

COMPARATIVE ELEMENTAL ANALYSIS OF SILKY WHITE AND BLACK MARBLE USING LASER-INDUCED BREAKDOWN SPECTROSCOPY

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Abstract

Laser-Induced Breakdown Spectroscopy (LIBS) is used for the elemental analysis of natural geological samples under atmospheric pressure. Plasma is generated using a Q-switched Nd:YAG laser operating at 1064 nm with a pulse duration of 5 ns, a repetition rate of 10 Hz, and a pulse energy of 400 mJ. The recorded emission spectra revealed the presence of calcium (Ca), magnesium (Mg), potassium (K), and barium (Ba) in both marble samples. To obtain representative spectra, multiple laser shots were acquired at different spatial locations on each sample and averaged. Plasma diagnostics were performed to investigate the temporal evolution of the laser-induced plasma. The electron temperature was determined using the Boltzmann plot method under the assumption of local thermodynamic equilibrium (LTE). The maximum electron temperature for Silky White Marble was 23,171.33 K at a delay time of 279 ns, whereas that for Black Marble was 16,203.78 K at 285 ns. The electron number density, estimated from the Stark broadening of the Ca II emission line at 393.36 nm, exhibited a decreasing trend with increasing delay time. For Silky White Marble, the electron number density decreased from $8.402 \times 10^{16} \text{ cm}^{-3}$ to $6.13 \times 10^{16} \text{ cm}^{-3}$, while for Black Marble it decreased from $8.21 \times 10^{16} \text{ cm}^{-3}$ to $5.99 \times 10^{16} \text{ cm}^{-3}$. The plasma frequency, calculated from the electron number density, also decreased with increasing delay time, confirming its direct dependence on electron density. These results demonstrate the capability of LIBS for rapid elemental analysis and plasma diagnostics of marble samples.

1. INTRODUCTION

The generation of high temperature, high density plasma by focusing a high-power laser pulse onto a material surface has attracted significant attention in engineering, fundamental sciences and material processing technology (MPT) [1]. Laser-Induced

Breakdown Spectroscopy (LIBS) is a powerful analytical technique for both (Qualitative and Quantitative) analysis of elemental composition. Laser-Induced Breakdown Spectroscopy is a powerful technique for rapid elemental analysis of materials. In this technique, a high energy laser

light is focused on the target sample. As a resulting in ablation and the formation of plasma plume. The plasma contains excited atoms and ions from the sample [2][3]. On the recombination, as the plasma cool down and emit light (characteristic radiation), which is collected and analyzed to determine elemental composition as well as plasma properties such as electron temperature (Te) and electron number density (Ne).

The plasma characteristics strongly depends on laser properties such as (Laser intensity, wavelength as well as pulse duration) and sample properties such as (optical properties as well as thermodynamics properties) [4][5]. LIBS offers several advantages, including rapid analysis, minimal sample preparation, non-contact operation and applicability to solids, liquids, and gases. Previous studies have applied LIBS to geological materials including marble and rocks for the identification of various elements such as (Ca, Mg, Fe, Na, Al and Si) have been reported by different research groups. Zeshan et al. [6] investigated granite rocks using Laser-Induced Breakdown Spectroscopy (LIBS) and Laser Ablation Time-of-Flight Mass Spectrometry (LA-TOF-MS), reporting the presence of elements such as (Si, Ca, K, Fe, Mg, Al, Na, and Li). P. M. Kalaitzaki et al. [7] applied LIBS to marble samples and observed that (Fe, Si, and Ti) concentrations decrease with depth in pollution-derived encrustations, whereas soil dust and patina layers retain Si and Al throughout. Fontana et al. [8] analyzed rock samples using LIBS with a 532 nm Nd: YAG laser and identified elements including (Al, Ca, Fe, K, Mg, Na, Si, and Ti). Mahmood et al. [9] reported that pigments responsible for color variations in marble are mainly composed of different elemental oxides, which can be effectively analyzed using LIBS. In another study, Mahmood et al. [10] showed that onyx (white spot) marble is rich in Ca, whereas green marble is dominated by Mg. Taher et al. [11] quantitatively determined 22

elements, including (Mg, Ca, V, Na, Mn) and rare earth elements, in marble samples from Saudi Arabia using Instrumental Neutron Activation Analysis (INAA). Furthermore, Bhatt et al. [12] identified emission lines of rare earth elements such as (Ce, La, Nd, Y, Pr, Sm, Eu, Gd, and Dy) in geological material using LIBS. Although LIBS has been extensively applied to rocks and marble from different geographical region, relatively limited has focused on the elemental characterization and plasma diagnostics of marble from Pakistan. Since marble composition varies significantly with local geology, results from other regions cannot accurately represent Pakistani marble. Moreover, relatively limited studies have focused on the elemental characterization and plasma diagnostics of locally available marble from Pakistan, particularly Silky White and Black Marble. In the present study, LIBS was employed to determine the elemental composition and plasma parameters of Silky White and Black Marble samples.

2.Experimental Setup.

The qualitative elemental composition of Silky White and Black Marble samples was determined by analyzing the optical emission spectra of laser-induced plasma generated on the sample surfaces. Plasma was generated using a Q-switched Nd:YAG laser operating in the fundamental mode at 1064 nm, with a pulse duration of 5 ns, a repetition rate of 10 Hz, and a pulse energy of 400 mJ. The laser pulse energy was measured using a Joule meter (Nova-Quantel, P/Niz 01507). The experimental arrangement is shown in Fig. 1. The laser beam was focused onto the sample surface using a focusing lens with a focal length of 15 cm to generate the plasma plume. The optical emission from the plasma was collected through an optical fiber positioned at approximately 90° to the plasma plume and coupled to a LIBS 2000+ spectrometer. The recorded emission spectra were subsequently analyzed using OriginLab software.

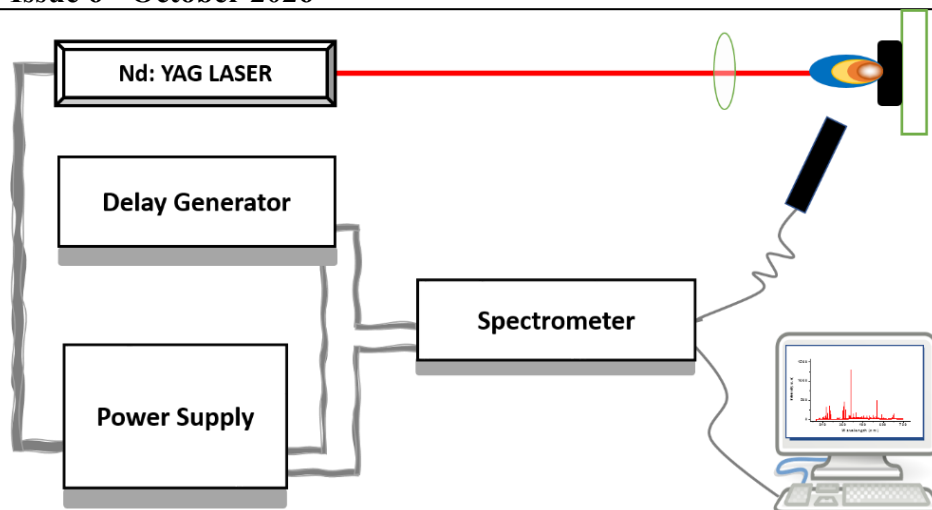


Fig 1. The experimental setup of LIBS.

3. Results and Discussion

3.1 The Atomic Emission Spectrum of Silky White Marble.

In the experiments, a plasma was generated using Q-switched Nd: YAG laser at 1064 nm in atmospheric pressure, with a laser irradiance of $4 \times 10^{10} \text{ W/cm}^2$. The emission spectrum of Silky White Marble consisted of prominent atomic and ionic emission lines. The identified Ca I lines were observed at 428.20, 428.93, 429.98, 430.77, 431.68, 442.54, 445.47, 457.85, 458.14, 458.53, 487.81, 518.88, 526.17, 526.42, 526.54, 534.94, 551.19, 558.19, 558.87, 559.44, 559.84, 560.28,

585.74, 610.27, 612.22, 616.21, 616.95, 643.91, 644.98, 645.56, 646.25, 647.16, 649.36, 649.96, 671.76, and 714.81 nm. The Ca II lines were identified at 315.88, 317.93, 370.60, 373.69, 393.36, and 396.86 nm, while Mg II lines were observed at 279.55, 280.27, and 285.21 nm. In addition, Ba I and K I emission lines were observed at 452.31 and 532.23 nm, respectively. The identified transition lines were assigned using the NIST Atomic Spectra Database are given in Fig 2 (a – e).

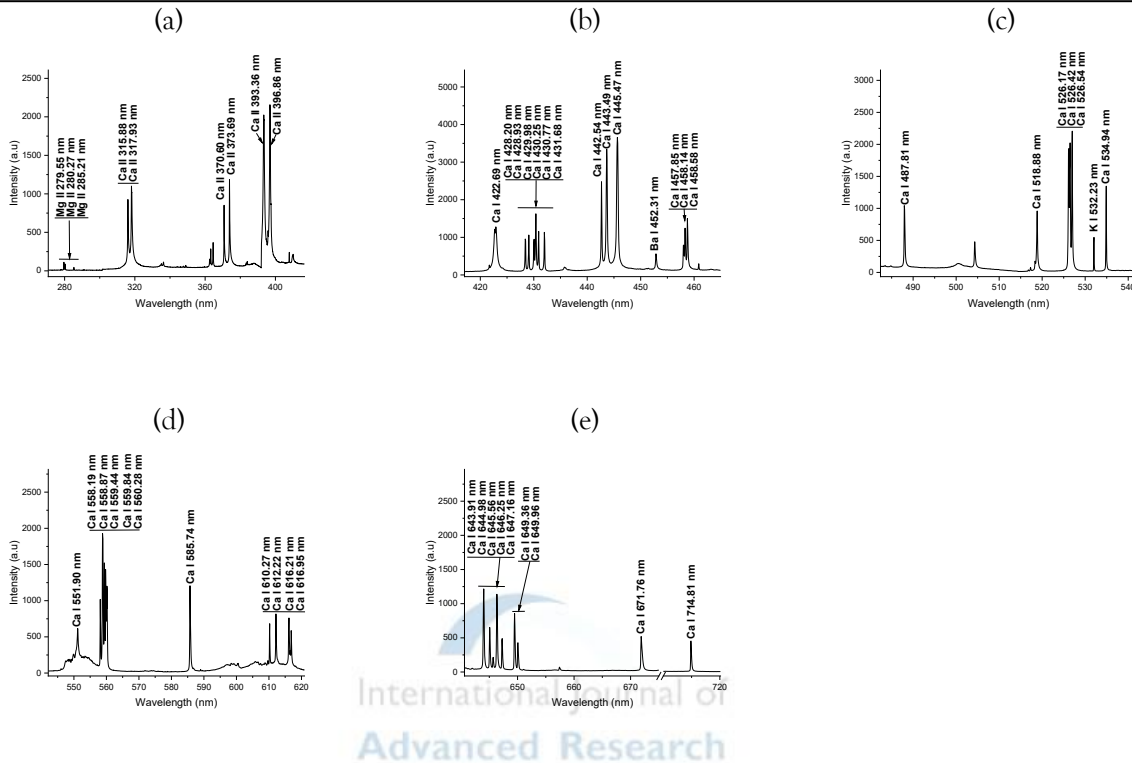


Figure 2 (a - e): Laser-induced emission spectra of Silky White Marble in different wavelength regions.

3.2 The Atomic Emission Spectrum of Black Marble

The emission spectrum of Black Marble consisted of prominent atomic and ionic emission lines. The identified Ca I lines were observed at 422.69, 428.20, 428.93, 429.98, 430.25, 430.77, 431.68, 442.54, 443.49, 445.47, 457.85, 458.14, 458.58, 487.81, 518.88, 526.17, 526.42, 526.54, 534.94, 551.90, 558.19, 558.87, 559.84, 560.28, 585.74, 610.27, 612.22, 616.21, 616.95, 643.91, 644.98,

645.56, 646.25, 647.16, 649.36, 649.96, 671.76, and 714.81 nm. The Ca II lines were identified at 315.88, 317.93, 370.60, 373.69, 393.36, and 396.86 nm, while Mg II lines were observed at 279.55, 280.27, and 285.21 nm. In addition, Ba I and K I emission lines were observed at 452.31 and 532.23 nm, respectively. The identified transition lines were assigned using the NIST Atomic Spectra Database are given in Fig 3 (a - e).

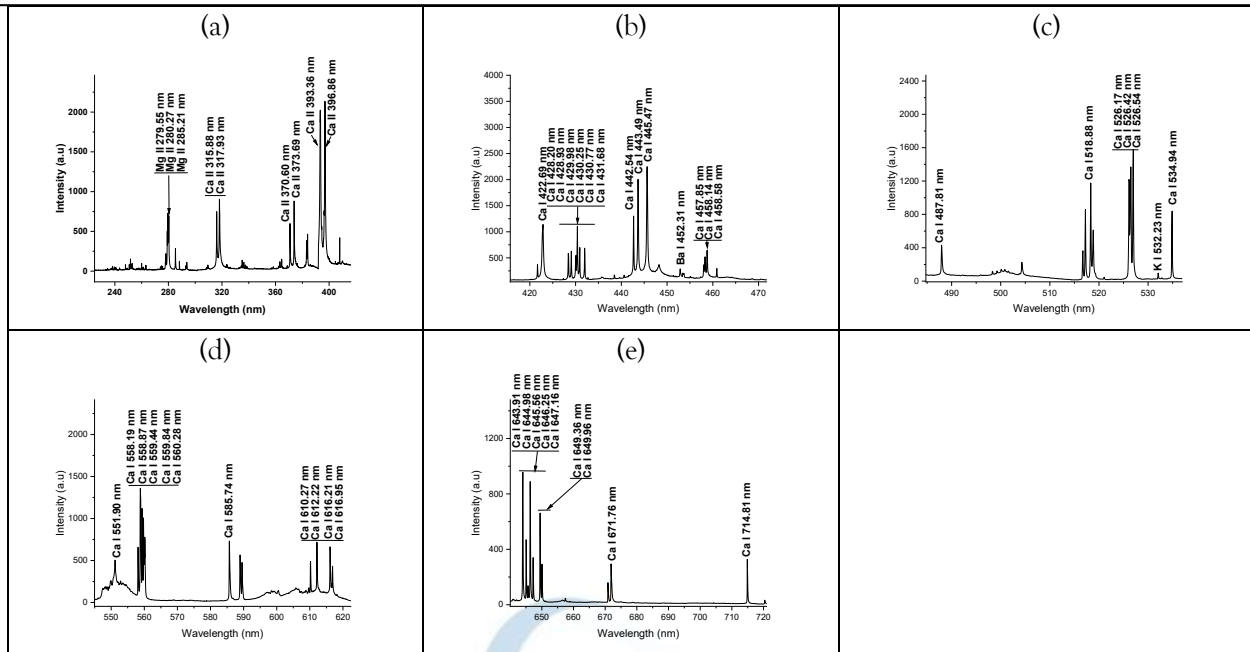
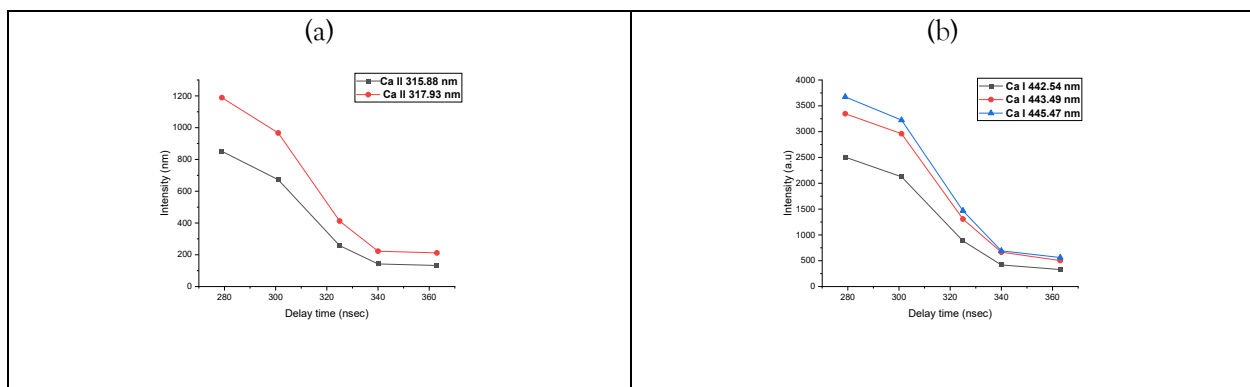


Figure 3 (a - e): Laser-induced emission spectra of Black Marble in different wavelength regions.

3.3 Temporal Variation of Silky White Marble and Black Marble in Plasma

To investigate the temporal evolution of the laser-induced plasma from Silky White and Black Marble, emission spectra were recorded at different delay times. The intensities of the observed transition lines were generally higher at shorter delay times and gradually decreased with

increasing delay time. This behavior can be attributed to plasma expansion, cooling, recombination, and associated changes in the population of excited states. Fig. 4 illustrates the temporal variation of selected Ca I and Ca II emission lines for both marble samples.



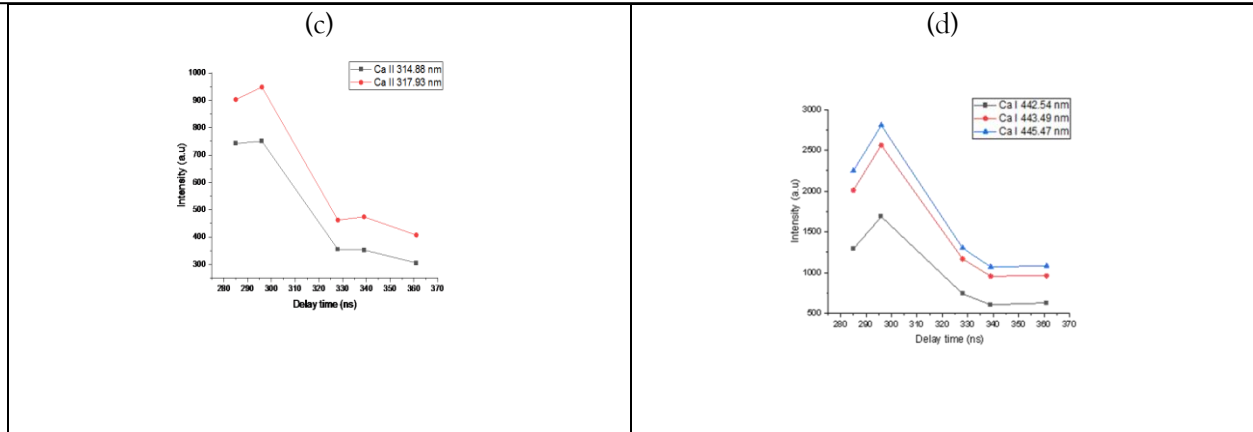


Figure 4: Variation of emission-line intensity with delay time for Silky White and Black Marble.

The overall variation of intensity in three dimensional view is given in Fig. 5.

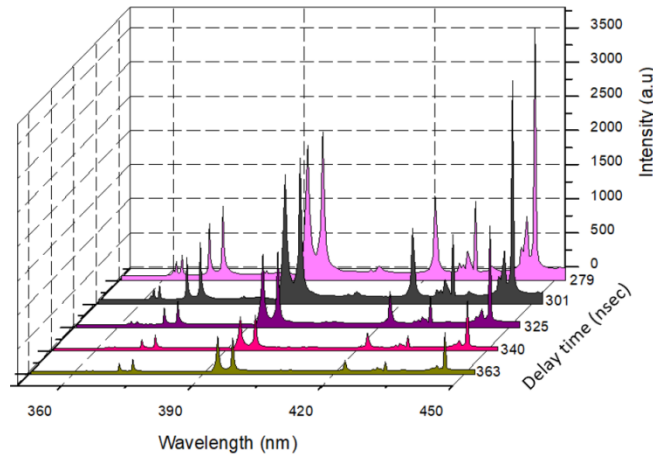


Figure 5: Three-dimensional representation of emission-line intensity as a function of wavelength and delay time.

3.4. The Electron Temperature (T_e)

Electron temperature is an important plasma parameter in Laser-Induced Breakdown Spectroscopy (LIBS) because it provides information about the excitation and thermal characteristics of the laser-induced plasma. The Q-switched Nd:YAG laser generates a high-temperature plasma in which excitation and ionization processes occur. In the present study, the electron temperature was determined using the Boltzmann plot method under the assumption of local thermodynamic equilibrium (LTE) [13].

For this work, The Boltzmann plot method was applied to the observed Ca I emission lines generated by the Nd:YAG laser. Under the

assumption of LTE, the electron temperature can be obtained from the slope of the linear relationship between the logarithmic term of the measured emission intensity and the upper-level energy. Equation (1) represents the Boltzmann plot relation [14].

$$\ln \left(\frac{I_{ij} \lambda_{ij}}{A_{ij} g_i} \right) = - \frac{E_i}{k T_e} + \ln \left(\frac{N}{Z(T_e)} \right) \quad (1)$$

where λ_{ij} is the wavelength of the transition, I_{ij} is the measured spectral-line intensity, A_{ij} is the transition probability, g_i is the statistical weight of the upper energy level, E_i is the upper-level energy, k is the Boltzmann constant, T_e is the electron temperature, N is the total number density of the emitting species, and $Z(T_e)$ is the partition

function. The Ca I emission lines at 443.49, 445.47, 526.56, 534.94, and 558.87 nm were selected for the electron-temperature determination. The calculated electron temperature decreased with increasing delay time, consistent with plasma expansion and cooling. As

shown in Fig. 6, the maximum electron temperature was 23,171.33 K for Silky White Marble at 279 ns and 16,203.78 K for Black Marble at 285 ns. A gradual decrease in temperature was observed with increasing delay time due to plasma expansion and cooling.

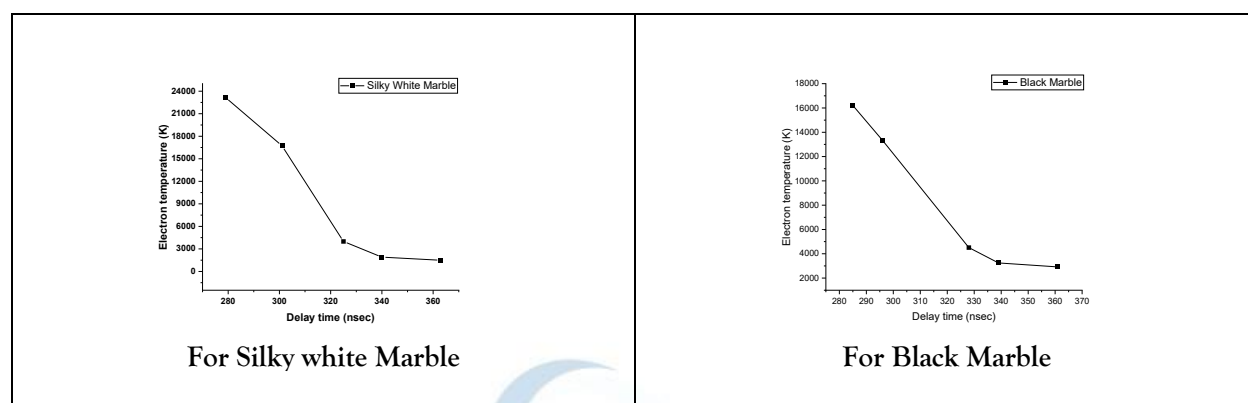


Figure 6: Variation of electron temperature with delay time for Silky White and Black Marble.

3.5 The Electron Number Density (N_e)

Electron number density is an important parameter for characterizing laser-induced plasma. In the present study, the electron number density was determined from the Stark broadening of the Ca II 393.36 nm emission line. The Stark broadening method relates the measured full width at half maximum (FWHM) of an emission line to the electron number density [15]. The corresponding relation is given in Equation (2).

$$\Delta\lambda_{FWHM} = 2\omega \left(\frac{N_e}{10^{16}} \right) \quad (2)$$

Where, N_e is the electron number density expressed in (cm^{-3}), ω is a constant called the impact parameter and $\Delta\lambda_{FWHM}$ is the Full-Width Half Maximum of the wavelength of the transition line. The FWHM was obtained by fitting the emission profile using a Lorentzian function, while the Stark broadening parameter was taken from the literature [16]. For Silky White Marble, the electron number density decreased from $8.402 \times 10^{16} \text{ cm}^{-3}$ to $6.13 \times 10^{16} \text{ cm}^{-3}$ as the delay time increased. For Black Marble, it decreased from $8.21 \times 10^{16} \text{ cm}^{-3}$ to approximately $5.99 \times 10^{16} \text{ cm}^{-3}$. The temporal variations are shown in Fig. 7.

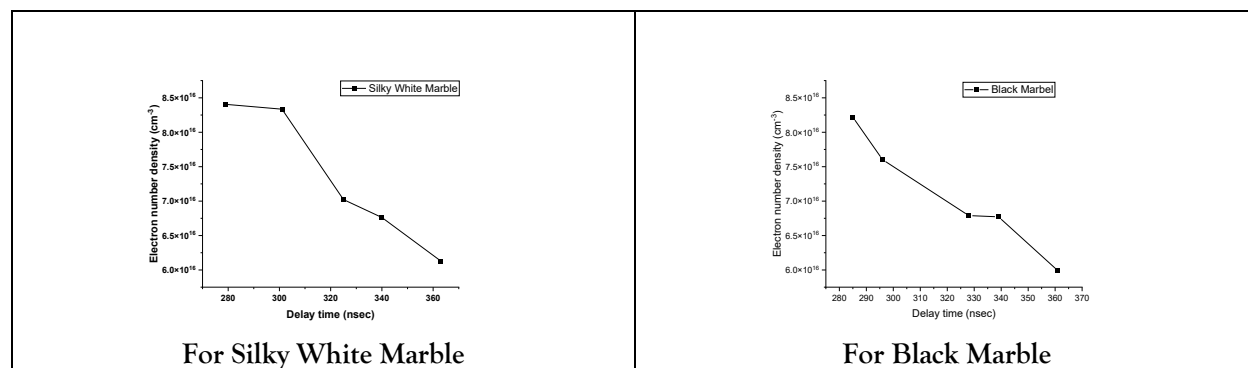


Figure 7: Variation of electron number density with delay time for Silky White and Black Marble.

3.6 Plasma Frequency

The plasma frequency is an important characteristic frequency of an electron plasma and is directly related to the electron number density. It represents the natural oscillation frequency of electrons in the plasma and can be calculated from the electron number density using Equation (3).

$$\omega_p = 9 \times 10^3 \sqrt{N_e} \quad (3)$$

where ω_p is the plasma frequency and N_e is the electron number density in cm^{-3} . For Silky White Marble, the plasma frequency decreased from 2.602×10^{12} Hz to 2.22×10^{12} Hz with increasing delay time. For Black Marble, it decreased from 2.57×10^{12} Hz to approximately 2.22×10^{12} Hz. The observed decrease in plasma frequency follows the decrease in electron number density, confirming their direct relationship. The corresponding variations are shown in Fig. 8.

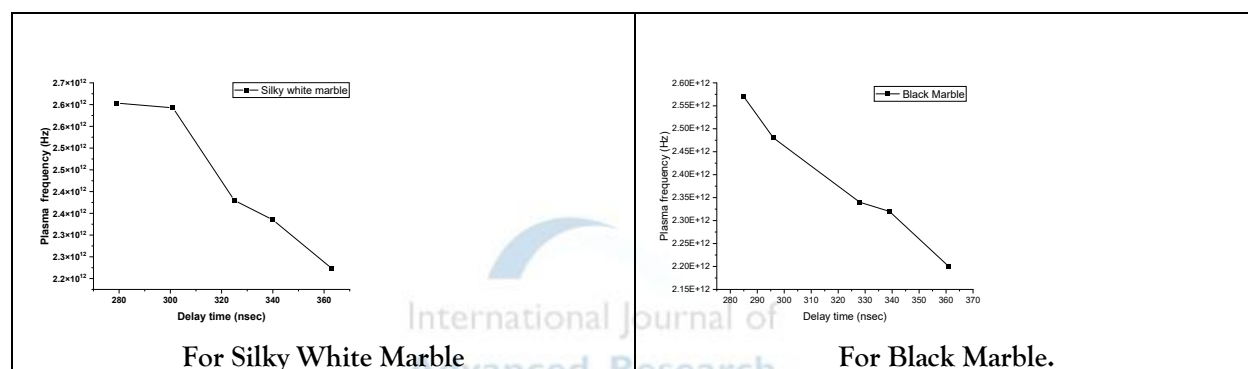


Figure 8: Variation of plasma frequency with delay time for Silky White and Black Marble.

4. Conclusion

The present study demonstrates the application of Laser-Induced Breakdown Spectroscopy (LIBS) for the elemental analysis and plasma characterization of Silky White and Black Marble. The emission spectra revealed the presence of calcium (Ca), magnesium (Mg), potassium (K), and barium (Ba) in both marble samples. The intensities of the observed emission lines generally decreased with increasing delay time, consistent with plasma expansion, cooling, and recombination processes. The electron temperature determined using the Boltzmann plot method reached maximum values of 23,171.33 K for Silky White Marble at 279 ns and 16,203.78 K for Black Marble at 285 ns. The electron number density, determined from the Stark broadening of the Ca II 393.36 nm emission line, decreased from $8.402 \times 10^{16} \text{ cm}^{-3}$ to $6.13 \times 10^{16} \text{ cm}^{-3}$ for Silky White Marble and from $8.21 \times 10^{16} \text{ cm}^{-3}$ to $5.99 \times 10^{16} \text{ cm}^{-3}$ for Black Marble. The plasma frequency also decreased with increasing delay time, from 2.602×10^{12} Hz to

2.22×10^{12} Hz for Silky White Marble and from 2.57×10^{12} Hz to approximately 2.22×10^{12} Hz for Black Marble. Overall, the results demonstrate that LIBS provides a rapid and minimally destructive approach for elemental analysis and plasma diagnostics of marble samples.

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