Short communication

Laser-induced breakdown spectroscopy of silicate, vanadate and sulfide rocks

J.M. Vadillo, J.J. Laserna*

Department of Analytical Chemistry, Faculty of Sciences, University of Malaga, 29071-Malaga, Spain

Received 14 March 1995; revised 26 September 1995; revised 30 November 1995; accepted 4 December 1995

Abstract

Laser-induced breakdown spectroscopy (LIBS) in air at atmospheric pressure has been used to study four geological samples belonging to different structural families. Atomic emission spectra of vanadinite, pyrite, garnet and a type of quartz (compostela’s quartz) are shown. The 532 nm line of a Nd:YAG laser at an irradiance of $18 \times 10^{11}$ W cm$^{-2}$ was used. The precise focus of the beam allowed microanalysis of a 0.02 mm$^2$ surface area working in single-laser shot mode. The use of an intensified gateable charge-coupled-device (CCD) detector permitted time-resolved studies. The spectral lines have been assigned to transitions in the neutral charge state of the corresponding atom of the material under investigation. The behavior of different transitions with time delay are shown. In experiments, minor components contained in several minerals have been detected. This fact has been used to demonstrate the applicability of the technique to characterize and identify similar minerals.

Keywords: Geochemical analysis; Laser-induced breakdown spectroscopy; Laser-induced plasmas; LIBS

1. Introduction

The effect of a short pulse of laser radiation focused on a sample produces an irradiance sufficient to vaporize a small spot of a solid on the surface, resulting in a high-temperature and electron-density plasma that can be spectrally analyzed by optical emission spectroscopy. This technique is called laser-induced breakdown spectroscopy (LIBS) [1].

The physics of laser/surface interaction is a well-known process. The surface reflects some of the energy and the remaining part is absorbed by the surface. Due to the short laser pulse duration, there is not enough time for thermal diffusion into the surface material outside the focal spot. This fact explains the quick heating of the surface, resulting in a rapid vaporization. The vapor moves outward from the surface and by a multiphoton absorption process; some of the material is ionized creating an appreciable ionic population. When a sufficient density of ions and electrons is created, an inverse Bremstrahlung process
causes the incident laser light to be absorbed minimizing the laser light reaching the sample surface. The electrons are heated causing an increase in temperature, and rapid energy transfer and electron–ion collisions which result in neutral species. Subsequent spectral analysis has been successfully used for elemental analysis in solids [2], gases [3], liquids [4] and aerosols [5]. Applications of LIBS for the analysis of solids include the detection of contaminants on electronic microcircuits [6], on-line process control [7] and analysis of noble and alloyed jewelry metals [8]. The advantages of improving the technique by working under high vacuum have been also described [9].

LIBS allows direct analysis of a wide range of solids, including minerals and rocks and shows great capabilities to perform routinely non-destructive identification of microscopic inclusions in their material hosts [10]. The simple requirements in sample-preparing-and-handling provide several advantages with respect to other widely used techniques including electron and ion microprobes [11]. LIBS can be used to identify, map out the distribution and determine the quantity of elemental constituents of the sample. The main advantage is the possibility of simultaneous multi-element analysis over a wide spectral range without pre-treatment or transport of the sample to the excitation source (inductively coupled plasma atomic emission spectrometry (ICP-AES)). Although the coupling of laser ablation to ICP-AES or ICP-MS (inductively coupled plasma mass spectrometry) systems is becoming a powerful tool in geochemical analysis, it can be said that LIBS is the right choice when the number of elements to be found is large or the composition of the sample is unknown [12].

The high performance of charge-coupled-device (CCD) detectors in terms of spectral range, quantum efficiency, integration time and gating, allows resolution of the complex spectra of geological samples better than using scanning spectrometers with photomultipliers tubes detectors [13]. Furthermore, because of the two-dimensional character of the CCD detector, spatial and spectral information can be achieved simultaneously. When combined with intensifier devices, extremely low light levels can be recorded without increasing acquisition times.

In this paper, time-resolved LIBS is used to obtain the spectra of minerals from different families including sulfides, vanadates and silicates. No sample preparation is required. In addition, time-resolved LIBS is used to improve the signal-to-noise ratio (SNR) as well as to reduce the Stark effect and continuum background often found in LIBS spectra. Examples are shown to demonstrate the capability to conduct geological taxonomy and to analyze a field sample.

2. Experimental

2.1. Apparatus

The experimental setup for time-resolved LIBS is shown schematically in Fig. 1. The second harmonic of a pulsed Nd:YAG laser (λ = 532 nm, pulse width 5 ns, 170 mJ pulse⁻¹, Continuum, Surelite SLI-20) was used to irradiate the samples. The beam was focused at normal incidence onto the sample surface with a glass planoconvex lens with a focal length of 100 mm and f-number of 4. The spot area was 0.012 mm², which resulted in an irradiance of 18 × 10¹¹ W cm⁻².

A 1:1 image of the plasma was focused using a planoconvex quartz lens with focal length of 100

Fig. 1. Schematic setup used in this paper. LH, laser head; CPU, cooling power unit; HG, second harmonic generator; BS, beam splitter; Phd, trigger photodiode; Sp, spectrograph; C, CCD detector; LS, linear stage; S, sample; PC, personal computer; M, monitor; Pr, printer; Lens #1, glass lens; Lens #2, quartz lens.
Fig. 2. Variation of peak intensity as a function of time delay. Sample: vanadinite; wavelength: 291 nm; gate width: 100 ns; laser energy: 170 mJ; MCP gain: 700 V.

mm and f-number of 4 into the entrance slit of a 0.5 m focal-length Czerny–Turner spectrograph (Chromex, 500 IS). Light was dispersed using a 2400 grooves mm⁻¹ holographic grating (250 nm blaze). The entrance slit width was 10 200 μm, and the height was 10 mm. The spectrograph was computer controlled using specific software (Chromex Host Control Software 2.21).

The dispersed plasma light is detected using a solid-state two-dimensional CCD (Stanford Computer Optics, 4 Quik 05). The CCD consists of 752(h) × 582(v) elements. The photoactive area is 6 × 4.5 mm². The device is equipped with an S 20 Q photocathode (spectral response from 180 to 820 nm) and an intensifier system (microchannel plate, MCP). The intensifier system allows a high photonic gain, better than 10⁸ electrons/photon. Extremely high system responses are achieved (50–500 000 ASA) with a 12 bit dynamic range. Operation of the detector was controlled by 4 Spec 1.20 Software. Shutter and delay times can be selected in 50 ns steps. A fast photodiode was used as the external trigger for exact synchroniza-

tion of the incident laser pulse and opening of the camera shutter.

The experimental conditions were optimized in order to obtain the best SNR. A gate width of 100 ns was used in all experiments, while the time delay was varied when required. The MCP gain was fixed in 700 V when single-shot experiments were run. When different shots were accumulated in order to improve the SNR, the gain was reduced.

Video image capture, processing and display were made using a PC-compatible monochrome frame grabber (Data Translation, DT2855). As images are captured, they can be displayed with 768 × 512 square pixels resolution and 256 gray levels. This number of pixels and gray levels produced a high-definition display with continuous tones to match real images. Later on, they can be output for real-time images processing and pseudo-color display into a VESA-ISA Local Bus PC specially equipped for fast capture and processing images.
2.2. Samples

Samples were directly taken from the field and analyzed without other treatment than washing the surface with deionized water to remove dust and mud. Four mineral species were analyzed: garnet, vanadinite, compostela’s quartz and pyrite. Details on chemical structures and atomic cells implants will be discussed in the results and discussion section.

Table 1
Designations of peaks labeled in Fig. 4. All signals correspond to \( \text{Fe}^{3+} \) transitions.

<table>
<thead>
<tr>
<th>Line</th>
<th>Wavelength (nm)</th>
<th>Upper energy level (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>370.9</td>
<td>34329</td>
</tr>
<tr>
<td>B</td>
<td>372.0</td>
<td>26875</td>
</tr>
<tr>
<td>C</td>
<td>372.7</td>
<td>34547</td>
</tr>
<tr>
<td>D</td>
<td>373.5</td>
<td>33695</td>
</tr>
<tr>
<td>E</td>
<td>374.9</td>
<td>34040</td>
</tr>
<tr>
<td>F</td>
<td>375.8</td>
<td>34329</td>
</tr>
<tr>
<td>G</td>
<td>376.4</td>
<td>34547</td>
</tr>
<tr>
<td>H</td>
<td>381.6</td>
<td>38175</td>
</tr>
<tr>
<td>I</td>
<td>382.0</td>
<td>33096</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Time-resolved analysis

Spectral analysis of geological samples obtained using LIBS involves complex spectra in the presence of a noisy background with many overlapped peaks due to band broadening (Stark effect). Spectral lines corresponding to high populated energy levels are the result of the elevated plasma temperature. Spectra can be drastically simplified and the SNR greatly improved by delaying observation of the plasma. Time-resolved LIBS is useful since three benefits are achieved. First, there is a considerable decrease of the continuum emission due to Bremstrahlung radiation occurring immediately after plasma formation. Second, it is possible to avoid spectral interferences between species that emit at different times during plasma decay allowing characterization of different species. Third, spectral resolution improves because the Stark effect contribution is minimized.

The temporal behavior of different atomic species of the plasma is illustrated in Fig. 2. As
shown, the 279.5 nm transition corresponding to Mn$^{3+}$ shows a different temporal behavior reaching its maximum intensity at 50 ns of delay while the rest of the lines decay immediately after plasma formation.

### 3.2. Spectral Analysis

Fig. 3 shows a pyrite (FeS$_2$) emission spectrum. The selected window does not allow the observation of sulfur lines and only Fe$^{2+}$ lines are plotted. Although the laser is a powerful mean of inducing plasmas and it is able to produce ionization states as high as other continuum plasma sources (ICP, microwave-induced plasma and other), these are often not visible. The explanation must be found in the pulsed nature of the laser-induced plasma that determines many secondary processes of recombination (with oxygen mainly involved). These processes reduce the lifetime of many ionic lines in the spectrum and can be minimized working under vacuum conditions. Table 1 summarizes the results and spectroscopical parameters of the most relevant lines [14].

In order to show the applicability of the method in the determination of mineral species, LIBS spectra of Compostela’s quartz and garnet were obtained. Fig. 4 shows line emission of quartz (top) and garnet (bottom). Both minerals contain the same silicate matrix with differences due to their three-dimensional structure. Garnet involves a large group of nesosilicates with many isostructural minerals. The general formula is $\text{A}_n\text{B}_3\text{SiO}_{3n}$, where $\text{A}$ refers to large divalent cations, mainly Mg$^{2+}$, Fe$^{2+}$ and Mn$^{2+}$, and B alludes to trivalent cations a few smaller in size, Al$^{3+}$, Fe$^{3+}$ and Cr$^{3+}$. On the other hand, compostela’s quartz is a very typical quartz variety from northern Spain, characterized by a light-red color due to iron insertions. Cr$^{3+}$, Mn$^{2+}$ and Mg$^{2+}$ can also be found [15]. Large similarities in spectral behavior of both samples are expected and only the analysis of insertions in the atomic cell can be fruitful to discriminate the samples. As Fe, Cr, Mn and Mg insertions can be found in both garnet and quartz, the presence of Al emission lines in the garnet spectrum provides information required to discriminate the minerals. For this purpose, experimental data were obtained by accumulating ten shots in order to avoid surface interferences and to improve the SNR. Fig. 4 shows lines corresponding to Fe$^{2+}$, Mn$^{2+}$, Mg$^{2+}$ and Si$^{4+}$ in both garnet and quartz as expected. However, a detailed comparison reveals an aluminum line at 281.8 nm in garnet, which is not found in the LIBS spectrum of compostela’s quartz.

### 4. Conclusions

In the present paper, the laser-induced plasma emission phenomenon described can be used to detect and identify atomic constituents on the
surface of inorganic minerals. Analysis can be performed quickly in air at atmospheric pressure with a comparatively simple experimental setup. Furthermore, the laser plasma light is collected and directed to the detection system using a lens or a fiber optic cable which allows direct field measurements from samples located in difficult sites.

Enhancement of spectral lines with respect to the plasma continuum has been achieved by time-resolved spectroscopy. The quick decay of continuum emission in the first 100 ns suggests that laser-induced plasma emission of neutrals is the dominant process. The development of similar experiments under vacuum conditions would be useful to enhance the lifetimes of the ionic lines. The applicability of the method has been illustrated in the characterization of two very similar mineral species. In a second study, quantitative results will be reported.

Acknowledgements

The authors would like to thank I. Vadillo (Dept. of Geology, Faculty of Sciences, University of Málaga) for obtaining the samples and for advice.

References