Self-absorbed Ca doublet lines for stand-off quantitative analysis by laser induced breakdown spectroscopy

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Abstract. Laser induced breakdown spectroscopy (LIBS) is one of the promising techniques for stand-off detection of element composition. However, it is somewhat limited by quantitative shortage. Absolute line intensity may be influenced by acquisition conditions, environmental variation, and sample surface conditions. Relative intensity may also fluctuate greatly. This study shows that the intensity ratio between Ca II doublet emission lines (393.37 nm and 396.85 nm) is stable, and changes with Ca concentration (or Ca atoms count within the laser spot). This is due to differences in self-absorption between the two transitions. A theoretical calibration shows a linear section for low species density and quadratic section for high species density. Experimental results confirm the linear section after density correction of CaO pellets. However, an equipment factor should be considered for numerical calibration in different laboratories. For Ca-containing samples, quantitative analysis could be based on the detected Ca spectrum. Ca is also shown to be suitable as an internal standard reference to determine other elemental concentration, such as Mg.

1. Introduction
Laser induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy that uses a high energy laser pulse as the excitation source. Elemental concentrations correspond to the intensity of particular emission lines, which allows quantitative analysis [1].

Stand-off LIBS techniques have developed rapidly in recent years, such as ChemCam on Mars Rover Curiosity [2], detection of historic buildings [3], and monitoring of pollutants on wind turbine surfaces [4]. However, stand-off LIBS signals can be somewhat unstable. Emission line intensity may be affected by various factors, such as dust, water, and voids on the sample surface [3], as well as the angle between the sample plane and excitation beam. In such cases, stand-off LIBS quantitative algorithms are usually based on relative absorption line intensities: 1) between significant lines belonging to different elements [3]; or 2) multivariate analysis based on selected intense emission line intensities of various elements [2, 5]. However, relative line intensity of different elements, even of the same element, also fluctuates, which weakens the persuasiveness of these algorithms.

This study shows a self-absorption relation in calcium doublet emission lines and applies this to quantitative stand-off LIBS measurements. Calcium concentration corresponded solely to the LIBS line intensity ratio regardless of matrix complex. The proposed approach could be applied successfully for
remote elemental detection of carbonate cliff rocks, small reefs, and karst caves [6] that are of great interest for geologists for paleoclimate research.

2. Theoretical calibration

The proposed model assumes the plasma has LTE and is spatially homogeneous. The emission intensity (erg s$^{-1}$ cm$^{-3}$) along the line profile corresponding to the transition between two atomic or ionic levels j and i (upper and lower, respectively) is [7]

$$I(\lambda) = \frac{8\pi\hbar c^2}{\lambda_0^5} \frac{n_j}{n_i} \frac{g_i}{g_j} \left(1 - e^{-k(\lambda)l}\right)$$

(1)

where $\hbar$ is Planck’s constant (erg s); $c$ is the speed of light (cm s$^{-1}$); $\lambda_0$ is the central wavelength (cm) of the transition; $n_j$, $n_i$, $g_j$ and $g_i$ are the number densities (cm$^{-3}$) and degeneracies of the upper and lower levels, respectively; $k(\lambda)$ is the absorption coefficient (cm$^{-1}$); and $l$ is the absorption path length (cm).

The occurrence of self-absorption can be checked through the intensity ratio of a pair of lines belonging to the same multiplet [6]. The ratio is expected to adhere to L-S coupling (where L is total orbital angular momentum; S is total spin angular momentum), and reduction of observed line intensity of the strongest line in the multiplet relative to the weaker indicates the presence of self-absorption [6]. Measuring the intensity ratio does not require additional equipment, and interpretation of the spectra is quite simple. In the case of good signal to noise ratio only a single recording of spectral lines is required (lines within a multiplet are, in most cases, spectrally close enough to record all, or at least two lines within multiplet, with a single ICCD exposure), and this is a great advantage for the study of plasmas with short lifetimes [7]. The width ratio of multiplet lines have also been shown to correspond to element concentration, due to broadening of the multiplet.

For an optically thin plasma, the emission intensity (erg s$^{-1}$ cm$^{-3}$) of $\lambda_0$ can be expressed as

$$I_0(\lambda_0) \approx \frac{8\pi\hbar c^2}{\lambda_0^5} \frac{n_j}{n_i} \frac{g_i}{g_j} k(\lambda_0) l,$$

(2)

and the intensity ratio of Ca II doublet lines for an optically thin plasma, is

$$R_{thin} = \frac{\lambda_0^5}{\lambda_2^5} e^{\left(-\frac{\lambda_0 - \lambda_2}{\lambda_2}\right)} \frac{f_2 \lambda_2^2 \Delta \lambda_2}{f_1 \lambda_1^2 \Delta \lambda_1},$$

(3)

where, $R_{min} = 2.11663$. When the concentration of Ca is very low, the ratio would be stable.

The upper energy level populations within the multiplet were assumed constant and the separation between upper energy levels within a multiplet was assumed to be small.

3. Experimental set-up and samples

3.1. Experimental set-up

Figure 1 shows a stand-off LIBS system that could be used for 2-D scanning and Raman spectra of samples. The integrated remote LIBS system comprises: telescope (Celestron C6-A-XLT-CG-5, 6 inch clear aperture, 25 mm 60x objective lens, Schmidt-Cassegrain type), frequency-doubled Nd:YAG laser source (Vlite-500, Beamtech, 532 nm, 10 Hz), four-way adjustable beam expander, intensified CCD detector (Andor, iStar DH320T-18U-03) and spectrograph with a 532 nm super notch filter (Sol instruments, MS-3504i).

The co-axial optical path with four reflection mirrors provides for automatically simultaneous excitation and acquisition when turning the laser to different targets. The beam expander was dedicated for flexibly focusing the laser at long distance. In this study, samples were placed at a fixed focus point.

The 532 nm pulsed laser beam excited a 1.5mm diameter region on the target 15 m away with a four-way beam expander. Laser power was electronically adjusted to 63 mJ/pulse. LIBS spectra were collected with integration time 4 s, equivalent to 40 laser-shot exposures. The gate width was fixed at 2 $\mu$s and the gate delay at 1.6 $\mu$s. ICCD gate control was optimized for adequate signal intensity, as well as avoiding excessive time evolution effects.
Background spectrum was first acquired without any sample and subtracted from all sample spectra. Peak heights, rather than integrated areas, were used to calculate the intensity ratios.

Figure 1. Schematic diagram of stand-off LIBS system.

3.2. Samples
The sample platform was set 15 m away from the telescope, with a 2-dimension displacement unit mounted on the platform. Uniformly distributed excited spots were obtained from each sample by moving the sample vertically and horizontally. Rocks were obtained from various locations in China, including major Ca-containing minerals. Limestone was the most common Ca-containing rock, composed largely of CaCO$_3$ in calcite or aragonite form, collected from Xinjiang and Hunan provinces, respectively. Dolostone was a common Ca and Mg-containing rock, in the form of dolomite, obtained from Yunnan province. Other rock samples with simple mineral compositions, including gypsum, anorthite, and wollastonite, were obtained commercially. Analytical grade pure CaO (97%, from Aladdin Co.,) was compacted manually into cylindrical pellets of ca. 200 mm$^2$ area and 5 mm thick using a hydraulic press. Planar surface of rocks and CaO pellets faced the laser beam perpendicularly. Rock samples were analyzed as raw material without further preparation. The CaO pellets were less compacted compared to natural rocks. Sedimentary rocks are formed deep in earth, with diagenesis pressure exceeding 10$^7$ Pa over periods of millions of years. On the other hand, the manmade CaO pellets experienced approximately 10$^6$ Pa for no more than 1 hour.

For the angle experiment, a rotation displacement unit was mounted on the sample platform and analytical grade pure copper slice (99%, from Aladdin Co.,), in the form of approximately 25 cm$^2$ cross-section area cylinder, 0.5 mm thick, mounted onto the displacement unit.

3.3. Data acquisition
All samples (six natural rocks and one manmade pellet) were uniform in minerals, color and features, and were regarded as identical in composition. Multiple laser pulses striking sample could damage the sample surface, forming a pit and significantly enhancing self-absorption. Thus, spectra were collected for each spot of a 7×7 grid with 2 mm intervals (49 spots) excited by laser. The Ca II doublet (393.37 nm, 396.85 nm) intensities were compared and fitted by simple linear regression (without intersect). The slope of the fitted line was considered the ratio. The slope represented data variance better than averaging 49 individual.

3.4. ICP-AES analysis
Rocks were also analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES), an established approach, to provide the calibration curve.

All the samples were subsequently powdered and concentrations of Sr, Mg, and Ca provided by South China Sea Institute of Oceanology, CAS, followed standard $<\text{GBT17413. (1-3)-1998. GB 3447.6-1982}>$. In summary, 0.5 g of powdered rock was mixed in flux and melted in a 900°C muffle. The ashes were dissolved in HCl and solvents were digested. Intensities of atomic lines (Sr II 216.596 nm, Sr II 407.771 nm, Sr II 421.552 nm; Mg II 279.553 nm, Mg II 280.270 nm, Mg I 285.213 nm; Ca II 318.127 nm, Ca I 430.253 nm, Ca I 445.478 nm) were compared with those of standard reference samples.
4. Results and discussion

4.1. Stability of stand-off LIBS emission lines

Stand-off LIBS is rarely applied for quantitative analysis because line intensities are not as stable as short range LIBS [6]. Sample features also influence the LIBS signal. For natural rocks, unrelated surface features could also contribute to instability, such as dust, water, and voids on the surface, and non-planar surfaces. The excited spots size was ~1.5 mm, so non-planar effects could introduce significant angle variation between the face and laser beam.

The instability was more severe for natural rocks. Several Ca lines were observed within the spectrum window 360–440 nm. The most intensive lines (Ca II, 393.37 nm; Ca II, 396.85 nm; Ca I, 422.67 nm; and Ca I, 430.77 nm) were chosen for analysis. Figure 2 shows the biplots of relative intensity among these lines. Only the Ca II doublet (393.37 and 396.85 nm, respectively) changed linearly; no other stable correlation was found. The linear correspondence indicates a constant intensity ratio between the Ca II doublet lines.

Uniform element composition was assumed for the study samples. This assumption facilitated using emission line intensity ratios of different elements for quantitative analysis. Figure 3 also shows the biplot of Mg I and Ca II (383.82 and 396.85 nm, respectively) was also approximately linear, suggesting a constant intensity ratio of these two lines corresponding to the concentration ratio of the elements.

![Figure 2. Ca II and Mg I emission line intensities. Scatters correspond to annotations in the same colors. Better linear relations are evident for Ca II, 396.85: Ca II, 393.37 and Mg I, 383.83: Ca II, 396.85.](image)

4.2. Intensity ratio of doublet Ca II lines

The theoretical calculation (Section 2) could apply to any pair of emission lines of the same elements (Eqs. 1-3). Therefore, in principle, the intensity ratio between any lines could be used to study the concentration of elements because suitable parameters could be found in an appropriate database (e.g. NIST). The intensity ratio changed with sample composition, as Ca concentration increased, the ratio decreased.

The ratio was the slope (without intersection) of the linear fit (Ca II vs. Ca II), as shown in Fig. 3. The stability of the slope (ratio) was evaluated by comparing with the standard deviation of individual ratios, and shown to represent the correlation better than an average of ratios. Table 1 shows standard deviation was mostly less than 3% for the slope, indicating good correspondence. A comparison test
was conducted to a lead-zinc ore which had large Ca composition variation. There is no clear relationship evident.

Figure 3. Fitted biplots for Ca II doublet lines. The slope was taken as the ratio for a particular sample. The determination coefficient ($R^2$) was used to evaluate the quality of fit.

Table 1. Sample descriptions and linear intensity fits for Ca II 393.37 nm and Ca II 396.85 nm

| Rock Item | Chemical Formula (stoichiometric) | Ca concentration (ICP-AES) | Mg concentration (ICP-AES) | Intensity ratio | Standard Deviation |
|-----------|----------------------------------|---------------------------|---------------------------|----------------|-------------------|
| CaO       | CaO                              | 71.43%                    | 0.00%                     | 0.9106         | 0.0198            |
| Limestone 1 | CaCO$_3$                        | 39.18%                    | 0.34%                     | 0.9336         | 0.0206            |
| Limestone 2 | CaCO$_3$                        | 38.83%                    | 0.19%                     | 0.9392         | 0.0123            |
| Wollastonite | CaSiO$_3$                      | 34.48%                    | 0.05%                     | 0.9469         | 0.0089            |
| Gypsum     | CaSO$_4$·2H$_2$O                 | 28.87%                    | 0.59%                     | 0.9672         | 0.0330            |
| Dolostone 3 | MgCa(CO$_3$)$_2$                | 25.10%                    | 13.13%                    | 0.9751         | 0.0352            |
| Anorthite  | CaAl$_2$Si$_2$O$_8$              | 2.50%                     | 0.49%                     | 1.0340         | 0.0526            |

1Limestone from Hunan; 2Limestone from Xinjiang; 3Dolostone from Yunnan.

4.3. Analysis of chemical composition

The Ca doublet line ratio was linear for low species density and quadratic for high species density. The maximum ratio should be 2.11663, where the Ca concentration was low enough to neglect self-absorption, and the minimum should be 1.069. The observed results match the theoretical trend. However, an equipment factor, including influences from excitation laser and acquisition parameters, should be considered for different laboratory results. Excitation conditions could affect plasma characteristics, such as temperature, and temporal or spatial variation. All these factors would change the plasma electron density and shift the curve along the x axis.

Total electron density in plasma was the result of ionization of all the atoms, i.e., the sum of electrons ionized from all the elements in the plasma. Electron composition was determined by partitioning the elements and plasma characteristics [7]. The energy required to ionize Ca II ions is so large that the number density of Ca III ions could be neglected, and the electron density ionized from calcium could be considered approximately equal to the density of Ca II ions.

Figure 6 shows fitted Ca concentrations to Ca II doublets intensity ratios. The ratio increases when Ca concentration decreases. Linear fitting is superior when the CaO sample was not included in the matrix (dotted blue line), but a quadratic function fits the seven samples well (dotted red line). The results agree well with the theoretical calculation (Figs. 1 and 6). However, another possible explanation could be that since manmade CaO pellet was less compacted than natural rocks, the mass density was somewhat lower. Since LIBS ablated an identical volume of sample, the total excited material in manmade CaO could be less. Thus, the nominal manmade Ca concentration was larger than the actual concentration within the laser spot.

Ca concentration could be used as an internal standard reference to determine other elemental concentrations. Magnesium is commonly present in Ca-containing rocks. Since the intensity ratio of
these four lines changes (Mg I 383.23nm, Mg I 383.82 nm, Ca II 393.37nm, Ca II 396.85nm) are correlated (see Fig. 2), the LIBS intensity ratio of Mg/Ca may be calculated as

$$ R_{\text{Mg/Ca}} = \frac{Mg \ I \ 383.23 \ + \ Mg \ I \ 383.82 \ + \ Ca \ II \ 393.37 \ + \ Ca \ II \ 396.85}{4} $$

Figure 4. Ca concentrations and Ca II doublet line intensity ratios. Dotted red line represents quadratic fit to all seven samples. Dotted blue line represents linear fit to six samples and density corrected CaO pellet. Samples are labeled in black text.

5. Conclusions
An ideal quantitative analysis method for stand-off sample detection, remains elusive. Absolute intensities are affected by many factors and most relative intensities for stand-off LIBS detection are unstable. The angle between the sample plain and laser beam could be one of the reasons.

A stable intensity ratio that varied with Ca concentration was identified between Ca II doublet lines 393.37 and 396.85 nm. The variation with concentration was due to self-absorption, since the lines have different self-absorption coefficients. The experimental outcomes matched theoretical predictions well for the expected linear relation for low species density and quadratic for high species density.

The results raised the possibility of using Ca as an internal standard reference to determine concentrations of other elements, such as Mg.

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