



## Technical note

## Enhancement of carbon detection sensitivity in laser induced breakdown spectroscopy with low pressure ambient helium gas



N. Idris<sup>a</sup>, M. Pardede<sup>b</sup>, E. Jobiliong<sup>c</sup>, Z.S. Lie<sup>d</sup>, R. Hedwig<sup>d</sup>, M.M. Suliyanti<sup>e</sup>, D.P. Kurniawan<sup>f</sup>, K.H. Kurniawan<sup>f,\*</sup>, K. Kagawa<sup>g,f</sup>, M.O. Tjia<sup>h,f</sup>

<sup>a</sup> Department of Physics, Faculty of Mathematics and Natural Sciences, Syiah Kuala University, Darussalam, Banda Aceh, 23111, Aceh, Indonesia

<sup>b</sup> Department of Electrical Engineering, University of Pelita Harapan, 1100 M.H. Thamrin Boulevard, Lippo Village, Tangerang 15811, Indonesia.

<sup>c</sup> Department of Industrial Engineering, University of Pelita Harapan, 1100 M.H. Thamrin Boulevard, Lippo Village, Tangerang 15811, Indonesia.

<sup>d</sup> Department of Computer Engineering, Bina Nusantara University, 9 K.H. Syahdan, Jakarta 14810, Indonesia

<sup>e</sup> Research Center for Physics, Indonesia Institute of Sciences, Kawasan PUSPIPTEK, Serpong, Tangerang Selatan 15314, Indonesia

<sup>f</sup> Research Center of Maju Makmur Mandiri Foundation, 40/80 Srengseng Raya, Jakarta 11630, Indonesia

<sup>g</sup> Fukui Science Education Academy, Takagi Chuou 2 chome, Fukui 910-0804, Japan

<sup>h</sup> Physics of Magnetism and Photonics Group, Faculty of Mathematics and Natural Sciences, Bandung Institute of Technology, 10 Ganesha, Bandung 40132, Indonesia

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## ABSTRACT

Carbon detection is usually difficult to carry out with high sensitivity and minimally destructive effect. While the conventional laser induced breakdown spectroscopy (LIBS) method operated with atmospheric ambient air is well known as a powerful and versatile analytical tool, it suffers nevertheless from the low sensitivity of C detection when measured in both atmospheric and low pressure ambient air with the more adverse effect found in the former case. This was shown to have its origin in the serious time mismatching effect between the formation of the shock wave plasma by the ablated major host elements and the premature fast passage of the much lighter ablated C atom. However, this study shows the result of high sensitivity C analysis of stone samples using LIBS technique with relatively low laser pulse energy of 60 mJ and low pressure He ambient gas without showing visible surface damage. The helium gas provides the additional delayed excitation by the He metastable excited states through the Penning-like ionization process. The C emission intensities measured from the jasper and black stone in 2.6 kPa He ambient gas are in general significantly higher than those measured in 0.5 kPa ambient air. The enhancement is shown to increase reaching an 8 fold enhancement with increased laser energy up to 60 mJ before undesirable surface damage is created. A further measurement of C emission using pelletized KBr mixtures with various CaCO<sub>3</sub> concentrations reveals a straight calibration line of rather large slope with extrapolated zero intercept and estimated detection limit of around 0.6 ppm, demonstrating its potential application for highly sensitive quantitative analysis of C with minimal destructive effect.

## 1. Introduction

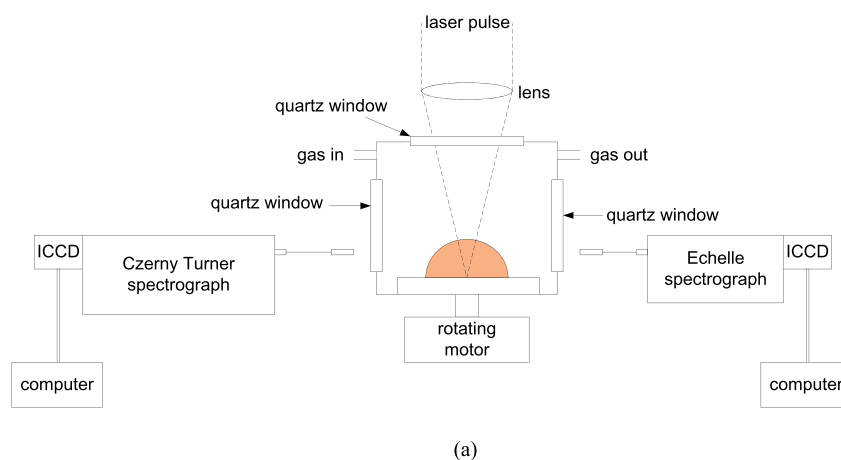
Carbon is one of the essential elements that determine the physical, mechanical and chemical properties of both metals such as steel as well as non metals such as stones and foods. The analytical methods commonly used for the detection and analysis of C in steel and other metallic samples are the spark discharge optical emission spectrometry and the classical combustion C analysis [1–2]. Meanwhile the analysis of C content in shale rock is normally carried out by means of instrumental neutron activation analysis (INNA), X-ray fluorescence (XRF), and inductively coupled plasma-optical emission spectroscopy (ICP-OES) [3–5]. However, INNA is not commonly available and it is time

consuming while the detection limit attained by XRF is relatively poor. Despite its reputation for uncomparably high accuracy, analysis using ICP-OES is both time and sample consuming as well as being totally destructive in nature. Thus, a more practical, minimally destructive and less expensive analytical tool with offering comparable high performance is very much in demand for C analysis of solid samples.

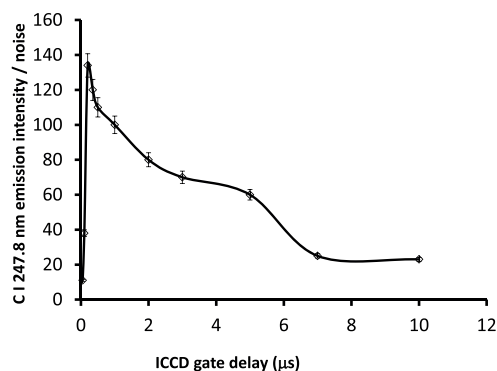
A potential alternative is basically offered by the laser-induced breakdown spectroscopy which is widely known as a powerful, versatile and practical analytical tool applicable to a large variety of samples in the forms of solid, liquid and gas [6–12]. It is also relatively free from tedious sample preparation and capable of performing rapid simultaneous multi-elemental analysis of samples having complex

\* Corresponding author.

E-mail address: [kurnia18@cbn.net.id](mailto:kurnia18@cbn.net.id) (K.H. Kurniawan).



(a)



(b)

Fig. 1. (a) Diagram of the experimental set up and (b) ICCD gate delay dependent of S/N ratios of C I 247.8 nm emission intensities detected using 60 mJ laser irradiation from black stone sample in He ambient gas at 2.6 kPa. The gate width of the ICCD is set at 50 μs.

compositions. The problem of weak emission and poor sensitivity in the detection of light elements such as hydrogen and deuterium in conventional LIBS due to the time mismatch effect in atmospheric ambient air has been overcome by the use of low pressure ambient He gas, thanks to the role of metastable excited He atoms created in the process. These excited He atoms were shown to provide the He assisted excitation (HAE) mechanism for the delayed excitation and emission of the ablated analyte atoms when the plasma becomes relatively cooled and free from the charged particles [13–26]. The benefits of using ambient He gas in LIBS applications have been amply demonstrated in a number of cases according to our previous works, [15–28] including C analysis of steel products [29–30]. Nevertheless its application to C analysis of stones has yet to appear in the literature.

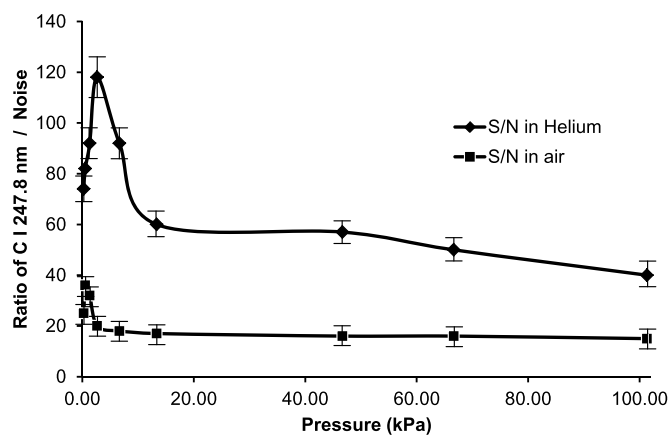
Recently there is a rising trend in Indonesia of collecting typical Indonesian precious stones of partially organic origin (jasper). Thousands of stone shops have recently sprout up all over the country to meet the growing market demand for this commodity. The most favorite choice of the collectors is a jasper with rather high content of C for spiritual need and other unexplained purposes. Therefore the stones of higher C concentration are the more expensive and sought after ones. In anticipation of its rapidly increasing commercial need, a fast and reliable C detection method with minimal destructive effect is highly desirable. The sensitive C detection for its concentration variation of less than 1% is generally required as the C content in jasper is known to vary from 0.5 to 3%. It is in response to this market need that the applicability of LIBS technique is investigated in this work. The work is

carried out by taking advantage of low pressure He ambient gas mentioned earlier and exploring the optimal irradiation energy and ambient He gas pressure for the most sensitive detection with least destructive effect. Further, the possibility for quantitative C analysis will also be examined.

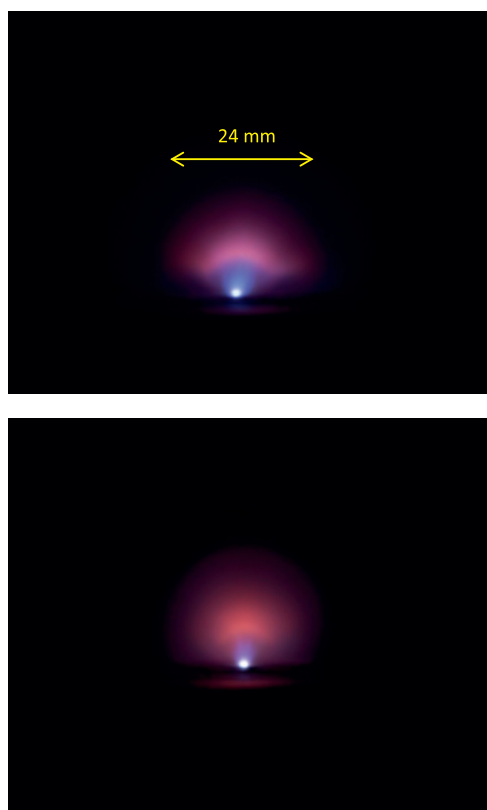
## 2. Experimental procedures

The experimental setup employed in this work is basically similar to those used in our previous works, [21–22] which is schematically presented in Fig. 1 for easy reference. The laser source is a nanosecond Nd:YAG laser Quanta Ray; LAB SERIES;  $\lambda = 1.064$  nm, 8 ns, 10 Hz with a maximum energy of 500 mJ which is operated in a Q-switched mode at 10 Hz repetition rate. In order to avoid undesirable surface damage marked by the appearance of crater size larger than 100 μm diameter, the laser output energy is lowered and varied below 60 mJ using a proper set of filters. The laser beam is focused by a moveable high density lens of  $f = +150$  mm and directed perpendicularly onto the sample surface.

Two stone samples used in this experiment are prepared from jasper (green stone of about 1% C content) and black stone of about 0.2% C content. Each sample is cut into a small slice of 20 mm × 20 mm × 5 mm and mounted on a sample holder in the metal chamber. The chamber is equipped with several windows allowing flexible observation and detection of the plasma emission as well as for the inlet and outlet of the gas line. The sample chamber is evacuated



(a)



(b)

**Fig. 2.** (a) Pressure dependent of S/N ratios of C I 247.8 nm emission intensities detected from black stone sample using 60 mJ laser irradiation. The gate delay and gate width of the ICCD is set at 200 ns and 50  $\mu$ s, respectively and (b) photograph of the plasma from black stone sample using 60 mJ laser irradiation. Upper part is for the case of 0.5 kPa ambient air and lower part is for the case of 2.6 kPa ambient He gas.

prior to its use and filled with certain ambient gases, including the high purity He gas (Air Liquid, 5 N) and ambient air at the desired pressures for comparison.

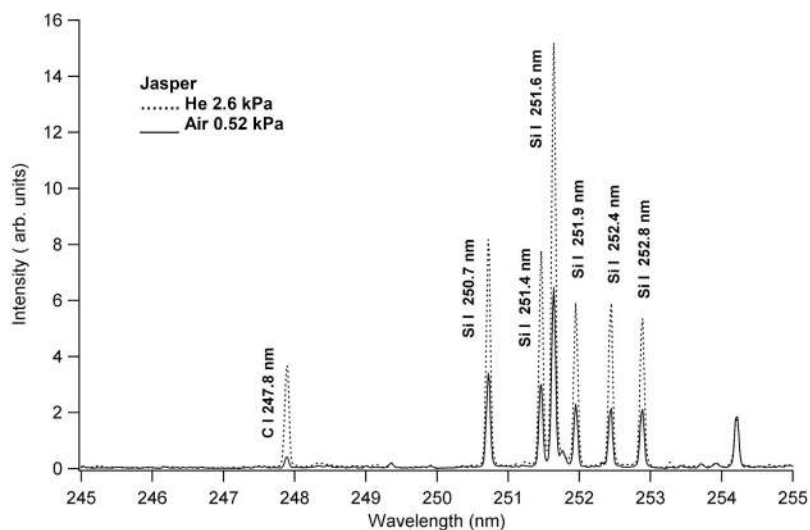
The plasma emission is collected by one end of an optical fiber positioned side wise at a distance of 80 mm from the plasma center with the other end of the fiber connected to the input port of the detection system consisting of an Echelle spectrograph (Mechelle M5000 made by

Andor) and intensified charged couple device (ICCD) detector (Andor iStar). Prior to its operation, a special experiment is carried out to ascertain the most favorable ICCD gating time. The resulted variation of the S/N ratio of C I 247.8 nm emission from the black stone versus the gating delay is displayed in Fig. 1(b). It is seen that the maximum S/N ratio is attained with 200 ns gate delay and followed by a gradual decrease thereafter. The 200 ns gate delay and 50  $\mu$ s gate width are chosen for the following experiment. The detection system has a spectral window covering the wavelength range from 200 nm to 975 nm. For the measurements aimed at exploring the possible existence of calibration curve, the Echelle spectrograph and the ICCD are replaced by Czerny Turner spectrograph (McPherson model 2061 with 1 m focal length, 1800 g/mm grating and f/8.6) and a different ICCD (Andor iStar 1024  $\times$  256 pixels) in the detection system, respectively, in order to attain a wavelength resolution of 0.01 nm. The accumulated data of 10 spectra obtained successively from each irradiated spot are monitored on a computer screen, and recorded to yield the averaged spectral results presented in this report.

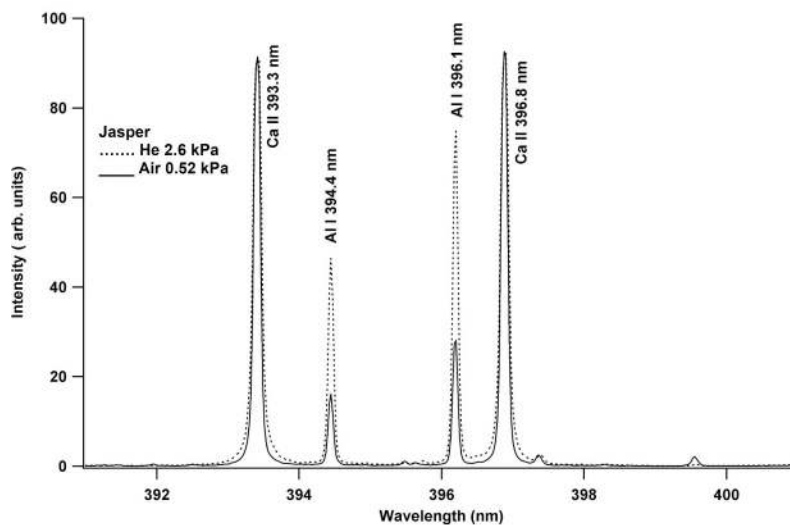
### 3. Experimental results and discussion

Since the He gas of high purity is relatively expensive and not readily available compared to air, it is necessary to show that the use of ambient He does offer the convincingly larger advantages over the use of ambient air. The emission spectra from the samples are separately measured by focusing 60 mJ laser irradiation onto the sample surface in 2.6 kPa He ambient gas and alternatively in 0.5 kPa ambient air for comparison. The He gas and air pressures are chosen on the basis of the pressure dependent intensity variations of the related plasma emission measured in a preliminary experiment. The result presented in Fig. 2 clearly shows the highest S/N ratios of the C I 247.8 nm emission line at the two gas pressures cited above. It should be noted that apart from the highest S/N ratios of the ambient air and helium gas, the different pressures also give the same gas density and the resulted plasma size as shown in Fig. 2(b).

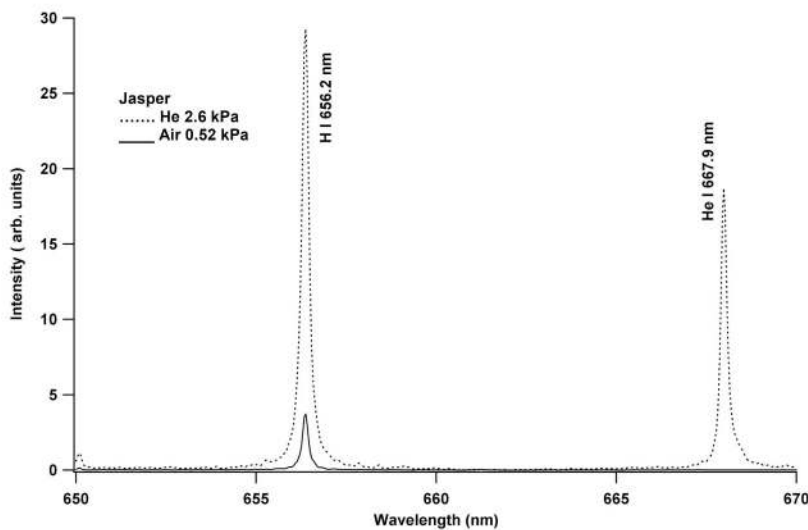
Figs. 3 and 4 show the emission spectra of jasper and black stone samples, respectively. In each case the spectra are presented in three different wavelength ranges covering (a) the C I 247.8 nm and Si I 251.6 nm emission lines, (b) the Ca II 393.3 nm and Ca II 396.8 nm emission lines and (c) the H I 656.2 nm and He I 667.8 nm emission lines. Note that different scales are adopted in the three spectral ranges. It should be noted that Si and Ca are among the major and heaviest host elements for both stones. The ablated Si and Ca atoms are therefore responsible for the generation of the shock wave plasma, and the associated emission lines do not suffer as much as the C emission from the time mismatch effect in ambient air. This effect was first revealed and reported in 2004 [31–34,14,17,24]. It was shown that the suppressed of H I 656.2 nm emission line in zirconium was mainly due to the ineffective shock wave induced thermal excitation of the ablated H in the plasma which was mainly generated by the other heavier host atom of Zr. Since the passage of the lighter and faster moving H atoms took place before the full formation of the shock wave plasma, the H atoms are bound to largely miss the thermal excitation process by the hottest part of the plasma right behind the shock wave front. That is why the emission lines of the light elements C and H are visibly weakened as shown in Figs. 3(a) and 3(c), respectively. Subsequently, a special experimental study on the time mismatch effect was performed using the agate sample. The specific measurements of the speeds of the ablated H, O and Ca yielded the results of 50 km/s, 10 km/s and 2.5 km/s. As explained above, the Ca atoms which is one of the host element in agate are among those responsible for the generation of shock wave plasma. This result therefore confirms the so called time mismatch effect [33]. Meanwhile the emission from both samples detected in ambient He gas



(a)



(b)



(c)

Fig. 3. Emission spectra measured from the plasma produced by focusing Nd:YAG laser beam of 60 mJ on a jasper in ambient He gas at 2.6 kPa and ambient air at 0.5 kPa; in the wavelength range of (a) 245 nm–255 nm, (b) 392 nm–400 nm and (c) 650–670 nm. The gate delay and gate width of the ICCD are set at 200 ns and 50  $\mu$ s, respectively.

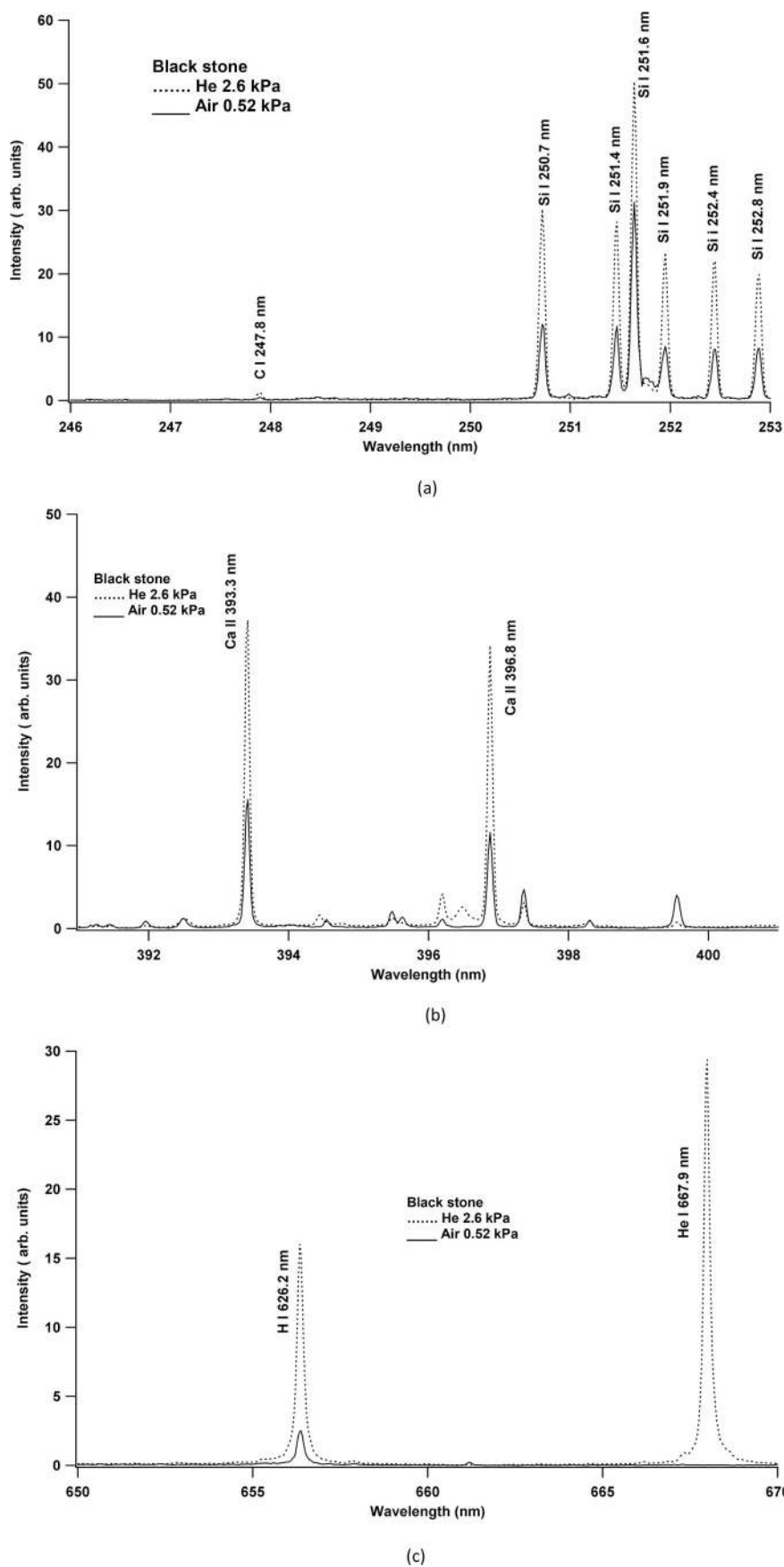


Fig. 4. Emission spectra measured from the plasma produced by focusing Nd:YAG laser beam of 60 mJ on a black stone in ambient He gas at 2.6 kPa and ambient air at 0.5 kPa; in the wavelength range of (a) 245 nm–255 nm, (b) 392 nm–400 nm and (c) 650–670 nm. The gate delay and gate width of the ICCD are set at 200 ns and 50  $\mu$ s, respectively.

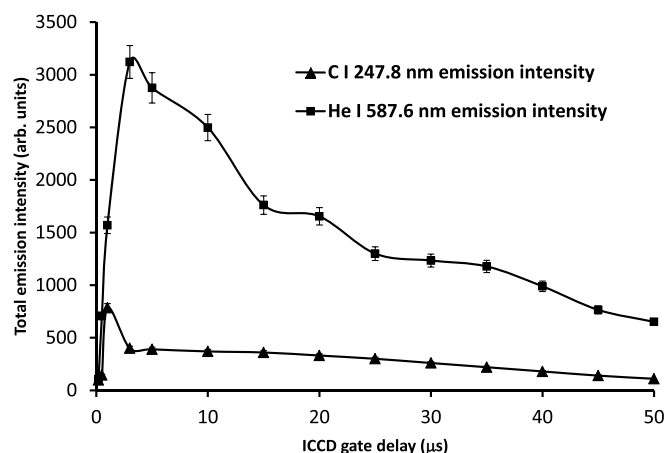


Fig. 5. Duration or emission life times of C I 247.8 nm and He I 587.6 nm lines. The He emission line is associated with transition from the metastable triplet excited state of He responsible for the HAE mechanism. The gate width of the ICCD is set at 500 ns.

are seen to be largely enhanced and exhibit generally much stronger and sharper emission lines. It is most remarkable that the intensity enhancement of C and H emission lines resulted from the replacement of ambient air by ambient He gas are marked by eight to ten fold increase as indicated in Figs. 3 and 4, respectively. This is in good agreement with the previous reports [14–15] of the effective role of HAE mechanism in the enhancement of light atom emission. This is further corroborated by the evidence of approximately the same lifetimes of the C I 247.8 nm and the metastable triplet He I 587.6 nm emission line responsible for the HAE process as depicted in Fig. 5.

In view of its purpose for spectrochemical analysis of precious stones, it is important to minimize the destructive effect on the sample surface due to excessive irradiations. Therefore it is necessary to investigate the possibility of retaining the appropriate emission intensities with lower ablation energies. Fig. 6 exhibits the energy dependent intensity variations of C I 247.8 nm emission from jasper and black stone samples measured separately in 2.6 kPa ambient He gas and 0.5 kPa ambient air. Apart from being obviously much weaker, the C emission intensities from both samples measured in ambient air are shown to be little affected by the pulse energy variation. In contrary, those emission intensities measured in ambient He gas are drastically reduced with decreasing pulse energy. This is clearly the result of reduced number of incoming photons for the excitation of He atoms. This

leads inevitably to less effective HAE mechanism at low ablation energies. Clearly, 60 mJ laser irradiation energy should be the optimal choice as it is the highest energy without causing unacceptable damage on the sample surface marked by craters exceeding 100 μm in diameter.

Since the quality and hence the price of the precious stone are largely determined by the C concentration in the stone, it is desirable to investigate the feasibility of applying our experimental setup for quantitative analysis of C in the stone samples. Unfortunately, stone samples with different known C concentrations are hard to come by. The samples used for this experiment are instead prepared by mixing KBr powder with CaCO<sub>3</sub> at various concentrations before being pelletized. These pellet samples are verified to show similar C emission lines from the black stone sample. Fig. 7 displays the resulted calibration curve for C in the pellet samples. It is seen to exhibit a linear relationship between C concentration and C I 247.8 nm emission intensity with extrapolated zero intercept and reasonably large slope for sensitive C detection. Depicted in the inset of Fig. 7 is the C emission line detected from KBr + CaCO<sub>3</sub> pellet, containing 0.3125% of CaCO<sub>3</sub> powder equivalent to a C concentration of about 5 ppm. The detection limit estimated from this spectrum is approximately 0.6 ppm. It is worth noting that the plasma temperatures and electron densities of the plasma generated from the black stone and the pelletized samples are found to be 9000 K and 10<sup>17</sup> cm<sup>-3</sup> and 8500 K and 4 × 10<sup>16</sup> cm<sup>-3</sup>, respectively. This result clearly shows the possibility of C analysis in precious stones using LIBS with low pressure He ambient gas.

#### 4. Conclusion

We demonstrate in this study the significant intensity enhancement (8×) of C emission line from jasper and black stone samples employing LIBS with low pressure ambient He gas compared to the results obtained with low pressure ambient air. This remarkable advantage is attributed to the He assisted excitation (HAE) mechanism due to the presence of metastable excited He atoms created in the plasma, and hence eliminating the time mismatch problem in the shock wave induced thermal excitation process. It is shown that 2.6 kPa low pressure ambient He gas provides the most favorable C emission intensity and highest S/N ratio. The intensity increases rapidly and monotonously in both samples with increased laser energy up to 60 mJ before surface damage begins to occur. Finally, repeating the experiment with KBr pellet of CaCO<sub>3</sub> also exhibits a linear calibration line with extrapolated zero intercept and reasonably high slope for the sensitive detection of C emission line as corroborated by an estimated detection limit of 0.6 ppm.

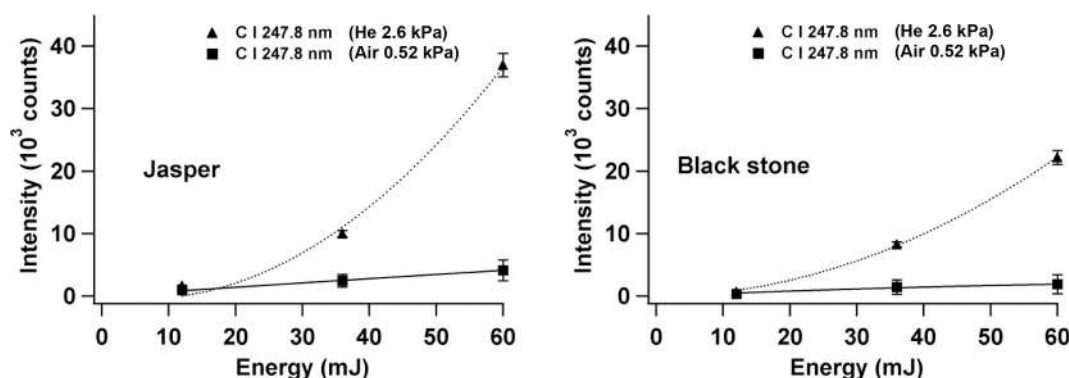


Fig. 6. Energy dependent of the emission intensity of carbon (C I 247.8 nm) detected from black stone and jasper samples in ambient He gas at 2.6 kPa and ambient air at 0.5 kPa. The gate delay and gate width of the ICCD is set at 200 ns and 50 μs, respectively.



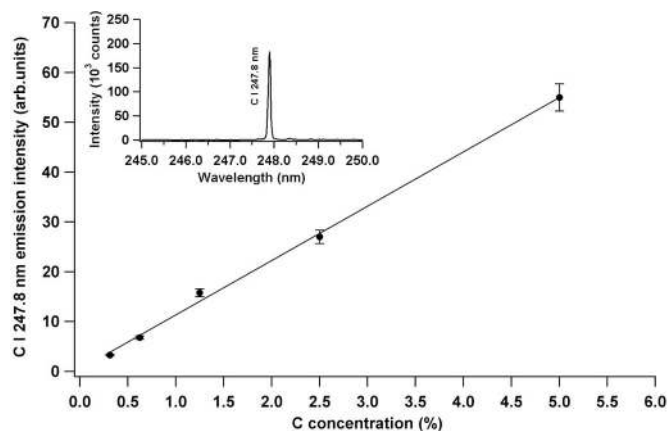


Fig. 7. Relationship between C concentration and C I 247.8 nm emission intensity detected from samples of KBr + CaCO<sub>3</sub> pellets containing various concentrations of C using the same setup and gating times. Given in the inset is the emission spectrum of C I 247.8 nm detected from the KBr pellet containing 0.3125 % of CaCO<sub>3</sub>.

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