some basic metals such as Cu, Zn, and Ni. This technique is, however, weakly sensitive to light elements (Z < 13). Besides, hyperspectral cameras, which are starting to be used for the identification of mineralogy, work for clay minerals and some other mineral groups depending on the bandwidth (VNIR, SWIR and LWIR). This technology is,

however, not well documented yet for carbonate, oxides, sulphides and native elements such as gold, silver and graphite [2].

Laser-induced breakdown spectroscopy (LIBS) appears to be a disruptive technology candidate for elemental analysis and imaging in real-time and under the harsh conditions of the mining environment. In addition, it requires low maintenance: for instance, the LIBS ChemCam system of the rover Curiosity runs without any maintenance under the extreme conditions of the planet Mars for the last five years. LIBS is an atomic emission spectroscopy (AES) technique, which consists of using a pulsed laser to create a micro-plasma onto a solid, liquid or vapor sample. When the laser fluence (energy per unit surface) exceeds the material's threshold, it vaporizes and atomizes a small area on the material surface to generate luminous plasma. The light emitted from the plasma is then collected and spectrally analyzed to determine the elemental chemical composition of the sample. The main advantage of LIBS over conventional analytical techniques is its capability to provide real-time analysis with minimal or no sample preparation, and under ambient atmosphere.

LIBS has already been applied to the analysis of ore samples. Some of these works focused on quantitative analysis of minor and major elements in the ore, some sought the identification and classification of the ore to distinguish valuable minerals from gangues, and others dealt with elemental imaging of the ore. Harmon et al. reviewed most of LIBS publications related to geochemical in environmental analysis till 2013 [3]. In 2010, Motto-Ros et al. obtained mappings of minor and trace elements in speleothem samples [4]. In that study, the scanning speed
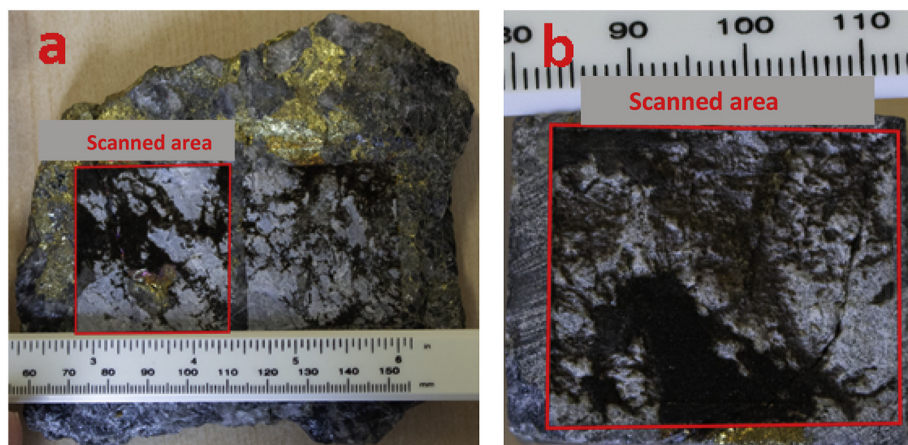
Fig. 1. Images of the two rocks samples, analyzed in this work. The LIBS-scanned zones are contained in the red perimeters representing areas of 40×40 mm^2 (a) and 30×25 mm^2 (b). The yellow areas in (a) is identified as pyrite (FeS_2). The eroded areas in both pictures are due to the laser scans. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of 1 Hz was limited by the readout of the detector. Later, the same group significantly improved the spatial resolution from 100 μm to 10 μm and the scanning speed from 1 Hz to 100 Hz [5]. On their side, Haavisto et al. reported the use of UV laser to analyze a drill core with a coarse scanning resolution of 1 mm and a moderate scanning speed of about 3 cm/min [6]. Furthermore, McMillan et al. report the chemical contour map of copper ore sample using LIBS [7]. Besides, Khajehzadeh et al. used a UV laser with a repetition rate of 20 Hz to identify different minerals [8]. In addition, Kahn et al. generated a LIBS chemical map of a drill core and compared it with the one obtained using energy dispersive X-ray fluorescence (EDXRF, ITRAX) [9]. The elemental mapping was performed using a prototype LIBS core scanner. Again, a modest acquisition speed of 20 Hz has been reported. Recently, Rifai et al. performed mappings of the gold content on the surface of drill cores, with a spatial resolution of 600 μm and scanning speed of 2 Hz [10].

In all the works cited above, LIBS elemental composition mappings were done at a spatial resolution from 15 to 1000 μm and at low to moderate scanning speed (1–100 Hz). It is, however, important to realize that, when it comes to analyzing large surfaces of drill cores, one should perform the scan as fast as possible for productivity reasons. For this purpose, Noll et al. reported for the first-time elemental mappings at 1000 Hz, using a Paschen-Runge LIBS spectrometer for inclusions detection in steel [11].

In this paper, LIBS elemental mappings of rock samples using Mission: Coriosity platform, commercialized by ELEMISSION inc. (Montreal, Canada), is reported [12]. The Mission: Coriosity platform presents cutting-edge features for the characterization of drill cores and other geological samples in term of scanning speed (up to 1000 Hz), spatial resolution (down to 50 μm) and elemental selectivity. In addition, the platform is coupled with novel software enabling the representation of the distribution of several elements at the same time on the sample surface. The unique capabilities of the platform are demonstrated in the case of two rock samples containing complex mineralogies.

2. Materials and methods

2.1. Mission curiosity benchtop

The Mission: Coriosity benchtop is fully automated from autofocus to mapping measurements. It integrates electronics, the laser source, the spectrometer and the ablation chamber in a single box. For this study, we used a 1064 nm laser source which can deliver up to 500 μJ/pulse at 1 kHz repetition rate. The standard focusing optics can deliver at target a laser spot size diameter of 50 μm. The focusing optics produces a Rayleigh zone of 5 mm (depth-of-field) to accommodate rock surface roughness. Resolution can be lowered to 100 μm as required or even more if speed of analysis is the priority. The plasma light was

collected by means of standard achromatic lenses (to ensure minimum chromatic shift over the full spectrum) and then sent by a 1-mm diameter optical fiber, to a spectrometer which covers wavelengths in the range 250–480 nm. The spectrometer was equipped with a simple cMOS (2048 px) controlled by custom-made electronics. The readout rate of the detector was 1 KHz. The optical window covers the emission lines of a large number of elements, but the system accommodates another spectrometer that can cover the range 620–950 nm. The ablation chamber can host samples up to 200×100 mm^2. The hole instrument is described in details elsewhere [13]. A line scanner (Gogater LMI Technology Inc., model 2340A-3R-01) was used to determine the roughness of the rock surface to be analyzed. The working distance between the optical window and the surface of the sample was about 150 mm. The platform was also equipped with an autofocusing system to ensure the sample positioning at the focal plane within < 30 μm.

Coupled to this instrument, the home-developed software ELEDIT allows depicting the distribution of up to 6 elements simultaneously on the same map, with distinct colors on the surface of the analyzed sample. ELEDIT provides also the possibility to divide each pixel into $n^2 = 4, 9, 16 \ldots$ subpixels whose colors are assigned to those of the elements investigated according to their estimated concentration in the pixel. Consequently, the proportion of subpixels having the same color with respect to n^2 subpixels reflects the relative abundance of the corresponding element in the pixel. ELEDIT first normalizes the intensity A_{ij} of the spectral line of the element j in the pixel i by dividing it by the largest value found among all i for a given j. Then ELEDIT assigns the number of subpixels as $m_{ij} = [n^2 \, a_{ij}/\Sigma_k \, a_{ik}]$, where a_{ij} is the normalized intensity ($0 \le a_{ij} \le 1$) and the brackets denote a near integer. A simple procedure is implemented to make sure that $\Sigma_j \, m_{ij} = n^2$. The software also allows enhancing the visibility of minor or trace elements on the map by multiplying their corresponding a_{ij} by some factor > 1 for all pixels i. In addition, ELEDIT represents each color with a level of saturation proportional to a_{ij}, thus providing information on the relative abundance of the element i over the map.

3. Ore samples

Two rocks samples provided by the Westwood gold mine (Val d'Or, Canada) were analyzed in this study. Their pictures are shown in Fig. 1. The rock shown in Fig. 1a was kept as is, without any preparation, while the one shown in Fig. 1b was cut into a parallelepiped form, using a diamond blade saw, to obtain 6 plane surfaces.

4. Results and discussion

Many chemical elements and mineralogies have been identified on the surface of both rock samples, including gold particles on the sample of Fig. 1b. Fig. 2 shows two spectra: the red one was obtained on a