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**LASER INDUCED BREAKDOWN SPECTROSCOPY IN OSTRACODS AND
GEOLOGICAL SAMPLES CHEMICAL ANALYSIS FOR
PALEOENVIRONMENTAL STUDIES**

Master's Final Thesis

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Introduction

Laser-induced breakdown spectroscopy (LIBS) is a fast, minimally destructive, and versatile analytical technique used for elemental analysis of solid, liquid, and gaseous samples[1]. It works by focusing a high-energy laser pulse onto the sample surface and creating plasma that emits light characteristic of the elemental composition of the material. The advantages of LIBS include no sample preparation, real-time data acquisition, and the ability to analyze all chemical elements. LIBS has been widely applied in fields such as metallurgy, cultural heritage and industrial quality control.

Despite these advantages, improvement of signal strength and analytical sensitivity remains an active area of research[2]. Novel research strategies, such as femtosecond multi-pulse LIBS setups or femtosecond burst-mode operation have not yet been widely explored in the field, even though they have a strong potential of signal enhancement by successive pulses[3]. These strategies may be especially advantageous for geological samples due to their complex composition, where accurate trace level detection requires reduced matrix effects and high spatial resolution.

Despite its broad applicability in geology, the use of LIBS in paleoenvironmental research still remains minimal. Paleoenvironmental studies rely heavily on the chemical and isotopic analysis of natural geological remains like mollusk shells, ostracods, corals, which often contain trace elements such as Mg, Sr, Ba and rare earth metals[4]. These elements can be used as proxies for past environmental conditions, including sea surface temperature and salinity, evaluations. Traditional techniques like Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and wavelength dispersive X-ray Fluorescence (WD-XRF) dominate the field but require complex instrumentation, sample preparation and are time consuming. Thus, LIBS might be a promising alternative for paleoenvironmental applications. However, signal quality, sensitivity, and reproducibility must be improved, especially when detecting trace-level elements in heterogeneous samples.

The main aim of this work was to investigate independently controlled femtosecond double-pulse LIBS as a signal enhancement strategy for ppm-level elemental detection in geological paleoenvironmental samples. The tasks of this work:

- Optimize the inter-pulse delay, energy distribution between the two pulses, plasma gating time and ambient gas conditions (air, argon) to maximize the signal-to-noise ratio (SNR) of LIBS emission.

- Evaluate the influence of the second-pulse energy on signal enhancement by relating SNR variations to crater morphology and ablated volume, thereby separating the contributions of plasma reheating and additional ablation.
- Compare the relative SNR enhancement factors of the independently controlled fs DP-LIBS setup and commercial GHz burst-mode configuration under equal total pulse-energy conditions.
- Apply the optimized fs DP-LIBS system to stratigraphic sample series and assess the correlation of LIBS spectral signals and elemental ratios (Mg/Ca, Sr/Ca, Sr/Ba) with reference LA-ICP-MS measurements.
- Validate the semi-quantitative suitability of the method for paleoenvironmental reconstruction using internal spectral normalization, leave-one-out cross-validation, and limit-of-detection (LoD) estimation, including the weak ionic emission lines of rare-earth elements.

1 Theoretical background

1.1 Laser-induced breakdown spectroscopy

Laser-induced breakdown spectroscopy, commonly abbreviated as LIBS, is a simple and all around adaptable spectroscopic method for elemental sample analysis[5]. When laser light interacts with any type of materials, whether it is in solid, liquid or gas form, plasma is formed which can be analyzed using a spectrometer. Excited and ionized atoms from the sample contribute to specific emission lines in LIBS spectrum and by analyzing the wavelengths and intensities – specific elements can be detected. Furthermore, laser-induced breakdown spectroscopy can detect all the chemical elements, even the lightest, such as lithium, helium, oxygen and so on. In addition to this, LIBS does not require scrutinizing sample preparation, is minimally invasive and does not require long acquisition times compared to other traditional chemical analysis methods – that makes it an attractive and emerging tool for elemental analysis[6].

Another well received feature of LIBS in science and industry is its adaptability from laboratory to on-field based environments, especially for geological and environmental research and analysis[5]. It can be easily integrated into in-situ compact, portable and robust systems, that offer real time elemental detection, simply employing a diode laser and fiber optics for

light collection. Furthermore, the achievable spatial resolution of analysis can be influenced by the choice of laser pulse duration and focusing optics, which can result in micron scale high resolution mineral, coating mapping[5], [7]. Though there also exists some drawbacks to this technique, and the main one is the sensitivity or, as it is often called, limits of detection (LoD). The usual value for it is around a few parts per million and in conventional setups cannot break through into parts per billion zone[5]–[7]. That is the main reason most laboratories, specializing in elemental analysis, still prefer techniques such as Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS), Secondary Ion Mass Spectroscopy (SIMS) or X-Ray Fluorescence (XRF).

A typical laser-induced breakdown spectroscopy setup consists of five key components, which includes a laser, beam focusing optical system, plasma emission collection system, a spectrometer coupled with a detector, usually gated and ICCD (intensified CCD), and computer system for laser control and spectra readings[6]. Most common laser systems used in LIBS analysis is the classic Q-switched Nd:YAG laser with the wavelength of around 1064nm, though there also are studies, where performances of its second, third and even fourth harmonics were compared, depending on the samples in an attempt to optimize experimental conditions[8]. Such lasers can provide high pulse energies and are market-proven for their stable and reliable operation. Typical focusing system can consist of only one plano-convex, though its focal length value cannot be extremely small, since it would hinder emission collection capabilities. Though considerations must be made since the power density for plasma ignition for different samples and regimes vary – for example on metal samples in ns regime it is on the order of 10^{10} W/cm², and for dielectrics in fs regime - 10^{12} W/cm²[9]. The emission is collected with a collimating lens, typically placed at around 45 degrees angle in reference to the sample and it travels through fiber optics into spectrometers and detectors. ICCD's and CMOS detectors also have to be gated and synchronized with laser pulses, since plasma evolution is ever changing. Such typical LIBS experimental setup can be seen in Figure 1.

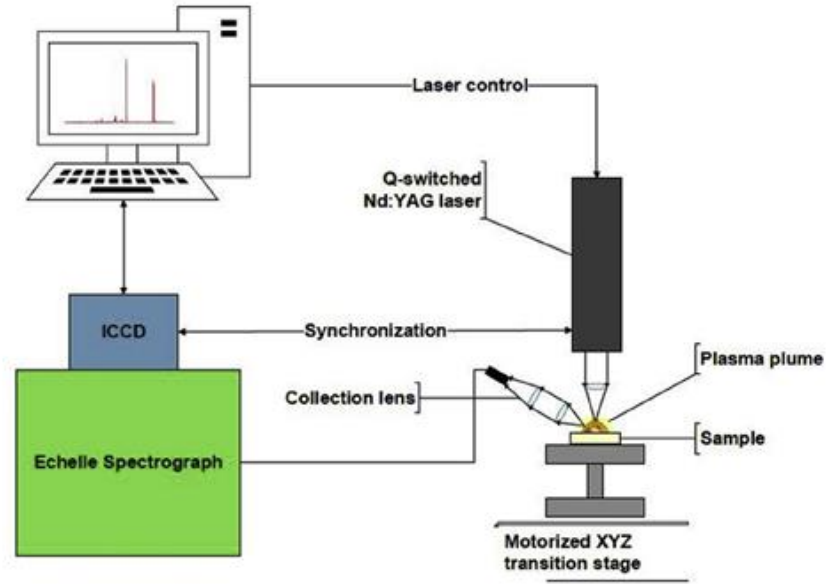


Fig. 1 Graphical depiction of simple and typical LIBS experimental setup. Figure taken from [6].

1.1.1 Pulse duration effects on laser-matter interaction and plasma physics

It is well established that nanosecond and femtosecond laser pulse-matter interaction is governed by different mechanisms[10]. While using short laser pulses (nanosecond, picosecond) the energy is deposited on the material over a comparatively long time scale, which leads to high thermal energy diffusion on the material. The ablation mechanism is attributed mainly to melting and vaporization, inducing stress, cracks and damaged zones to the surrounding areas. On the other hand, ultrashort pulses interact with matter on a different timescale: the pulse is shorter than electron-phonon interaction time, meaning ablation does not start until only after the end of laser pulse. Firstly the energy is absorbed by electron system, followed by its transmission to atoms and ions, with typical time for such system to reach thermal equilibrium being around 10 picoseconds[11]. Thus, such model, where a system is described by two distinct temperatures, is called a Two-Temperature-Model (TTM). In terms of ablation, it results in very localized and fast matter removal, leaving minimal heat affected zones (HAZ).

Speaking in terms of laser-induced breakdown spectroscopy method, ablation mechanism differences play a huge role for plasma dynamics[12][2]. When a high energy laser is focused onto a sample's surface, small spots are ablated, which through vaporization and excitation mechanisms forms a plasma plume. Depending on the laser pulse duration used, it can be heated and ionized even further to create hot plasma. After that, the plume starts to spread, cool down

and recombination mechanisms start to take part – that is where characteristic emission lines appear in LIBS spectra. Schematic representation of plasma dynamics is shown in Figure 2.

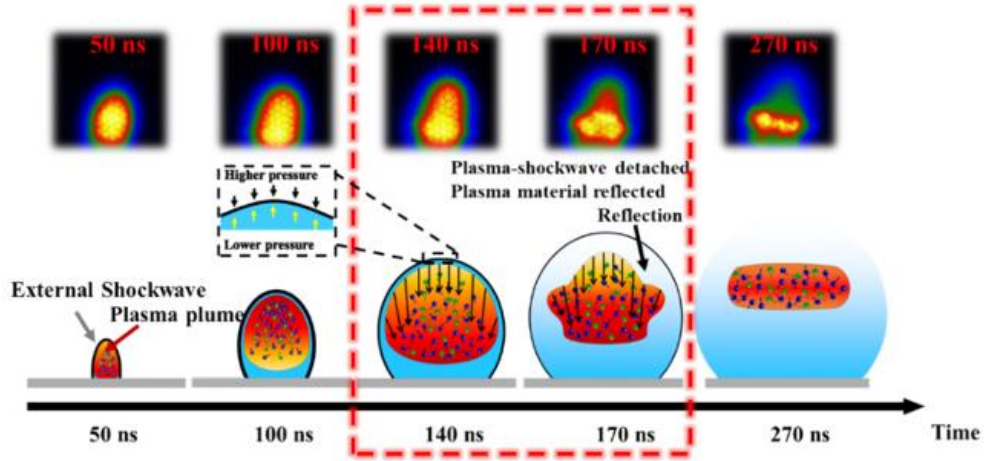


Fig. 2 Plasma expansion dynamics. Taken from [2].

When comparing LIBS generated spectra of short and ultrashort laser pulse, couple of main points can be made – the initial background continuum, and spectral line resolution. Since the trailing parts of nanosecond pulses interact with already existing plasma, it can prolong higher temperatures and higher electron densities, which can lead to higher order ionized transition lines in LIBS spectra[13]. However, this phenomenon also leads to higher background, the so-called continuum, emission, dominated by the Bremsstrahlung effect, which negatively affects the signal-to-noise ratio of spectral elements. Comparison of early-stage plasma LIBS spectra using nanosecond and femtosecond lasers on Ti sample is shown in Figure 3.

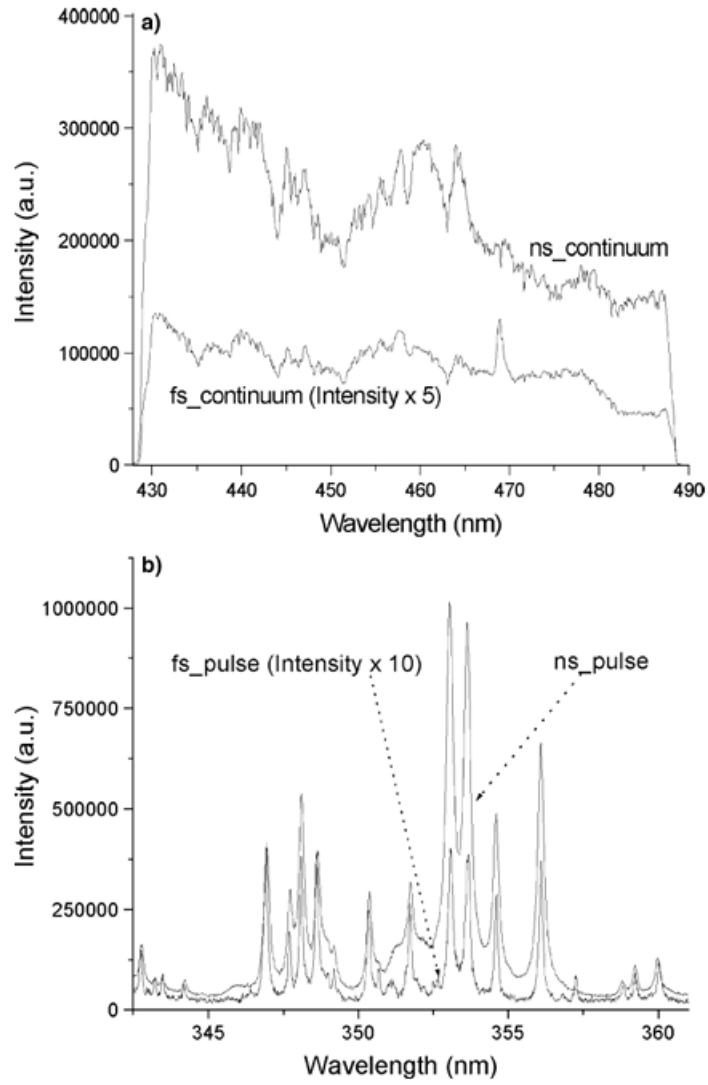


Fig. 3 a) Early stage (0 ns delay) continuum comparison employing fs and ns induced plasmas on Ti sample. b) Comparison of Ti characteristic lines from fs and ns induced plasmas. Taken from [12].

So, the femtosecond LIBS typically showcase weaker background emission, lower intensity, but higher resolution characteristic emission lines, while minimally damaging the sample. On the other hand, nanosecond LIBS can reach better sensitivity, though leading to sample modifications due to thermal energy deposition. A case can be made that ultrashort pulsed lasers are more useful for high resolution chemical analysis, whereas nanosecond laser effectiveness for simple material characterization remains unquestionable.

1.1.2 Main laser parameters for ultrashort pulse ablation

The characteristics and the efficiency of femtosecond laser ablation are strongly controlled by key, the so called working parameters such as pulse energy, repetition rate and

number of pulse per single processed spot, making their optimization an essential step in any laser micromachining task as these parameters are easily tunable in most modern femtosecond sources[14], [15].

Typically, crater sizes, in turn, ablated volumes increase with pulse energy, or fluence. As more energy exceed the ablation threshold, stronger material removal occurs[14]. A more interesting effect happens, when the number of pulses/shots per spot is increased. In such case, with increasing number, the ablation threshold is decreased through well-known incubation effect – defects, changed surface morphology, for example increased roughness, formed from primary pulses increase the absorption of the surface. And this effect is usually most pronounced in the first 100 pulses, after that, the ablation threshold is at near possible minimum.

Repetition rate also influences the ablation, though the effect is non-linear, due to the interactions between the laser pulses and ejected material/plasma[15]. At low repetition rates of around ~1kHz, plasma and other material diffuse before the successive pulse reaches the target so pulses act independently. Increasing repetition rate to the vicinity of 50 kHz can enhance the ablation due to heat accumulation and incomplete thermal relaxation between the pulse, leading to larger craters. However, if the repetition rate is increased by another order of magnitude – to a few hundred kHz, the pulses interact with dense plasma, which in turn reduces ablation efficiency and leaves rough structures on the surface.

Thus, these considerations highlight working parameters optimization necessity for controlled ablation's depth, volume and surface quality.

1.1.3 Local Thermodynamic Equilibrium

In terms of LIBS, Local Thermodynamic Equilibrium, known as LTE, is an important plasma condition, which allows us to not only qualitatively but also quantitatively analyze LIBS spectra[16]. Since laser induced plasma (LIP) evolves rapidly in temporal domain, it is not optically thick in all emissive frequencies, thus photon energies cannot be accurately described by Planck's law. Under Local Thermodynamic equilibrium state, electron velocities follow Maxwell-Boltzmann distribution, excited state populations – Boltzmann distribution and ionized states follow the Saha distribution, all at a common electron temperature. Unlike full thermodynamic equilibrium, the radiation field is not in equilibrium with plasma, because emitted photons escape from it. LTE condition is given by:

$$T_{exc} = T_e = T_H \neq T_v \quad (1)$$

T_{exc} , T_e , T_H , T_v – are respectively excitation, electron, atom/ion and photon distribution temperatures. LTE assumes that particles' collisions govern both population and depopulation of energy states and for that, the particle density must be high. Such this limit for electron density can be described by McWhirter criterion[16]:

$$n_e \geq 1.6 \cdot 10^{12} \cdot T^{1/2} \cdot \Delta E^3 \quad (2)$$

T – excitation temperature, ΔE - LTE state energy difference. Importantly, such density of electrons can only exist at short delay times after laser induced plasma ignition. When plasma expands, it cools and this density drops below thresholds, and LIBS analysis becomes very complex and inaccurate.

1.1.4 LIBS signal enhancement methods

Despite being a fast and economical chemical analysis tool, LIBS have not yet reached large commercial success because of lower measurements repeatability and accuracy when comparing to more complex methods[2]. Thus, scientists are continually seeking additional experimental LIBS signal enhancements. These include the usage of double-pulse, spark discharge assisted LIBS or choosing optimal ambient pressures.

Double-pulse method, sometimes abbreviated as DP-LIBS, usually involves two lasers pulses: one for plasma ignition and another following for plasma re-excitation[2]. Secondary pulse increases the electron density and temperature inside the plasma plume, which results in better sensitivity. Though a lot of considerations and optimization steps are necessary, since different parameters, such as each pulse time duration, wavelength and delay time between them can have significant impact on LIBS performance. Such setup also allows combining the advantages of femtosecond and nanosecond lasers: small laser ablated mass and high signal intensities (typical values in signal-to-noise ratio increase in literature is around one order of magnitude[2]), which are crucial in heterogenous sample chemical mapping.

Similarly as with the second pulse, a voltage can be applied to laser induced plasma for signal enhancement – as the plasma plume grows, it creates a closed loop for the discharge, thus plasma is re-excited[2]. This is called spark discharge LIBS (SP-LIBS). However, the temperature still cools way faster in comparison to DP-LIBS, thus signal enhancement is relatively modest.

Another signal enhancement method intensely studied by LIBS researchers, which still fails to give consistent and reproducible results, is the variation of gasses and their pressures in sampling environments. Zhang et al. investigated the effects and regularities of different atmospheric pressures on H and N atomic spectral lines' intensities and FWHM using a nanosecond laser[17]. Their finding consisted on two main results, the highest signal intensities were around atmospheric pressure of ~ 1.2 bar, because in lower pressures the overall excited species density in plasma becomes smaller leading to faster expansion and cooling – insufficient ionization. However, beyond 1.2 bar self-absorption effect started to really take place leading decreased intensities due to higher particle collisions count and reduced atomic line lifetime. The increased FWHM of H I 656 nm line from 0.5nm at 0.3 bar to 3 nm at 2.5 bar can also be attributed to the same self-absorption mentioned previously. Furthermore, higher pressures lead to rapid increase of standard deviation in FWHM, which can be attributed to a decrease in signal-to-noise ratio (SNR). Signal intensity and FWHM regularities on pressure can be seen in Figure 4.

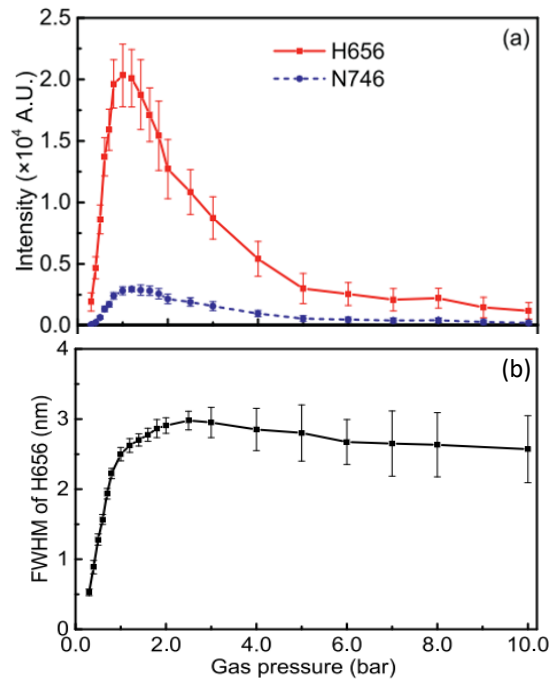


Fig. 4 Gas pressure effects on (a) peak intensity (H I 656 nm; N I 746 nm) and (b) FWHM (H I 656 nm). Taken from [17].

Another study conducted in 2013 by Nakimana et al. researched the effect of ambient conditions in fs-LIBS on Al[18]. They compared plasma parameters such as electron density and temperature using three gases: air, Ar and He. Their findings suggest that highest Al signal intensities can be achieved at pressures of around 20 mbar in all used environments, though due

to Ar characteristic of having low thermal conductivity, which sustains high plasma temperatures for longer periods of time, it yielded around 3 times stronger signals than other gases used.

1.2 Double-pulse LIBS

Double-pulse laser-induced breakdown spectroscopy (DP-LIBS) is an advanced LIBS configuration in which two laser pulses are applied sequentially with a controlled inter-pulse delay to enhance plasma emission intensity and improve analytical performance. Compared with regular - single laser pulse LIBS, DP-LIBS commonly provides higher signal intensity, improved signal-to-noise ratio (SNR) and lower limits of detection due to increased plasma temperature, electron density and ablated mass[2], [19].

The interpulse delay is one of the most critical parameters controlling signal enhancement in double-pulse LIBS, as it determines how the second laser pulse interacts with the evolving plasma generated by the first pulse. Different physical mechanisms dominate at different temporal regimes depending on the plasma density, temperature and expansion dynamics. At extremely short delays, the plasma produced by the first pulse is still highly dense and optically thick, causing strong plasma shielding effects that reduce transmission of the second pulse toward the sample surface and limit enhancement efficiency. As the plasma expands and its electron density decreases, the delayed pulse can interact more effectively with the plasma plume through inverse Bremsstrahlung absorption, resulting in plasma reheating, increased electron temperature and enhanced excitation of atomic and ionic species[19], [20].

In femtosecond DP-LIBS systems, optimal inter-pulse delays are typically observed within the picosecond to low nanosecond range because the plasma plume remains spatially confined close to the sample surface during this period[21]. Ahamer et al. reported that enhancement factors increased with interpulse delay up to approximately 200 ps and remained relatively stable for delays around 300 ps, indicating efficient energy coupling of the second pulse into the plasma[21]. The second pulse may not only simultaneously interact with the expanding plasma, but also with vaporized material and laser-generated nanoparticles, contributing to increased emission intensity. At longer delays, plasma cooling and expansion reduce the efficiency of energy transfer from the second pulse, causing the enhancement effect to decrease.

Several models describe the enhancement mechanisms associated with interpulse delay in DP-LIBS. Among the most widely accepted is the plasma reheating model, in which free electrons absorb energy from the delayed pulse via inverse Bremsstrahlung processes, increasing plasma temperature and promoting higher populations of excited states[20], [21]. The efficiency of this mechanism strongly depends on the temporal overlap between the delayed pulse and the plasma conditions required for efficient laser energy absorption.

Another important contribution arises from increased material ablation. The second pulse may interact with a molten or partially vaporized surface generated by the first pulse, producing larger crater volumes and increasing the number of emitting species within the plasma plume[19]. In femtosecond DP-LIBS, nanoparticle formation additionally influences plasma dynamics. Nanoparticles generated during the initial ablation stage can absorb energy from the second pulse and undergo atomization or ionization, further increasing optical emission intensity[21].

The geometrical configuration of the laser beams also affects enhancement behavior. DP-LIBS systems are commonly categorized into collinear and orthogonal configurations (shown in Figure 5). In collinear configurations, both pulses are directed onto the same location on the sample surface, often increasing ablation efficiency - but also enlarging crater size. In orthogonal reheating configurations, the second pulse interacts predominantly with the plasma plume rather than directly with the sample surface, emphasizing plasma reheating effects[19]. Dual-color DP-LIBS systems using different wavelengths, such as 400 nm and 800 nm, are particularly effective because plasma absorption through inverse Bremsstrahlung is generally stronger at longer wavelengths[21].

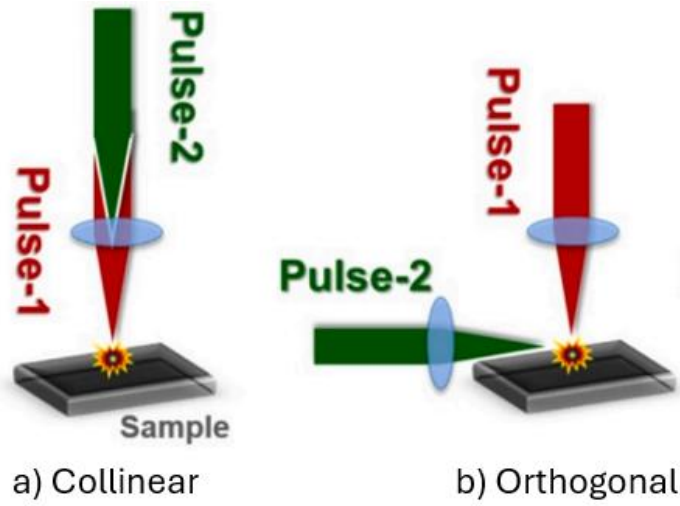


Fig. 5 Schematic diagram of typical DP-LIBS configurations: a) collinear, b) orthogonal. Taken from [19].

Another technological way to achieve double-pulse LIBS (or multi-pulse LIBS) is by the use of burst-mode laser [3]. The typical femtosecond burst-mode laser operation diagram is shown in Figure 6. Usual femtosecond lasers operate at a repetition rates from a couple of kHz to a few MHz. For example, in 100 kHz the pulses are separated by a period of 10 μ s (Figure 6, a), while burst mode allows to separate the pulses in to more sub-pulses, separated by intra-burst repetition rates. In the MHz burst, the separation is usually in the nanosecond range (Figure 6, b). The GHz regime allows even shorter – ps separation between sub-pulses (Figure 6, c). Combining these two modes, the user can achieve a Biburst (burst-in-burst) pulse structure (Figure 6, d), allowing for fine control of temporal energy distribution.

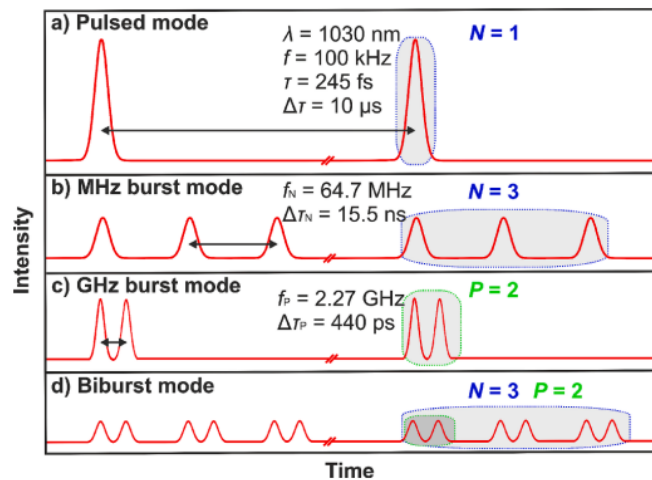


Fig. 6 Schematic diagram of femtosecond burst-mode laser operating modes (a – normal pulsed mode, b – burst MHz mode, c – burst GHz mode, d – combined burst-in-burst mode). Taken from [22].

Overall, double-pulse LIBS provides significant advantages over single-pulse LIBS through improved emission intensity, enhanced excitation efficiency and better analytical sensitivity. Proper optimization of the inter-pulse delay conditions enables efficient plasma reheating and energy coupling effects. Due to these characteristics, DP-LIBS has become an important approach for high-sensitivity elemental analysis and applications requiring improved spatial resolution and signal quality.

1.3 Paleoenvironmental analysis

Studies of biological remains, that were preserved in sediments are recognized as key indicators for reconstructing past environmental conditions[4]. The most popular proxies are ostracods - small shells, that are very useful in freshwater environments due to their ecological diversity and wide salinity tolerance. Their carbonate shells have geochemical information that can reflect changes in temperature, salinity and redox conditions, making them valuable proxies for paleoenvironmental studies - paleolimnology and paleoclimatology.

Traditional proxies used are stable oxygen $\delta^{18}\text{O}$ and carbon $\delta^{13}\text{C}$ isotopes, along with elemental ratios such as Mg/Ca and Sr/Ca, which are commonly used in geological samples of different stratigraphic depths – corals[4], [23]. In recent years, these methods have been increasingly applied to ostracods, offering new potential for reconstructing conditions in lake systems. Mg/Ca ratios serve as proxies for bottom water temperature, while Sr/Ca ratios reflect changes in water chemistry and evaporation rates. Redox sensitive elements trace elements such as U and Mo and most of the rare earth metals can also provide insights into past oxygenation levels and water column thermal layering. Thus effective and reliable chemical analysis tools are crucial for paleoenvironmental studies.

2 Overview of the literature on LIBS optimization in paleoenvironmental studies

2.1 Standard paleoenvironmental analysis techniques

Since geochemists are mostly interested in trace element detection for past environmental condition studies, accurate and very sensitive techniques are required for sub-ppm element concentration detection. Here I am going to talk about a couple of most widely used methods[24].

Probably the most widely used technique in most of the environmental studies (rocks, earth, ocean etc.) is the Inductively-Coupled-Plasma Mass-Spectrometry (ICP-MS). A schematic depiction is shown in Fig 7. Its basic operational principle is as follows: a sample is introduced into a high-temperature argon plasma, where it is atomized and ionized. The resulting ions are then directed into a mass spectrometer, where they are separated based on their mass-to-charge ratios, allowing for the measurement of trace, low concentration with extremely high sensitivity. However, samples have to be dissolved and external standard solutions must be employed, especially for geological samples, which compositional heterogeneity is very vast.

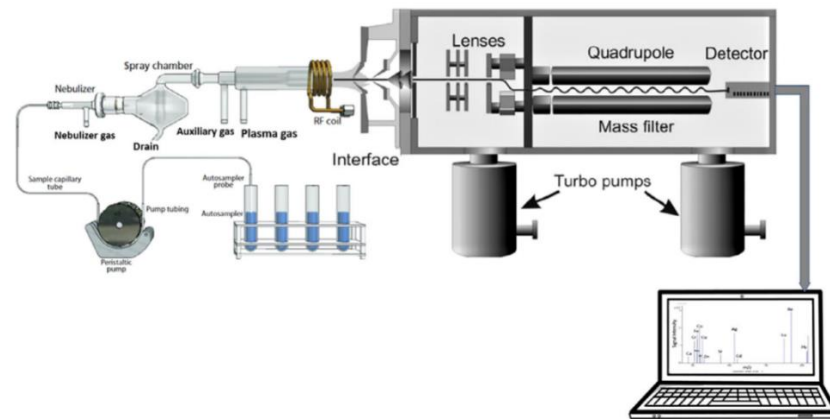


Fig. 7 Inductively coupled ion mass spectrometry typical setup. Taken from [24].

An extension of previously mentioned ICP-MS method is called Laser-Ablation Inductively-Coupled-Plasma Mass-Spectrometry. It employs a pulsed laser for sample for analyte collection, which also makes it applicable to solid samples - vast majority found in geological studies. The principle is simple: laser ablated particles are collected and transported by assist argon gas into the ICP-MS part. A huge advantage of the method is its spatial resolution capabilities, which can be determined by laser spot diameter and in-situ measurement capabilities. Principle operation setup is shown in Figure 8.

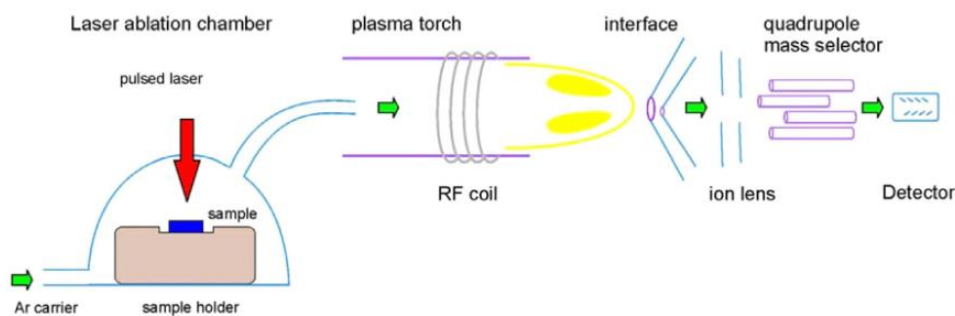


Fig. 8 Laser ablation inductively coupled ion mass spectrometry principal operation. Taken from [24].

Another widely employed method is called Wavelength Dispersive X Ray Fluorescence (WD-XRF). It is the oldest technique using X rays for chemical analysis. However, it cannot detect the lightest elements such as Li, H etc. and isotopes. It works as such: X rays are directed onto a sample, causing it to emit secondary X rays characteristic of its elemental composition, which are separated, based on Bragg's law, by wavelength using diffraction crystals and measured by detectors. Schematic representation shown in Figure 9.

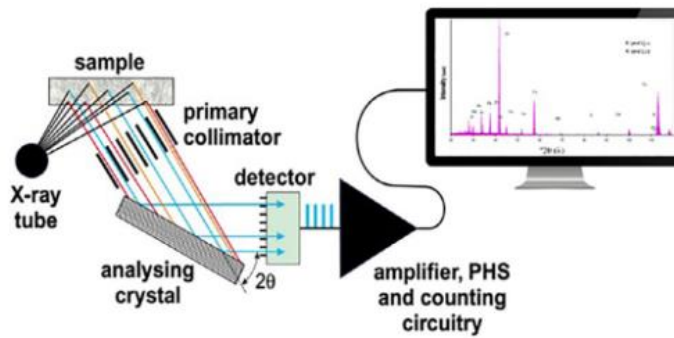


Fig. 9 Schematic picture of typical WD-XRF setup. Taken from [24].

It is obvious, that most techniques require quite complex instrumentation including ion lenses, X ray sources or assist gasses, which makes them expensive and difficult to operate. Furthermore, most of them require sample preparation, such as dissolution, thus making them a destructive method. The advantages of LIBS such as all element detectivity, fast analysis with no sample preparation required could provide a relatively cheap option for geochemical and paleoenvironmental studies[25], [26].

2.2 Double-pulse LIBS and ultrafast burst mode LIBS optimization studies

Double-pulse LIBS (DP-LIBS) is a well-established technique, with the classical ns-ns configuration being the most widely studied, where signal enhancement mainly arises from thermal plasma reheating and well-understood ablation dynamics. In contrast, fs-fs DP-LIBS is a relatively recent and less explored regime, where ultrashort pulses produce mainly non-thermal ablation and rapidly evolving plasma on sub-nanosecond timescales. This makes fs-fs schemes attractive for higher spatial precision and reduced matrix effects, but their interaction mechanisms and optimal operating conditions are still not fully understood compared to ns-ns systems.

Although relatively new, fs-fs double-pulse LIBS has been experimentally demonstrated. It is a method, which uses two or more subsequent ultrashort pulses, where first one ignites the plasma and trailing pulses re-excite it[2]. Skruibis et al. in their 2019 study of multiple-pulse

LIBS for monitoring the glass micromachining process used a beamsplitter and optical delay to achieve a sequence of femtosecond pulses[27]. They reported a maximum Na I 589 nm line signal increase of 2.5 times using multiple pulses in comparison to single pulse at 80 μ J total pulse energy, however, the groove depth did not increase significantly, meaning that the enhanced emission comes from plasma heating by subsequent pulses.

Furthermore, fs-fs DP-LIBS involves ultrafast pulse to material and pulse to plasma interactions with substantially different plasma evolution dynamics and timescales. So, in femtosecond double-pulse LIBS, there were a lot of studies done to investigate the optimal inter-pulse delay time for highest signal-to-noise (SNR) gain and the answer varies from sample to sample and environmental conditions[19]. In 2019 Wang et al. investigated glass the LIBS signal intensity of glass dependency on inter-pulse delay time in air. They observed that optimal timing was around 150 ps for an SNR enhancement of 4 times[29]. The same group using two harmonics of Ti:Sapphire laser, second for plasma reheating, found that for Fe the enhancement was and order of magnitude higher at 100 ps pulse delay in comparison to 0 ps[30]. In other studies, the optimal delay time vary from 0 ns to 1 ns, indicating, that fine tuning of this parameter for best results is important[31].

Ahamer et al. investigated signal enhancement mechanisms in femtosecond double-pulse LIBS using a dual-color configuration consisting of tightly focused 400 nm femtosecond pulses combined with delayed 800 nm pulses separated by approximately 300 ps[21]. Under optimized conditions, double-pulse excitation produced significantly higher emission intensities than single-pulse excitation. Enhancement factors depended strongly on pulse energy, reaching values between approximately 10 and 30 at low fluences and stabilizing near factors of 2-3 at higher pulse energies. Time-resolved plasma measurements showed that double-pulse plasmas exhibited elevated temperatures and electron densities during the early stages of plasma evolution. The study also examined crater morphology and nanoparticle formation, demonstrating that enhancement originated not only from plasma reheating but also from increased ablated mass and partial atomization of nanoparticles generated during the first pulse interaction.

Other studies, like Ciobotea et al. in 2024, optimized a femtosecond double-pulse LIBS setup for examining biological – liver and muscle tissues[32]. Their study showed that signal enhancement strongly depended on delay time, with biggest intensity growth occurring below 200 ps, which was followed by a broad enhancement saturation extending approximately from 200 ps to 2000 ps. Maximum enhancement was obtained near 1100 ps, where Ca II emission

increased almost five, Ca I - four and molecular bands by more than three times compared with single-pulse excitation at equivalent total energy. The authors linked this behavior to plasma plume evolution and improved coupling of the second pulse into the expanding plasma through inverse Bremsstrahlung absorption after the initial shielding phase.

Another study showcased how the SNR of LIBS emission line could be increased by an order of magnitude, while maintaining the advantages of femtosecond LIBS - spatial resolution and minimized matrix effects using a more sophisticated two laser fs-ns DP-LIBS setup. In 2020, Meng et al. used a femtosecond laser for sampling and a nanosecond for plasma reheating in the orthogonal direction[33] on Al grid sample. Using such system they managed to increase their SNR value up to 70 times higher than single pulse LIBS, while creating 500 nm wide craters. The calculated absolute limit of detection reached 20 fg and they successfully visualized the microstructures at nanometer resolution (Figure 10).

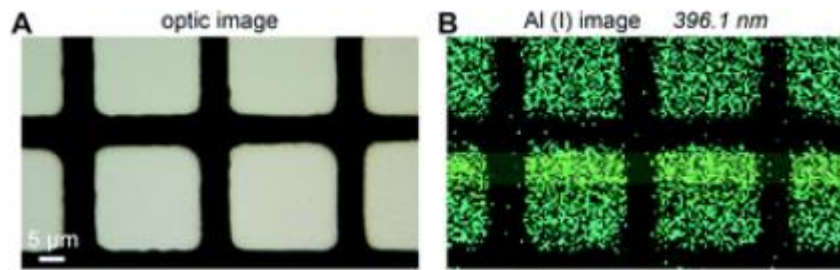


Fig. 10 Nanometer scale LIBS imaging examples of Al grid samples. Taken from [33].

Femtosecond burst mode LIBS though is a new and unexplored area with only a few studies employing real burst modes from a single laser. Noor et al. in 2025 were the first group to investigate femtosecond burst mode laser performance in GHz repetition rate pulses on stainless steel LIBS[3]. They compared different intra-burst pulse number dependence on spectral line signal to noise ratio (SNR) in the energy range from 6 to 45 $\mu\text{J}/\text{burst}$. However, they only used high number of pulses per burst, from ~ 200 to 700. The group concluded that their lowest number of intra-burst pulses lead to highest SNR, as higher number (lowest energy per pulse) lead to plasma behaving like a blackbody, which produced a broad and continuous spectra. At lower pulse number and in turn higher individual pulse energy, the plasma reached a higher temperature, enhanced ionization and produced sharp atomic and ionic emission lines (plasma temperature dependence on pulse number and energy are shown in Figure 11).

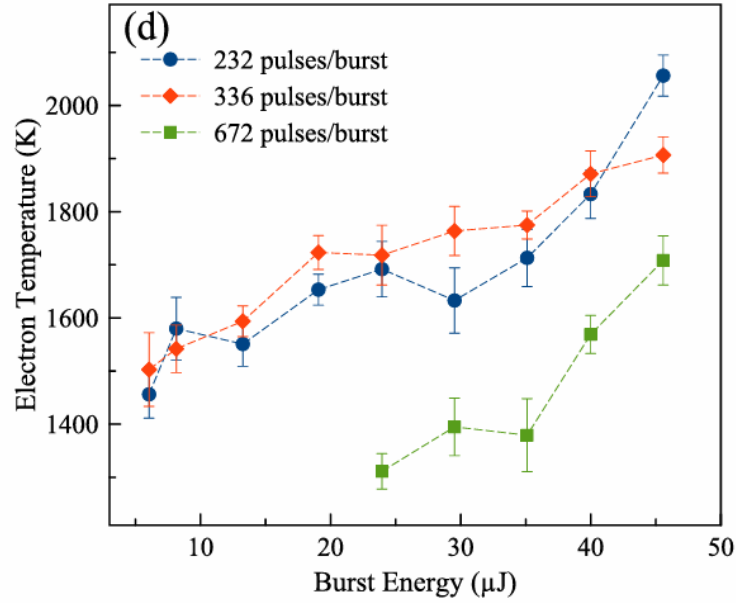


Fig. 11 Variation of plasma temperature at different intra-burst pulse number and total envelope energy. Taken from [3].

These studies suggest that multiple pulse or burst-mode LIBS can improve signal to noise ratio. While the first pulse removes the material, later pulses reheat the plasma, in turn increasing emission intensity without inducing additional thermal damage to the sample. Such method is in particularly advantageous to geological sample, where high heterogeneity could lead to enhanced matrix effects and reduced accuracy – important for paleoenvironmental analysis, where trace elements are the main interest. However, careful inter-pulse delay should be chosen for the optimal enhancement of signal and detectability.

2.3 LIBS as paleoenvironmental analysis tool

In 2007, Fabre et al. explored the potential of hypercalcified sponges as paleoenvironmental proxies using high-resolution micro laser induced breakdown spectroscopy (micro-LIBS)[25]. They investigated these samples, since they were once misclassified as corals, but exhibit distinct growth bands over time within their calcium carbonate skeletons. Micro-LIBS provided excellent spatial resolution of 5 μm and broad spectral coverage from 190 nm up to 1100 nm, allowing precise elemental mapping of Ca, Mg and Sr across growth layers – some of the most useful elements, whose ratio is used for past environmental conditions evaluation. The chemical heterogeneities seen in layers were interpreted as being time-dependent and possibly linked to seasonal or annual environmental changes such as water

temperature and chemistry (Figure 12). Thus, their results prove that LIBS could be used for elemental ratio analysis in paleoenvironmental studies context and can even provide the possibility of spatial reconstruction of marine environment with great temporal resolution.

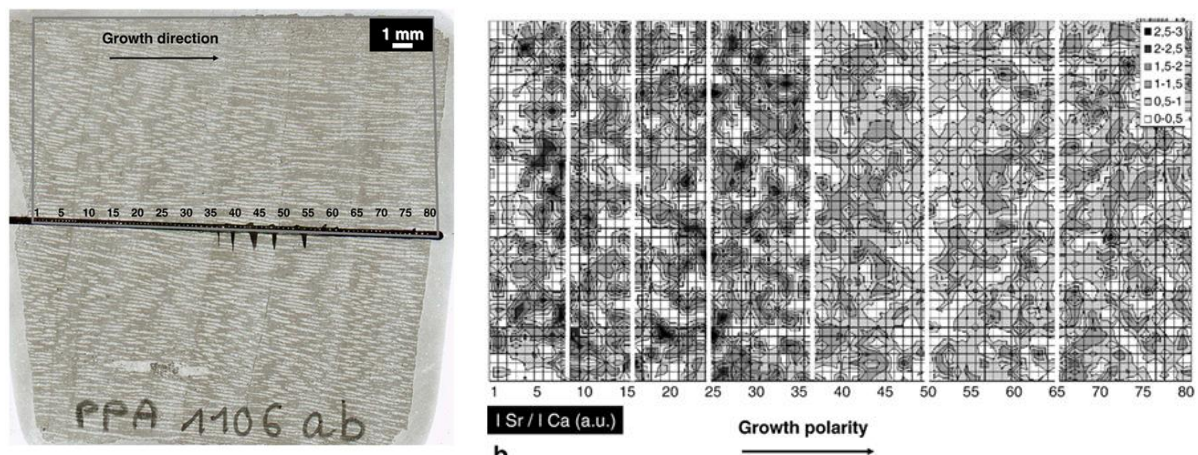


Fig. 12 (Left) Sample, with distinct growth bands, studied in Fabre et al. article. (Right) LIBS cartography of the same sample. Different shades depict different Sr/Ca ratio, indicating how water environments changed in the past. Taken from [25].

Another study, conducted by Martinez-Mincherio et al. in 2022, evaluated the effectiveness of calibration-free LIBS for Mg/Ca ratios in shells by comparing it to the standard LA-ICP-MS method. Instead of using Mg and Ca etalon samples for spectral line intensity calibration, they used Boltzmann and Saha equations, calculated electron temperature and electron density and derived elemental concentration. Results from four shells revealed a strong correlation between LIBS and LA-ICP-MS measurements – LIBS produced molar ratios with less than 10% error relative to the more established technique (Table 1). Both methods captured similar temporal patterns of shell growth, reflecting seasonal environmental changes. This work confirms, that LIBS could be employed as an efficient technique for geochemical analysis.

Table 1. Comparison of calibration-free LIBS and LA-ICP-MS results of Mg/Ca concentration ratios in Martinez-Mincherio et al. study. Taken from [26].

Sample	LAN.563	LAN.565	LAN.566	LAN.567
Maximum CF-LIBS (mmol Mg/mol Ca)	25.6	27.4	26.1	27.7
Minimum CF-LIBS (mmol Mg/mol Ca)	15.1	14.1	14.8	14.2
Maximum LA-ICP-MS (mmol Mg/mol Ca)	29.5	26.4	27.2	26.3
Minimum LA-ICP-MS (mmol Mg/mol Ca)	14.0	12.8	13.2	12.5

In the study of Ma et al., they used a conventional – nanosecond micro-LIBS system on stalagmite sample (266 nm, 5 ns pulse duration, 18 mJ per pulse) focused to a $\sim 100\ \mu\text{m}$ spot size to create elemental maps[34]. Elemental line intensities (Ca, Mg, Sr, Na, Fe, Al, Si, K) were converted into relative concentration maps, revealing chemically correlated clusters: a Ca-Mg-Sr group representing the carbonate matrix and an Fe-Al-Si group linked to clay phases - distinguishing mineralogical components spatially. They justify semi-quantitative interpretation by showing stable plasma conditions (electron density and temperature) across heterogeneous layers indicating minimal matrix effects, so intensity variations mainly reflect true compositional changes.

In 2024, Saha et al. demonstrated that femtosecond LIBS can successfully map the spatial variation of trace elements such as Mg, Sr, Si, Al, K and Na along the growth axis of a stalagmite[35]. They detected Mg/Ca and Sr/Ca ratios that aligned with carbon isotope records, indicating that femtosecond LIBS can output paleoenvironmental data with high accuracy. Furthermore, the authors noted that ultrashort pulses offer[31] high spatial resolution (in the micron range), minimal heat affected zones, and reduced matrix effects compared to longer pulse LIBS, enabling rapid, in situ analysis of complex geological samples with accuracy comparable to conventional reference methods.

Talking about LIBS performance evaluation for such applications, it is important to note that most of the articles use classical ns-LIBS studies without advanced chemometric processing and commonly report moderate quantitative performance for geological materials due to matrix effects and plasma variability. For relatively simple major and trace elements such as Ba, Sr, Mg or Ca measured in homogeneous matrices, reported correlations are typically in the range of $R^2 \sim 0.6-0.7$ [37]. In paleoenvironmental applications, elemental ratios such as Mg/Ca and Sr/Ca are often preferred over absolute line intensities because ratio-based analysis partially compensates plasma fluctuations and matrix-dependent effects, leading to more stable correlations with reference methods[38].

Rare-earth element analysis is considerably more difficult because REE emission lines are weaker and strongly affected by spectral overlap and matrix effects. As a result, univariate REE correlations in geological samples are commonly limited to approximately $R^2 \sim 0.5-0.7$ [39]. For this reason, many studies employ internal-standard normalization, lithology clustering, PCA or PLS approaches, where multiple spectral regions and sample grouping are used to compensate matrix-dependent plasma behavior and overlapping spectral features. Such approaches can increase quantitative performance to $R^2 > 0.9$ for REE analysis[40].

More recently, ultrafast double-pulse LIBS approaches have attracted attention due to their potentially reduced matrix sensitivity. Minimizing matrix effect in uranium polymetallic ores by orthogonal femtosecond-nanosecond laser induced breakdown spectroscopy demonstrated that fs-ns DP-LIBS produced lower matrix dependence and improved analytical stability compared to conventional ns excitation regimes, improving the R^2 by almost twofold - from 0.5 to 0.9[41]. These results suggest that ultrafast plasma reheating schemes may be advantageous for low-level trace-element and REE analysis in heterogeneous geological and paleoenvironmental samples.

These examples not only show, that laser induced breakdown spectroscopy offers a rapid, low-cost, and calibration independent alternative to traditional methods, but can also drive novel research in the realm of paleoenvironmental studies.

3 Experimental methodology

3.1 Setup of the experiments

Experimental setup employed in this work is depicted in Figure 13. Femtosecond Yb:KGW laser PHAROS from Light Conversion Ltd. that has the pulse width of around 250 fs at 1030 nm was focused on the sample with a 50 mm lens to induce plasma. Maximum average output power of the laser is 6W at repetition rates from 1 kHz to 1000 kHz. Beam diameter on the sample resulted in around 30 μm (measured using Liu's method[42]). The laser pulse was split using two polarization-variable beam splitters and a delay was controlled by mounting a retroreflector on a V-508 High-Precision linear motor stage from Physik Instrumente (PI), allowing precise adjustment of the optical path length and enabling delays in the 0-1 ns range.

In previous projects, we additionally employed in Femtosecond Yb:KGW laser CARBIDE with BiBurst mode from Light Conversion Ltd. that has the pulse width of around 330 fs at 1030 nm. Maximum average output power of the laser is 80W at repetition rates from 1 kHz to 40 kHz. The BiBurst mode allows to control number of pulses in GHz (440 ps) and MHz (16 ns) burst and adjust its inter-burst amplitude slope. Result with this laser are compared to double-pulse LIBS in this work.

The scanning of the samples in these measurements was realized using LIBS interaction chamber - Sci-Trace from AtomTrace Inc, which has a motorized XYZ translation stage with 5 μm minimal step width. A vacuum pump included in this chamber can also create different pressures in the sample's vicinity: from 3 to 1300 mbar. Mechelle ME5000 spectrograph

equipped with iStar ICCD 334T from Andor Technology Co. camera acquired the spectra of the plasma. These instruments have the wavelength range of 380-800 nm with spectral resolution of 0.05 nm. The ICCD camera has built-in cooling system, so during our measurements its temperature was constant at -20 °C. For the UV part of the spectra, Freedom HR-UV spectrometer was used from Ibsen Photonics, which can acquire in the range of 190 to 435 nm at 0.2 nm resolution. The acquisitions of femtosecond LIBS spectra were performed using different delays after its plasma's ignition with the use of digital delay generator AC-DDG-4 from AtomTrace Inc. which synchronizes the ICCD camera and UV spectrometer with the PHAROS laser. It provides a resolution of 10 ns and the delay between 0 and 1000 s can be achieved.

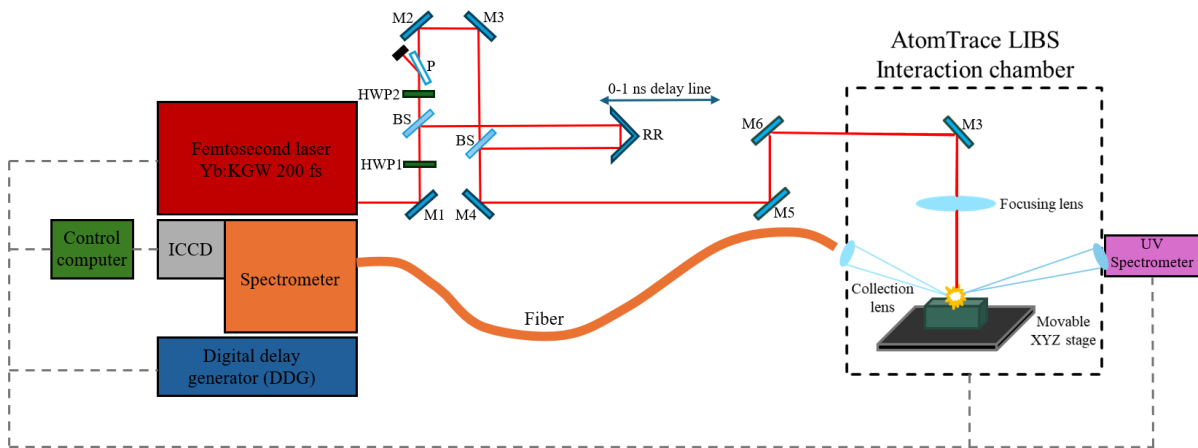


Fig. 13 Experimental setup used in LIBS experiments. M1-M6 – HR@1030nm mirrors; HWP1, HWP2 – half-wave plates, P – Brewster's polarizer, RR – retroreflector.

Laser shooting, sample moving by a motorized stage and delay generation were realized using AtomController software. AndorSolis (for VIS spectrometer) and Ibsen (for UV spectrometer) software allowed the adjustment of acquisition settings: acquisition number and exposure time, which typically were one acquisition per sampling spot and the exposure time depended on the number of pulses used per one spot on the sample surface.

The profiles of the ablated surfaces were investigated with OLS5100 from Olympus, which is a confocal laser scanning microscope. It operates at a wavelength of around 400 nm, providing a resolution of 0.03 μm with a 20 times magnifying objective and 0.012 μm at 50x objective.

3.2 Experiment conditions

To make accurate comparisons between ignited plasma spectra at different ambient pressures, instrumentation was calibrated, and similar experimental conditions were kept during the measurements. Firstly, the Mechelle spectrometer together with ICCD camera were calibrated using calibration source, a mercury lamp HG-2 (Ocean Optics) with known spectral lines. This step ensured that camera pixels were assigned to the correct wavelengths. Furthermore, relative efficiency correction between different wavelengths was performed with a continuous halogen-deuterium lamp DH-200-BAL (Ocean Optics). The room temperature was controlled using air-conditioning unit to keep it as close as possible to the calibration temperature.

Additionally, argon gas was inserted in the chamber, and 1000 mbar was used for the measurements.

3.3 Samples for the experiment

Geological samples provided by collaborators from Vilnius University, Faculty of Chemistry and Geosciences were analyzed and are referred to by their original field labels (e.g., Fröjel 1-25, MB 1-6, BLA 1-12), which denote the sampling location and individual samples of different stratigraphic depth. The material of these samples was collected from four outcrops on Gotland: Väsändeojk, Mulde Täglen-Brock, Blåhäll and Djupvik, representing Homeric strata of the Slite and Halla formations deposited in a shallow marine shelf environment. The studied rocks mainly comprise limestone, marl, marly limestone, and bioturbated argillaceous mudstones, locally containing organic-rich and bentonite-bearing intervals. LIBS measurements were carried out on the samples as received, without further preparation. Representative images of the different sample series are shown in Figure 14.



Fig. 14 Types of geological samples used in LIBS experiments for elemental composition detection.

4 Experimental results

4.1 Sample characterization

Firstly, the samples were investigated by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) method by our colleagues from Faculty of Chemistry and Geosciences, Vilnius University, which allowed us to have the correct ppm-level elemental concentrations across elements from different depths as a reference for LIBS measurements. In Tables 2-4 contains information about most paleoenvironmentally significant element concentration across every sample series used in this work, examined by LA-ICP-MS.

Table 2. LA-ICP-MS chemical analysis of Fröjel series samples. The table depicts the constituent elements and their amount in parts per million (ppm) or %.

SAMPLE	Ba	Ce	Cr	La	Nd	Sr	Ti	Zr	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
DESCRIPTION	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	%	%	%	%	%
FRÖJEL-1	318	59.5	74	31.2	23.9	181	0.41	165	46.9	13.9	5.27	9.46	5.12
FRÖJEL-2	41.9	23	11	11	9.9	879	0.06	18	5.56	1.56	1.14	50.3	1.42
FRÖJEL-3	238	53.2	56	26.2	22.4	363	0.29	124	38.1	10.9	4.26	19.25	4.68
FRÖJEL-4	285	56.8	66	29.1	23.7	254	0.36	150	43.6	12.5	5.08	13	5.08
FRÖJEL-5	275	58.3	63	29	24.5	291	0.35	143	40.6	11.8	4.81	14.15	4.78
FRÖJEL-6	297	63.7	70	31.1	27.9	153	0.39	159	47.5	14	5.49	8.92	5.41
FRÖJEL-7	272	69	75	33.7	30.7	160	0.4	146	45	14.05	6.21	9.35	5.65
FRÖJEL-8	282	71.7	67	33	32.6	191	0.36	158	45	12.65	5.45	12.15	5.76
FRÖJEL-9	265	66.4	60	29.6	27.6	163.5	0.32	154	42.7	10.7	4.5	12.65	5.86
FRÖJEL-10	210	62.5	36	26.9	28.1	306	0.24	139	33.3	7.59	2.92	22.7	5.3
FRÖJEL-11	286	64.4	78	32.1	26.8	141	0.41	155	45.9	14.25	5.83	8.34	5.4
FRÖJEL-12	736	63.3	62	29.2	28.7	226	0.34	142	44.5	11.55	5.12	12.85	6.17
FRÖJEL-13	284	66.3	73	32.9	28.6	144	0.39	151	45.4	13.45	5.57	10.25	6.06
FRÖJEL-14	168	79.8	18	29.4	34.1	183	0.15	163	29.7	3.75	2.12	27.2	7.06
FRÖJEL-15	157	74.6	20	27.3	31.5	178	0.15	163	29.9	3.7	1.91	26.6	6.74
FRÖJEL-16	266	67.2	30	26.1	31.8	221	0.2	148	33.7	5.79	2.59	22.8	6.55
FRÖJEL-17	199	70.8	31	27.8	31.6	182	0.21	172	35.6	5.56	2.4	22.3	6.39
FRÖJEL-18	271	62.5	58	28.9	28.2	157.5	0.33	151	41.5	10.4	4.53	13.3	6.59
FRÖJEL-19	199	66.6	23	25.4	30.9	178	0.16	143	35.1	5.3	2.09	23.9	6.91
FRÖJEL-20	144.5	43	13	17.4	19.3	392	0.11	76	20.5	2.86	1.08	35.1	5.24
FRÖJEL-21	196.5	57.3	29	24.1	25.6	190	0.19	115	32.6	5.73	2.69	22.6	7.62
FRÖJEL-22	117.5	35.8	10	15.6	16.1	420	0.08	72	16.9	2.52	0.9	37.4	5.44
FRÖJEL-23	124	38	10	15.7	17.4	398	0.07	44	17.4	2.57	0.87	37.6	5.15
FRÖJEL-24	114	32.7	13	15.8	13.5	359	0.09	66	16.4	2.67	1.07	36.1	5.01
FRÖJEL-25	181	23.6	10	11	10.8	470	0.06	56	14.15	1.97	0.6	40.9	4.58

Table 3. LA-ICP-MS chemical analysis of BLA series samples. The table depicts the constituent elements and their amount in parts per million (ppm) or %.

SAMPLE	Ba	Ce	Cr	La	Nd	Sr	Ti	Zr	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
DESCRIPTION	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	%	%	%	%	%
BLA-1	354	68.3	84	34.9	29.7	219	0.43	148	48.4	14.9	5.92	8.94	4.46
BLA-2	335	69.6	78	34.4	31.3	248	0.41	138	45.4	13.65	5.26	10.9	4.26
BLA-3	324	67.3	75	33.6	30.4	249	0.4	137	45.1	13.45	5.38	12.1	4.14
BLA-4	254	63.2	57	30.2	28.3	441	0.3	114	34	9.79	4.02	22	3.32
BLA-5	308	66.3	69	32.6	30.3	298	0.38	137	43.1	12.25	4.89	14.05	4.03
BLA-6	301	69.1	63	32.9	31.1	333	0.35	133	39.9	11.3	4.4	17.2	3.82
BLA-7	294	58.3	49	27.3	25.1	504	0.27	95	29.2	8.48	3.53	26.5	3.01
BLA-8	358	73	79	35.4	31.7	229	0.39	142	44.7	13.9	5.51	11.15	4.17
BLA-9	261	62.3	54	29.2	27.5	361	0.31	126	36.4	9.8	4.26	20.1	4.02
BLA-10	275	61.2	54	29.2	27.8	379	0.3	116	35.1	9.54	4.13	21.7	3.69
BLA-11	268	61.2	54	28.5	27.7	400	0.3	125	35.7	9.42	4.37	23.1	3.95
BLA-12	369	68.8	79	32.7	29.3	274	0.37	127	44.2	13.6	5.76	13.95	4.24

Table 4. LA-ICP-MS chemical analysis of BLA series samples. The table depicts the constituent elements and their amount in parts per million (ppm) or %.

SAMPLE	Ba	Ce	Cr	La	Nd	Sr	Ti	Zr	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
DESCRIPTION	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	%	%	%	%	%
MB-1	268	60.8	47	26.5	26.6	181.5	0.28	123	37.8	8.77	3.86	17.3	6.7
MB-2	293	56.4	68	28.7	23.2	138.5	0.36	153	43.9	12.15	4.83	11.4	6.21
MB-3	270	56.3	54	26.5	22	145.5	0.31	140	42	10.3	4.14	14.35	6.47
MB-4	284	60.9	69	31	25.2	134.5	0.37	152	44.1	12.7	5.3	11.1	6.29
MB-5	216	57.6	26	24	26.3	248	0.15	102	27.3	4.77	2.38	27.4	6.8
MB-6	341	53	66	27.8	22.9	142	0.35	161	40.1	11.1	4.63	12.55	6.38
MB-7	325	52.4	56	25.9	23.2	161.5	0.31	136	38.8	9.68	4.18	15.25	6.91

The optimization of the double-pulse LIBS setup parameters was initially performed by examining five randomly selected samples from the Fröjel series using single-pulse LIBS. All samples showed several strong and similar of intensity Ca spectral lines. Based on that, the Ca

I line at 616.4 nm was selected for signal-to-noise ratio (SNR) evaluation under varying experimental conditions. This particular line was chosen due to the absence of nearby interfering lines from other elements, minimizing the risk of spectral overlap.

Signal-to-noise ratio (SNR) in this work is defined as the ratio between the integrated spectral line intensity and the standard deviation of the background noise. For each selected emission line, the signal is obtained by numerical integration of the line area after local background subtraction. The noise level is evaluated from a nearby spectral region without emission lines under the same measurement conditions, where the standard deviation of the intensity is calculated. The SNR is then expressed:

$$SNR = I_{line}/\sigma_{noise} \quad (3)$$

Where I_{line} is the integrated line intensity and σ_{noise} is the standard deviation of the baseline region.

The effects of double-pulse delay, energy ratio between the pulses and plasma gating timing were systematically investigated. These optimization experiments were conducted using the Fröjel25 sample, whose characteristic spectra are presented in Figure 15.

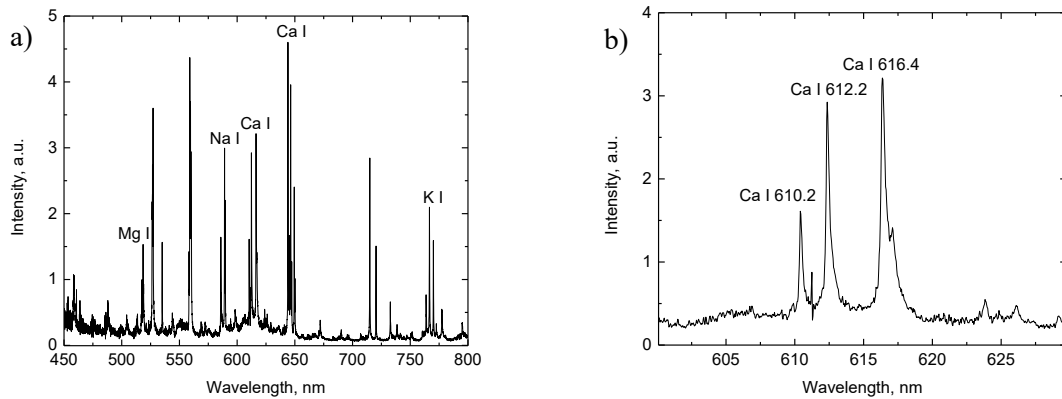


Fig. 15 a) Single pulse LIBS emission spectra of Fröjel25 sample, showing its main constituent elemental composition. b) Zoomed in fraction of the spectra, showcasing Ca I spectral lines. Spectra was acquired at 150 ns plasma gating time, geological samples of different stratigraphical depth at 150 ns delay time, using 125 $\mu\text{J/pulse}$ fluence of 35 J/cm^2 and 4000 pulses of 1030 nm laser wavelength in atmospheric pressure.

4.2 Characterization of double-pulse LIBS parameters

4.2.1 Constant total energy with varied pulse energy distribution

In the first part of the double-pulse LIBS optimization performed on the Fröjel25 sample, the total laser energy delivered by the two pulses was kept constant, while only the energy distribution between the first and second pulse was varied. The double-pulse delay was systematically adjusted from 0 ps (corresponding to a single-pulse condition where the full energy is delivered in one pulse) up to 800 ps. This delay range was selected to examine how the second pulse affects the plasma, from single-pulse conditions to cases where it reheats the already formed plasma and enhances emission intensity.

In parallel, the plasma gating delay was varied from 0 ns (the start of plasma formation) to 1 μ s in order to capture the temporal evolution of the emission signal and to identify optimal detection conditions as the plasma cools and continuum emission decreases.

The energy distribution between the two pulses was varied while maintaining a constant total average power of 300 mW at a repetition rate of 4 kHz in atmospheric pressure air. This corresponds to pulse energies ranging from 37.5 μ J/ 37.5 μ J to 15 μ J/60 μ J for the first and second pulse, respectively, where increasing the energy of the second pulse was accompanied by the decrease in the first pulse energy. Given a laser spot diameter is around 30 μ m this results in fluence values ranging from approximately 4 to 17 J/cm² depending on the pulse combination. All measurements were performed using 4000 laser shots per spot and one acquisition was averaged from 5 spots on the sample.

The results of 19 μ J/56 μ J ratio are presented in Table 5 as a heat map. The horizontal X axis represents the increasing delay between the two pulses from left to right, while the vertical Y axis shows increasing plasma gating delay from top to bottom. The color scale corresponds to the signal-to-noise ratio of the selected Ca I 616.4 nm emission line, red meaning highest SNR and green the lowest allowing visualization of how double-pulse delay and detection timing influence plasma reheating efficiency and signal enhancement.

Table 5. Signal-to-noise ratio (SNR) values for the Ca I 616.4 nm emission line obtained from the double-pulse LIBS heat map at an energy distribution of 19 μJ / 56 μJ (first/second pulse), corresponding to a fluences range of 5 J/cm^2 and 16 J/cm^2 as a function of double-pulse delay (DP delay) and plasma gating time (Gating). Measurements were acquired in air atmospheric pressure at 4 kHz repetition rate, values averaged from 4000 shots per spot, 5 different spots.

DP delay, ps \ Gating, ns	0	50	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800
0	15.0	14.0	16.8	16.0	13.4	16.9	12.5	15.5	15.7	15.2	16.0	17.0	16.6	14.1	14.6	14.4	15.9
50	33.9	30.3	32.2	24.1	30.2	30.5	34.7	39.8	38.9	34.8	32.4	43.6	36.6	31.4	32.5	37.7	41.4
100	46.0	35.8	40.0	46.1	48.1	42.7	46.0	35.3	50.6	44.9	38.1	45.9	52.1	55.2	47.8	39.7	44.7
150	33.1	28.0	46.9	35.3	49.7	50.0	44.9	50.0	49.0	50.4	42.9	56.5	53.5	52.1	48.5	48.5	51.1
200	44.6	35.1	48.6	51.8	68.7	72.6	82.0	69.6	60.9	66.0	62.5	60.6	55.8	62.5	71.2	59.3	59.0
250	21.3	25.4	28.6	30.8	29.6	36.5	49.4	44.8	44.3	36.1	34.8	49.9	48.4	46.7	59.3	49.2	42.7
300	25.8	20.9	23.0	19.3	20.9	25.5	33.3	20.4	32.3	24.0	17.5	31.1	17.4	31.9	28.1	35.5	28.1
350	15.1	12.4	20.0	16.4	18.4	17.6	18.0	22.4	23.0	24.0	14.0	27.2	20.2	21.9	20.0	19.8	18.2
400	12.1	14.2	15.2	12.0	13.1	20.1	16.1	13.3	15.2	16.1	13.7	18.5	12.4	15.8	17.4	14.3	12.4
450	6.6	10.3	9.7	11.0	9.2	12.6	11.2	14.8	11.9	9.8	12.9	17.2	11.5	15.1	12.4	15.7	14.9
500	10.6	8.2	9.2	9.2	10.2	12.8	15.3	10.6	17.6	10.2	11.6	14.1	8.2	10.3	9.1	14.3	10.7
550	6.0	5.8	9.2	8.5	9.0	9.7	12.9	8.5	13.8	8.2	5.8	10.1	10.0	11.5	12.1	14.4	13.2
600	4.9	5.9	8.0	8.4	6.5	7.0	8.7	8.2	9.6	5.6	6.7	10.9	5.5	8.8	9.9	9.3	10.6
650	3.8	6.1	8.5	6.8	8.5	6.5	7.3	8.4	10.9	9.4	8.2	11.6	7.3	9.4	7.4	11.2	5.1
700	4.7	3.3	8.1	6.4	4.1	8.0	8.1	7.9	6.3	6.2	8.5	7.2	6.1	6.9	12.2	9.0	0.1
750	2.8	3.4	5.3	3.9	7.2	7.0	7.2	8.9	5.8	6.7	5.1	8.3	5.3	9.2	7.5	8.3	3.6
800	1.9	4.1	5.2	7.2	6.9	5.0	6.7	4.7	7.5	5.0	9.1	4.7	6.3	3.7	7.2	8.9	6.6
850	4.2	4.0	4.7	1.6	5.9	5.7	4.7	7.8	6.8	5.8	3.9	5.3	6.5	7.2	8.6	10.4	7.7
900	3.2	2.2	5.4	4.0	8.3	2.6	8.2	4.4	6.8	4.8	5.6	7.6	5.3	5.2	5.5	6.3	6.0

The heat map above summarizes the signal-to-noise ratio (SNR) of the Ca I 616.4 nm emission line as a function of inter-pulse delay and plasma gating time for a fixed double-pulse energy distribution. The values in the table allow for a more quantitative identification of the optimal experimental conditions.

A clear dependence of the SNR on both double-pulse delay and gating time is observed. At short delays approaching the single-pulse regime, the SNR is relatively low, indicating that the second pulse does not significantly contribute to plasma reheating. As the delay increases, the SNR increases strongly, reaching a maximum at intermediate delay values. This behavior indicates efficient interaction between the second laser pulse and the expanding plasma plume, leading to enhanced excitation of Ca species.

Importantly, the region of maximum SNR is not confined to a single sharp point but extends over a relatively broad delay window, approximately from 300 ps up to 450 ps. Within this range, only minor variations in SNR are observed, suggesting that plasma reheating efficiency remains high and stable over a wide window. The observed behavior can be explained by the interplay between plasma reheating and temporal evolution of the plasma plume. Optimal conditions are achieved when the second pulse efficiently reheats the plasma while detection is performed after sufficient decay of the continuum background but before significant loss of atomic emission intensity.

In addition to the temporal optimization, the influence of the energy distribution between the two pulses was evaluated by averaging the SNR over the optimal delay window (300–450 ps). The corresponding results are presented in Figure 16 as a function of pulse energy ratio. The results show a clear dependence of the averaged SNR on the energy distribution. A gradual increase in signal quality is observed when the second pulse energy is increased at the expense of the first pulse, reaching a maximum for the 19 μJ / 56 μJ configuration. This suggests that plasma reheating efficiency is enhanced when a larger fraction of the total energy is delivered in the delayed pulse, which interacts more effectively with the already formed plasma plume. At very high energy asymmetries, the SNR begins to decrease, likely due to insufficient initial plasma formation by the first pulse, which reduces the effectiveness of subsequent plasma reheating.

Overall, these findings confirm that optimal LIBS performance is achieved through a combination of a relatively broad temporal window for efficient plasma reheating and a strongly weighted second-pulse energy distribution, rather than through a single narrowly defined set of parameters.

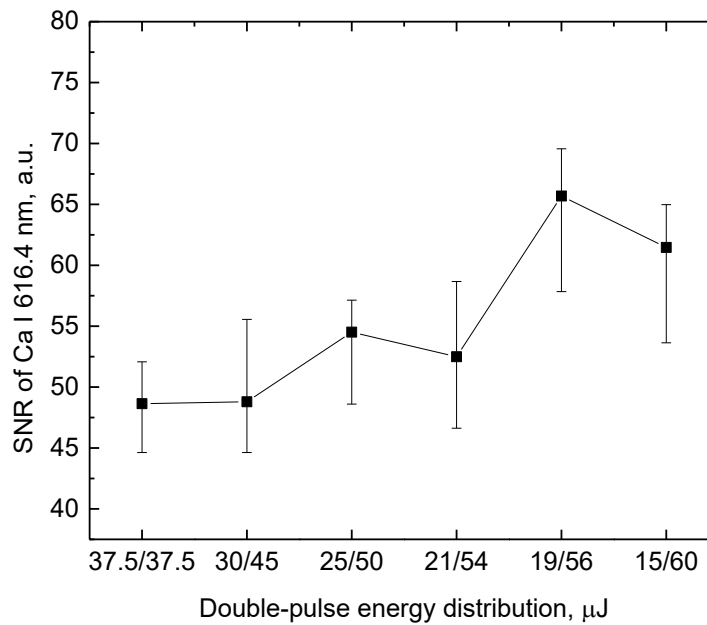


Fig. 16 Dependence of Ca I 616.4 nm emission line SNR on energy distribution between two double pulse LIBS pulses in atmospheric air pressure for a fixed total pulse energy of 75 μJ . The data represent the maximum SNR values averaged from the corresponding heat maps within the optimal double-pulse delay range of 300–450 ps.

Furthermore, the same double-pulse parameter study was performed in 1000 mbar argon atmosphere using the previously identified optimal energy distribution (19 μ J / 56 μ J). The resulting heatmap (Table 6) confirms that the overall temporal behavior remains consistent with that observed in air, with the maximum SNR again occurring at double-pulse delay of approximately 300 ps, however gating time shifted to a larger value - around 250 ns. This indicates that the optimal inter-pulse timing for plasma reheating is not largely affected by the surrounding gas environment and is governed by plasma dynamics, though the shift of optimal plasma gating time is due to the nature of argon.

In addition to the optimal temporal window, a significant enhancement in signal quality is observed under argon conditions. The maximum SNR increases from approximately 70 in air to around 115 in argon. This improvement can again be attributed to the higher mass and inert nature of argon, which reduces energy losses through molecular reactions and leads to more efficient plasma confinement. As a result, the plasma remains denser for a longer time, promoting stronger excitation and higher emission intensities.

Although the optimization procedure was primarily performed using the Ca I 616.4 nm transition due to its high signal stability and strong emission intensity, additional evaluation using the Mg I 518.5 nm line showed a similar broad optimum region under the same set of double-pulse delay and plasma gating conditions (Table 7). This suggests that the selected operating region is not exclusively specific to Ca emission alone. Nevertheless, different atomic and ionic species possess different excitation and ionization energies, and therefore the exact optimum conditions may vary for individual elements.

Based on these clear improvement in SNR, further experiments were subsequently performed in argon to exploit the enhanced signal conditions for improved analytical performance.

Table 6. Signal-to-noise ratio (SNR) values for the Ca I 616.4 nm emission line obtained from the double-pulse LIBS heat map at an energy distribution of 19 μJ / 56 μJ (first/second pulse), corresponding to a fluences range of 5 J/cm^2 and 16 J/cm^2 as a function of double-pulse delay (DP delay) and plasma gating time (Gating). Measurements were acquired in 1000 mbar argon pressure at 4 kHz repetition rate. Each heatmap value represents a single accumulated spectrum obtained from measurements across five sampling locations, with a total of 4000 laser shots accumulated per experimental condition. Values are reported with one decimal place to preserve visual contrast within the heat map and should not be interpreted as the true analytical precision of the measurements.

DP delay, ps \ Gating, ns	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300	320	340	360	380	400
0	2.6	5.2	1.7	2.2	2.4	3.2	6.6	4.6	2.2	2.7	8.6	1.6	3.5	6.1	4.5	5.5	2.7	1.1	3.6	2.0	6.1
50	25.3	24.7	17.0	21.4	22.8	22.0	26.8	26.2	17.9	24.2	19.9	24.3	17.6	20.9	21.9	24.7	24.2	22.6	20.4	20.2	18.7
100	42.4	55.3	53.7	43.3	56.2	48.4	78.8	54.9	41.8	46.7	52.7	44.6	48.9	41.5	54.3	50.5	62.3	58.1	50.6	51.9	46.2
150	50.8	55.6	65.4	72.5	57.0	75.6	58.2	79.6	70.3	64.3	65.9	88.4	69.4	54.5	60.2	78.1	65.6	61.8	62.9	70.8	70.5
200	48.3	56.9	59.1	62.3	70.6	69.9	65.3	65.5	67.2	85.1	62.1	58.7	74.6	72.5	67.1	55.4	62.9	68.4	74.8	70.8	86.2
250	69.6	71.5	85.7	84.6	97.3	110.7	84.9	103.6	92.5	88.6	113.5	109.4	112.4	108.8	125.9	103.2	126.0	115.7	109.2	99.7	109.6
300	46.8	53.4	56.0	52.0	78.4	64.2	63.0	84.6	66.3	66.8	56.8	66.6	79.3	69.7	75.8	80.0	82.1	65.1	68.9	76.6	81.1
350	21.2	30.8	36.1	39.2	42.7	45.1	40.5	44.8	46.0	44.7	45.9	44.3	49.0	49.6	40.7	52.9	41.2	38.1	45.6	41.6	50.4
400	16.5	20.3	21.1	26.8	31.8	22.0	25.3	24.7	22.1	29.2	41.8	29.7	41.1	20.7	35.2	34.7	30.8	35.2	31.9	25.5	30.0
450	15.3	13.8	17.1	23.6	18.2	19.1	23.8	19.8	20.0	19.0	23.4	20.0	30.8	30.3	28.7	29.8	30.9	29.4	27.6	20.1	21.2
500	14.9	13.5	18.1	15.8	20.3	16.7	15.6	15.9	24.0	17.2	20.3	18.0	24.4	21.1	22.3	14.4	23.3	18.5	19.8	16.2	21.0
550	5.3	12.8	13.6	19.7	17.1	11.9	14.7	12.9	20.0	19.3	17.0	15.2	23.7	18.9	18.9	17.0	12.2	18.3	14.9	12.5	14.1
600	9.6	13.4	11.5	11.4	17.1	16.1	16.1	15.8	13.5	17.6	15.6	14.6	14.4	14.8	12.8	12.8	12.8	14.8	9.3	12.4	13.2
650	4.7	8.2	7.2	10.2	15.1	15.5	10.5	15.5	10.0	14.9	11.4	9.7	10.4	11.7	11.3	12.7	15.3	13.0	11.9	12.1	14.4
700	8.9	10.1	6.9	9.7	13.0	11.6	9.1	11.2	8.0	15.2	11.0	12.8	11.5	14.1	14.6	10.2	13.8	13.9	9.2	17.0	12.4
750	3.1	7.8	7.5	10.7	11.3	7.7	8.3	13.4	16.1	13.6	10.6	13.2	9.7	10.0	11.4	6.9	14.3	10.3	11.2	8.4	10.0
800	7.8	7.4	7.8	6.6	9.6	9.9	7.5	11.1	8.0	7.9	7.2	8.4	6.1	7.6	11.1	8.3	9.6	12.4	5.8	10.7	13.2
850	7.1	3.6	10.4	7.7	9.8	8.7	6.1	6.9	7.9	10.7	11.4	14.1	13.0	11.3	14.7	11.6	10.4	6.6	10.4	11.6	
900	3.6	6.7	4.0	6.3	8.1	10.6	10.2	7.4	7.0	7.7	15.3	11.7	7.2	11.4	11.6	9.9	9.3	9.0	9.7	11.2	13.1

Highest SNR

Lowest SNR

Table 7. Signal-to-noise ratio (SNR) values for the Mg I 518.5 nm emission line obtained from the double-pulse LIBS heat map at an energy distribution of 19 μJ / 56 μJ (first/second pulse), corresponding to a fluences range of 5 J/cm^2 and 16 J/cm^2 as a function of double-pulse delay (DP delay) and plasma gating time (Gating). Measurements were acquired in 1000 mbar argon pressure at 4 kHz repetition rate. Each heatmap value represents a single accumulated spectrum obtained from measurements across five sampling locations, with a total of 4000 laser shots accumulated per experimental condition. Values are reported with one decimal place to preserve visual contrast within the heat map and should not be interpreted as the true analytical precision of the measurements.

DP delay, ps \ Gating, ns	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300	320	340	360	380	400
0	0.6	0.0	-0.8	0.0	2.9	2.5	2.8	0.9	1.3	0.6	5.3	3.1	0.2	3.5	1.4	2.4	1.9	0.8	0.7	5.4	4.0
50	3.1	4.2	1.5	3.4	2.4	3.5	6.3	4.2	3.1	2.7	8.2	1.5	4.8	4.9	5.5	6.8	3.0	1.3	3.8	2.6	4.6
100	12.6	11.3	11.9	12.9	14.2	15.3	11.8	10.9	11.4	14.8	9.5	11.4	9.3	13.0	12.4	15.1	12.2	10.7	14.9	15.2	11.2
150	13.2	14.2	13.8	18.6	17.2	17.2	15.0	17.6	17.5	12.4	15.1	18.1	14.9	19.6	14.9	16.5	25.2	16.0	21.0	13.4	16.7
200	14.3	14.9	17.6	18.2	19.7	16.3	19.2	13.7	12.4	18.8	17.5	15.9	17.3	21.4	17.3	19.4	21.6	24.3	21.2	20.1	20.2
250	13.1	11.1	18.9	15.9	15.9	20.4	16.7	12.5	15.4	16.4	17.9	19.2	21.4	16.2	25.4	20.9	21.9	20.6	20.6	20.3	17.3
300	11.3	7.8	10.3	13.1	9.9	10.8	11.5	14.8	16.1	11.7	12.5	15.5	13.6	11.2	10.5	10.6	14.7	14.8	16.7	11.4	15.5
350	4.1	5.8	5.2	5.8	5.8	7.0	5.9	4.6	6.5	5.5	6.8	6.2	6.7	6.4	6.2	8.7	6.1	9.4	6.2	4.2	8.9
400	1.1	4.1	1.9	2.3	2.0	1.4	4.3	3.6	3.8	3.3	3.6	1.0	4.5	1.9	5.1	2.7	4.0	3.4	4.4	2.9	4.1
450	1.8	1.6	1.2	2.4	4.4	2.2	1.6	2.8	2.6	2.3	2.3	2.9	0.8	0.2	5.6	3.3	2.2	2.0	4.6	2.6	2.9
500	2.8	1.8	0.6	1.0	0.8	2.6	2.0	2.4	1.7	1.8	3.6	3.9	3.1	0.9	2.4	2.9	3.3	1.2	2.0	2.8	2.0
550	4.2	0.0	5.7	0.3	3.8	1.0	0.4	1.2	0.3	2.7	1.5	0.7	3.5	4.2	3.2	-0.4	3.4	0.7	2.3	1.3	2.4
600	1.7	0.3	1.8	3.4	1.2	1.5	1.8	1.5	2.1	0.7	1.2	0.1	3.1	2.2	3.7	3.0	0.1	2.1	1.0	1.0	1.3
650	0.6	2.6	1.7	1.1	3.7	2.7	4.7	0.9	3.5	2.1	0.6	1.3	2.6	3.7	1.3	0.4	2.3	1.9	-0.5	1.4	3.1
700	0.0	1.3	1.2	1.3	2.5	3.2	1.5	1.7	1.4	4.4	0.4	1.5	0.4	1.9	2.3	2.5	2.6	0.5	1.2	4.1	2.5
750	5.0	4.0	0.0	1.1	1.4	4.2	1.7	3.8	0.9	3.4	1.8	2.1	2.7	2.3	3.1	1.6	3.5	1.5	2.3	3.5	1.3
800	-1.3	2.0	0.8	0.1	0.4	1.6	-0.7	1.6	3.7	2.7	3.6	3.5	2.3	1.2	2.0	0.5	3.8	0.8	2.5	3.0	2.6
850	4.3	2.9	2.4	-0.8	1.1	3.8	0.7	2.1	-0.4	0.6	2.1	0.4	0.4	1.1	1.9	1.8	3.0	1.4	0.8	5.1	1.7
900	1.5	-0.6	1.8	1.1	2.1	1.6	0.2	0.1	0.7	1.9	2.5	2.4	3.4	2.5	1.4	5.2	2.7	3.4	2.4	4.6	3.9
950	3.2	-0.9	0.1	1.8	3.5	0.4	2.9	2.1	1.8	0.9	5.1	2.7	-0.2	1.1	4.4	4.4	2.0	4.9	2.3	2.4	1.2

Highest SNR

Lowest SNR

4.2.2 Effect of increased second pulse energy

Based on the previous optimization experiments, the second pulse was identified as the dominant contributor to plasma reheating and signal enhancement. Therefore, further experiments were performed in argon atmosphere while maintaining the first pulse energy at 25 μJ and progressively increasing the second-pulse energy from 75 μJ to 140 μJ . This approach allows the initial ablation conditions and plasma to remain unchanged, so variations in spectral intensity can be associated primarily with the interaction of the second pulse to plasma. The double-pulse delay range was restricted to 300 - 450 ps, corresponding to the previously identified optimal reheating region. Signal enhancement was evaluated using the SNR of the same Ca I 616.4 nm emission line.

Previous experiments indicated that lower energies (~ 15 μJ) produced weaker initial plasma formation and reduced signal stability – lower SNR. Therefore, a first-pulse energy of 25 μJ was selected as a compromise between efficient plasma generation and effective coupling of the second pulse for plasma reheating.

Table 8 shows the SNR heat map obtained using a 25 μJ /113 μJ pulse energy combination in argon atmosphere, where SNR values were the best. In comparison to lower second-pulse energies, the increased reheating pulse produced a broader high-SNR region and improved overall signal intensity. The optimal plasma gate delay was observed near 250 ns, indicating prolonged plasma emission in argon atmosphere.

Table 8. Signal-to-noise ratio (SNR) values for the Ca I 616.4 nm emission line obtained from the double-pulse LIBS heat map at an energy distribution of 25 μJ / 113 μJ (first/second pulse), corresponding to a fluences range of 7 J/cm² and 32 J/cm² as a function of double-pulse delay (DP delay) and plasma gating time (Gating). Measurements were acquired in 1000 mbar argon pressure at 4 kHz repetition rate, values averaged from 4000 shots per spot, 5 different spots. Values are reported with one decimal place to preserve visual contrast within the heat map and should not be interpreted as the true analytical precision of the measurements.

DP delay, ps \ Gating, ns	300	350	400	450	
50	27.9	29.0	23.6	33.8	
75	62.1	56.1	51.9	57.7	
100	71.8	62.1	61.5	64.3	
125	74.5	80.1	83.0	90.9	
150	76.8	95.8	93.7	88.2	
175	104.7	90.0	108.3	102.9	
200	91.8	103.7	108.3	94.1	
225	103.9	126.8	119.6	130.3	
250	145.0	188.0	169.7	169.5	Highest SNR
275	143.6	158.0	160.0	145.6	
300	124.2	121.5	155.6	176.4	
325	123.3	130.0	129.4	140.1	
350	99.8	96.2	88.7	101.8	
375	80.1	108.2	119.7	100.7	
400	79.2	75.6	89.4	77.2	
425	62.0	75.2	71.3	92.4	
450	66.0	65.1	66.2	64.3	
475	50.9	63.6	47.9	60.6	
500	67.1	44.9	54.8	46.0	
525	54.8	39.0	56.9	46.7	Lowest SNR

Figure 17 shows the SNR values as a function of second pulse energy. The value is averaged from all data-points in 300-450 ps double-pulse delay range and 200-250 ns plasma gating time. The signal intensity increases with second-pulse energy up to 113 μJ , while further increases result in only marginal improvements in SNR, indicating a saturation of plasma reheating efficiency. Although higher pulse energies introduce additional energy into the system, a progressively smaller fraction is effectively coupled into excitation of emitting species, because at elevated laser energies, hot and dense plasma effects become more significant, as the dense plasma formed after the first pulse increasingly absorbs and scatters the incoming laser radiation. Additionally, stronger continuum emission and increased plasma turbulence may contribute to higher background levels, limiting further improvement of the analytical signal. Therefore, the 25/113 μJ pulse combination was selected as the optimal condition for subsequent experiments.

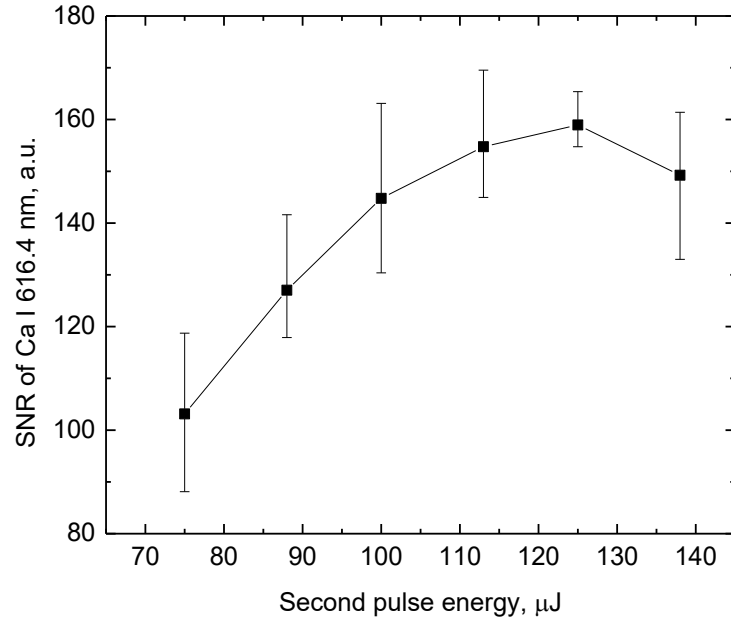


Fig. 17 Dependence of Ca I 616.4 nm emission line SNR on second pulse energy in argon atmosphere for a fixed first pulse energy of 25 μJ . The data represent the maximum SNR values extracted from the corresponding heat maps within the optimal double-pulse delay range of 300–450 ps.

To support the observed SNR trends, crater morphology and ablated volumes were analyzed for different second-pulse energies. Figure 18 presents crater profiles for selected pulse energies, while Figure 19 summarizes the corresponding ablated volume as a function of second-pulse energy.

The crater profiles indicate generally deeper ablation features at higher second-pulse energies, although noticeable shot-to-shot variability is present, likely due to the heterogeneous nature of the rock matrix and local variations in absorption and coupling efficiency. Despite this variability, an overall increase in crater depth with increasing second-pulse energy can be observed when comparing lower (75 μJ , 88 μJ) and higher (113 μJ , 138 μJ) energy conditions.

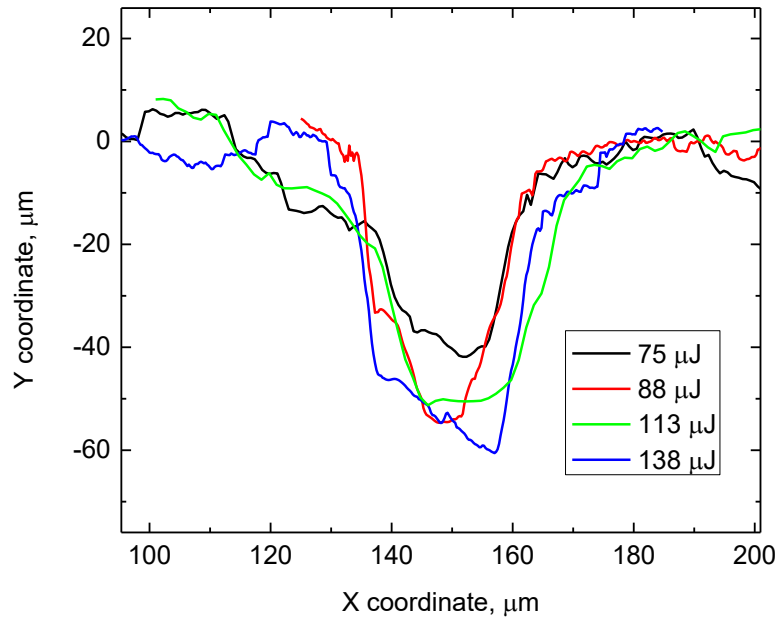


Fig. 18 2D cross-section of ablated craters using different sets of double pulse energy distribution (25 μJ / 75 μJ , 25 μJ / 88 μJ , 25 μJ / 113 μJ , 25 μJ / 138 μJ , 4000 shots per spot at 4kHz in argon.

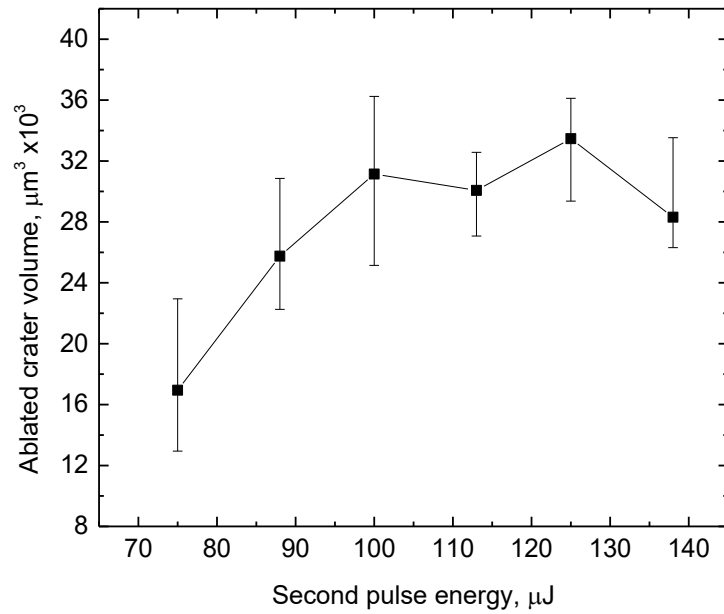


Fig. 19 Dependence of crater ablated volume on second pulse energy in argon atmosphere for a fixed first pulse energy of 25 μJ . The data represents the average ablated volume of 5 craters at 400 ps double pulse delay.

The increase in ablated volume with second-pulse energy up to 113 μJ indicates more efficient coupling of laser energy into the plasma-sample system, leading to enhanced material removal and plasma reheating. The additional SNR versus ablation volume and SNR/V over second pulse energy analyses (Figure 20) further demonstrate that the observed signal enhancement is not governed solely by increased ablated material volume. While the total SNR generally increases with second-pulse energy, the normalized SNR/V behavior shows a more complex dependence related to plasma excitation efficiency. Initially, SNR/V decreases slightly between 75 and 100 μJ , suggesting that part of the additional pulse energy is inefficiently coupled due to energy redistribution within the expanding plasma. Between approximately 100 and 125 μJ , SNR/V increases fast, indicating more effective plasma reheating and excitation enhancement beyond simple ablation increase. However, further increase in pulse energy does not result in proportional growth of either ablated volume or normalized emission efficiency. In this higher-energy regime, spectral broadening and continuum growth becomes increasingly significant, as the dense plasma formed by the first pulse absorbs and scatters a larger fraction of the incoming second pulse before it reaches the sample surface. Additionally, self-absorption of the spectral lines could start taking place. The gradual saturation behavior in SNR/V therefore suggests that the system approaches a regime where further increases in pulse energy no longer translate into substantially improved analytical performance.

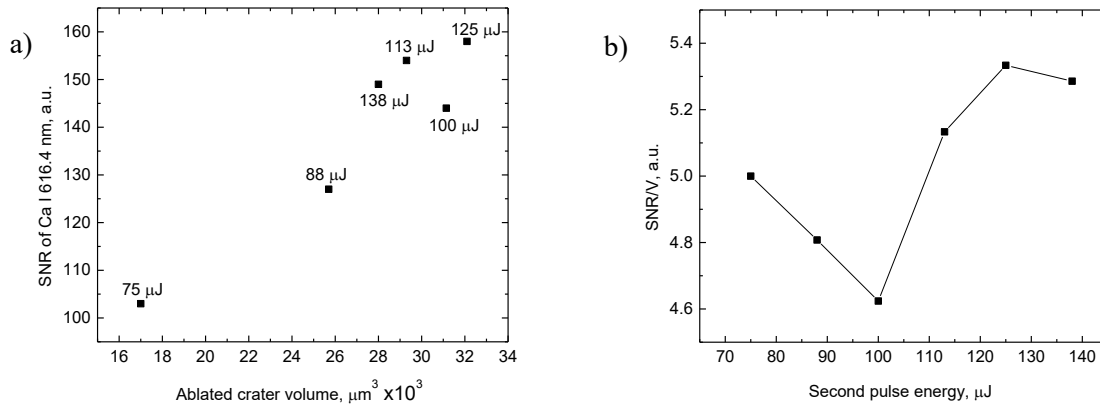


Figure 20. (a) Relationship between LIBS signal-to-noise ratio (SNR) and estimated ablation volume V for different second-pulse energies. Energy values are indicated next to the corresponding data points. (b) Dependence of normalized emission efficiency (SNR/V) on second-pulse energy.

4.3 Double-pulse LIBS comparison with GHz burst LIBS

A comparison with a previously investigated GHz burst LIBS configuration was performed in order to evaluate the relative signal enhancement achieved using different plasma reheating approaches. In the earlier work, a burst-mode laser source was employed, where each laser burst consisted of two sub-pulses separated by a fixed inter-pulse delay of 450 ps. Due to the laser architecture, the pulse energy distribution within the burst could only be adjusted within a limited range, approximately from 3:1 to 1:1, with the first pulse always remaining equal to or higher in energy than the second pulse.

In contrast, the present double-pulse LIBS setup allows independent control of both pulse energies and double-pulse delay, enabling a broader optimization of plasma reheating conditions. The optimization experiments performed in this work demonstrated that the most efficient signal enhancement was achieved using a weaker first pulse followed by a stronger second pulse, indicating that the independently controlled DP-LIBS configuration provides greater flexibility for optimization of laser-plasma coupling.

The previous GHz burst experiments were performed using the same Ca I 616.4 nm emission line as the evaluation metric, but different laser parameters, therefore, direct comparison of absolute SNR values between the two systems is not appropriate. Instead, the comparison presented in this section focuses on relative SNR enhancement factors with respect to the corresponding single-pulse LIBS measurements in both air and argon atmospheres. Full set of different parameters used in two configurations are listed in Table 9.

Table 9. Experimental parameters used for comparison of GHz burst and independently controlled double-pulse LIBS configurations.

Parameter	GHz burst LIBS	DP-LIBS
Laser architecture	GHz burst laser	Independently controlled double-pulse
Repetition rate	5 kHz	4 kHz
Inter-pulse delay	450 ps (fixed)	Optimized 300 ps - 450 ps
Investigated pulse ratios	75/25 μJ , 60/40 μJ	19/56 μJ , 25/113 μJ
Total pulse energy	100 μJ	75 μJ / 138 μJ
Fluence	$\sim 60 \text{ J/cm}^2$	25 - 40 J/cm^2
Spectra sampling number	20 spectra from 20 spots, 4000 shots per spot	20 spectra from 20 spots, 4000 shots per spot
Atmospheres	Air, Ar	Air, Ar
Spectral line used for evaluation	Ca I 616.4 nm	Ca I 616.4 nm

Figure 21 summarizes the maximum achieved SNR enhancement factors for both excitation configurations. In the GHz burst system (a), the use of argon resulted in a moderate improvement compared to air, with an overall enhancement factor of approximately 1.5 relative to the single-pulse baseline when 3/1 energy distribution between two inter-pulses was employed. In contrast, the independently controlled DP-LIBS configuration (b), evaluated under the same total pulse energy conditions as the single-pulse reference, achieved a significantly higher enhancement factor of approximately 2.5 in argon. However, it should be noted that the GHz burst and independently controlled DP-LIBS configurations were operated under different experimental conditions, including pulse fluence, repetition rate, and available pulse-energy range. Therefore, the observed differences represent performance trends under

the investigated conditions rather than a strict fundamental comparison between excitation schemes.

The improved performance of the DP-LIBS system can be attributed to its greater flexibility in controlling both double-pulse delay and pulse energy distribution. Unlike the energy ratio constraint of the burst configuration, the independently controlled system enables optimization of a weak first pulse followed by a stronger second pulse, which is more efficient for plasma reheating and excitation enhancement.

When the second-pulse energy is further increased beyond the energy of a single pulse reference, the DP-LIBS configuration enables even higher enhancement factors exceeding 3.5 (Figure 20 (b) DP-LIBS 25/113 μJ). This indicates that additional signal gain can be achieved by further strengthening the reheating pulse. This behavior shows that plasma reheating efficiency depends mainly on the second-pulse energy. A weaker first pulse helps to form the initial plasma with less shielding, while a stronger second pulse couples more effectively into the expanding plasma and improves excitation. Overall, the results highlight the benefit of independently controlling pulse timing and energy in DP-LIBS for improving laser-plasma interaction and signal enhancement, although a fully equivalent comparison between excitation regimes would require matched fluence and pulse-energy conditions.

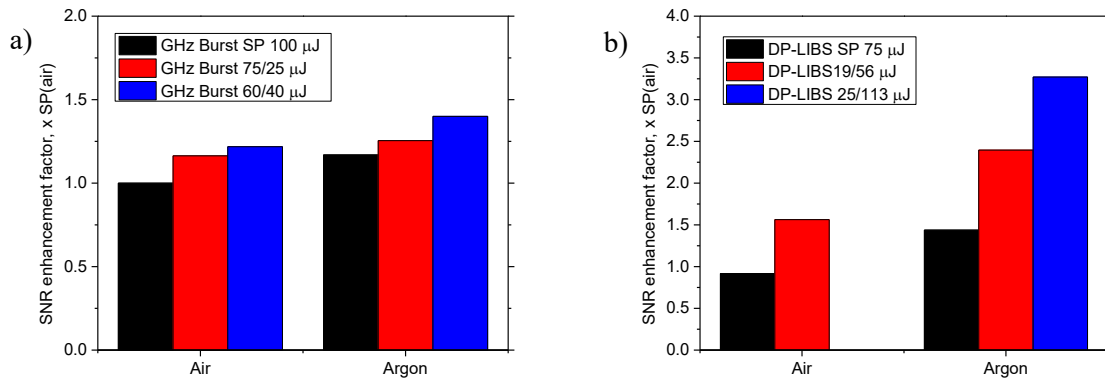


Fig. 21 SNR enhancement factors (relative to single-pulse LIBS, SP = 1) for (a) GHz burst and (b) independently controlled DP-LIBS configurations in air and argon atmospheres. Burst ratios of 75/25 μJ and 60/40 μJ and DP ratios of 19/56 μJ and 25/113 μJ are shown. Values are enhancement factors based on Ca I 616.6 nm (DP-LIBS) and K I 769.9 nm (GHz burst) emission lines.

4.4 Correlation between LIBS and ICP-MS results

The DP-LIBS measurements were further evaluated in the context of a real paleoenvironmental application by comparing LIBS spectral responses with reference LA-ICP-MS measurements obtained from the same stratigraphic series. The measurements were performed on approximately 0.5×0.5 cm sample regions by accumulating 100 spectra for each stratigraphic depth (one spectrum per 4000 pulses). Since no matrix-matched calibration standards were used, absolute LIBS intensities were not interpreted quantitatively. Instead, integrated spectral line intensities were compared with corresponding elemental concentrations obtained by LA-ICP-MS in order to evaluate whether the selected DP-LIBS measurement conditions preserve relative geochemical variations between samples. Firstly, univariate correlation analysis was performed, where each elemental signal or elemental ratio was evaluated directly from a single selected LIBS spectral line without additional normalization or multivariate chemometric processing. The correlation analysis between LIBS signals and LA-ICP-MS concentrations was performed for the most paleoenvironmentally relevant elemental ratios. This comparison provides an assessment of the applicability of fs DP-LIBS for paleoenvironmental and paleoclimate investigations.

The Figures 22-24 show the results for all investigated series for Sr/Ca, Mg/Ca and Sr/Ba ratios. In the double-Y graphs LIBS SNR and LA-ICP-MS concentrations are plotted at independent Y axes. The best previously obtained laser parameters and ambient conditions were employed: 1000 mbar argon gas vicinity, 25/113 μ J pulse energy distribution, 375 ps double-pulse delay at 250 ns plasma gating time. Correlation coefficients (R^2) (equal to squared Pearson correlation coefficient r [43]) are also shown in these graphs.

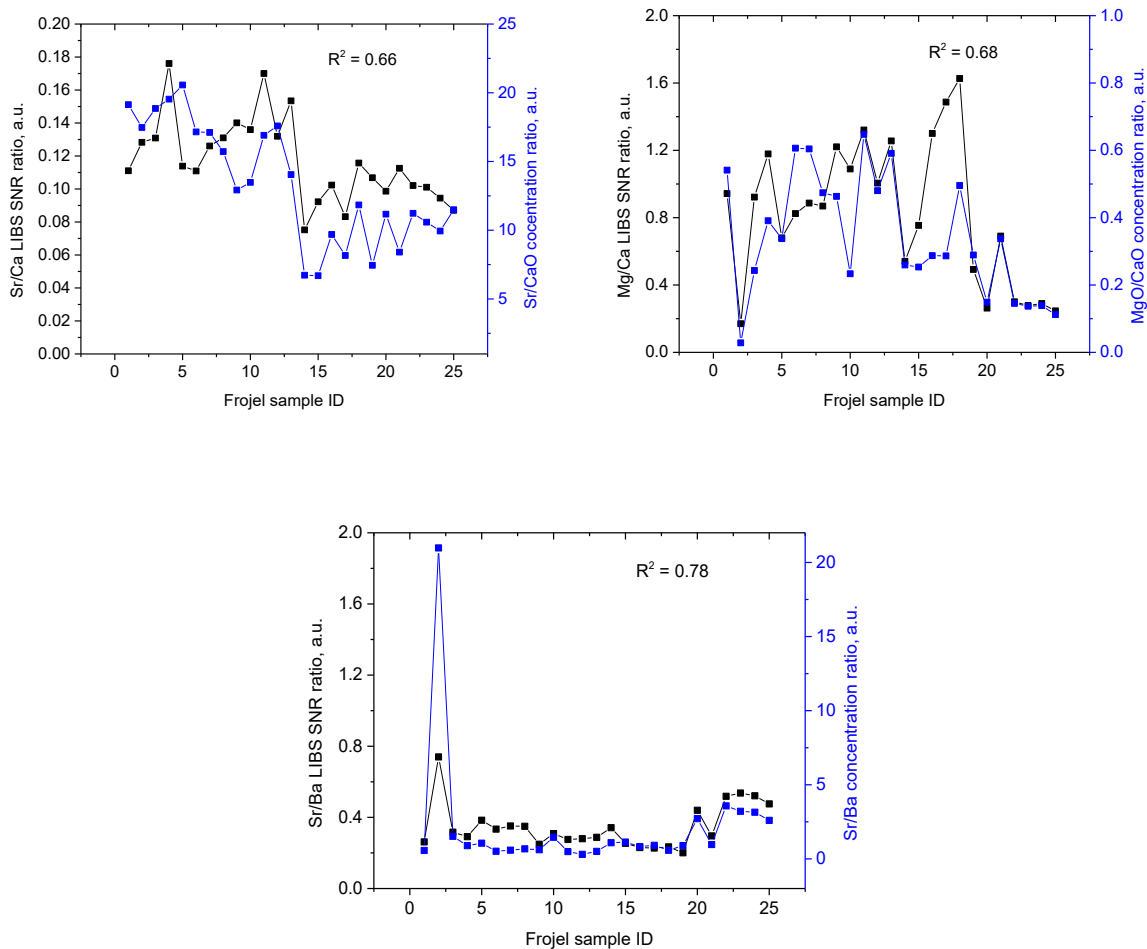


Fig. 22 DP-LIBS SNR ratio correlations to the LA-ICP-MS measured concentration values for Fröjel sample series. LIBS spectra accumulations were done in 1000 mbar argon gas vicinity, 25/113 μJ pulse energy distribution, 375 ps double-pulse delay at 250 ns plasma gating time.

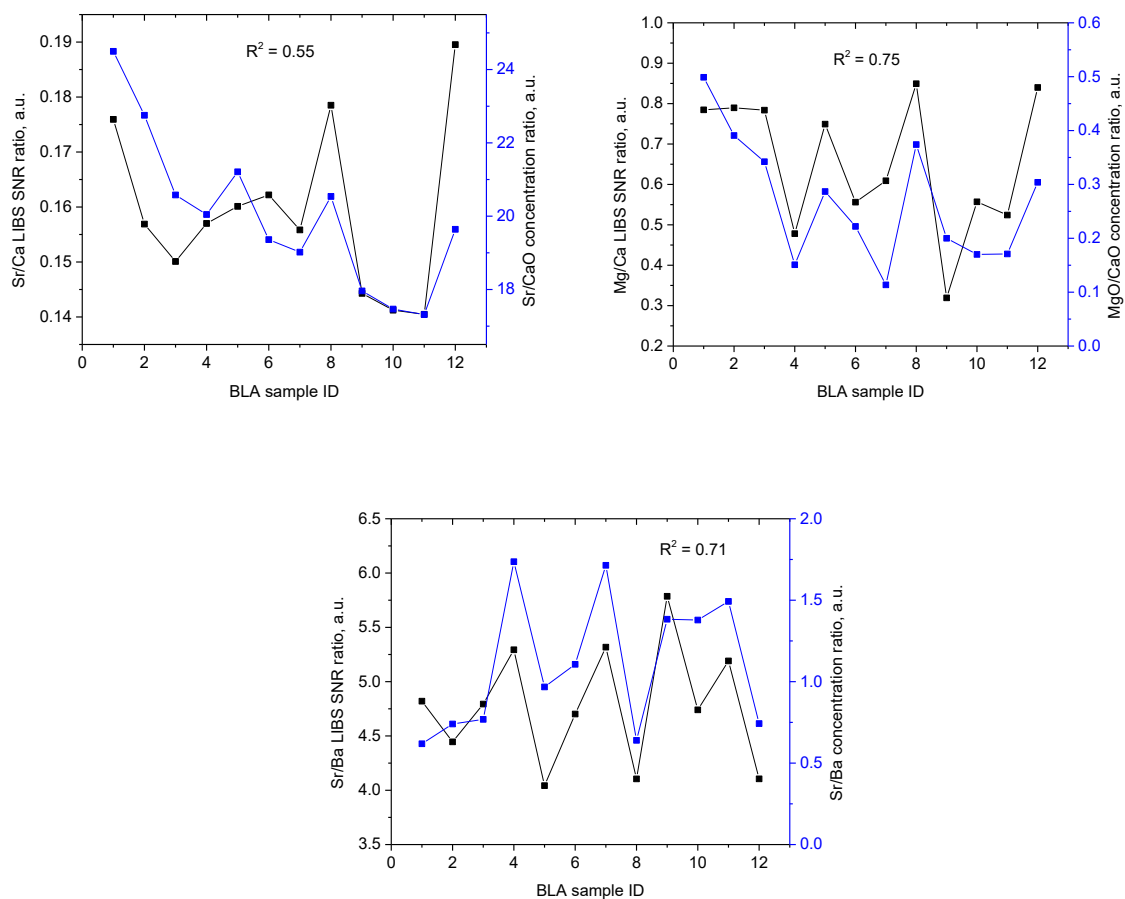


Fig. 23 DP-LIBS SNR ratio correlations to the LA-ICP-MS measured concentration values for BLA sample series. LIBS spectra accumulations were done in 1000 mbar argon gas vicinity, 25/113 μJ pulse energy distribution, 375 ps double-pulse delay at 250 ns plasma gating time.

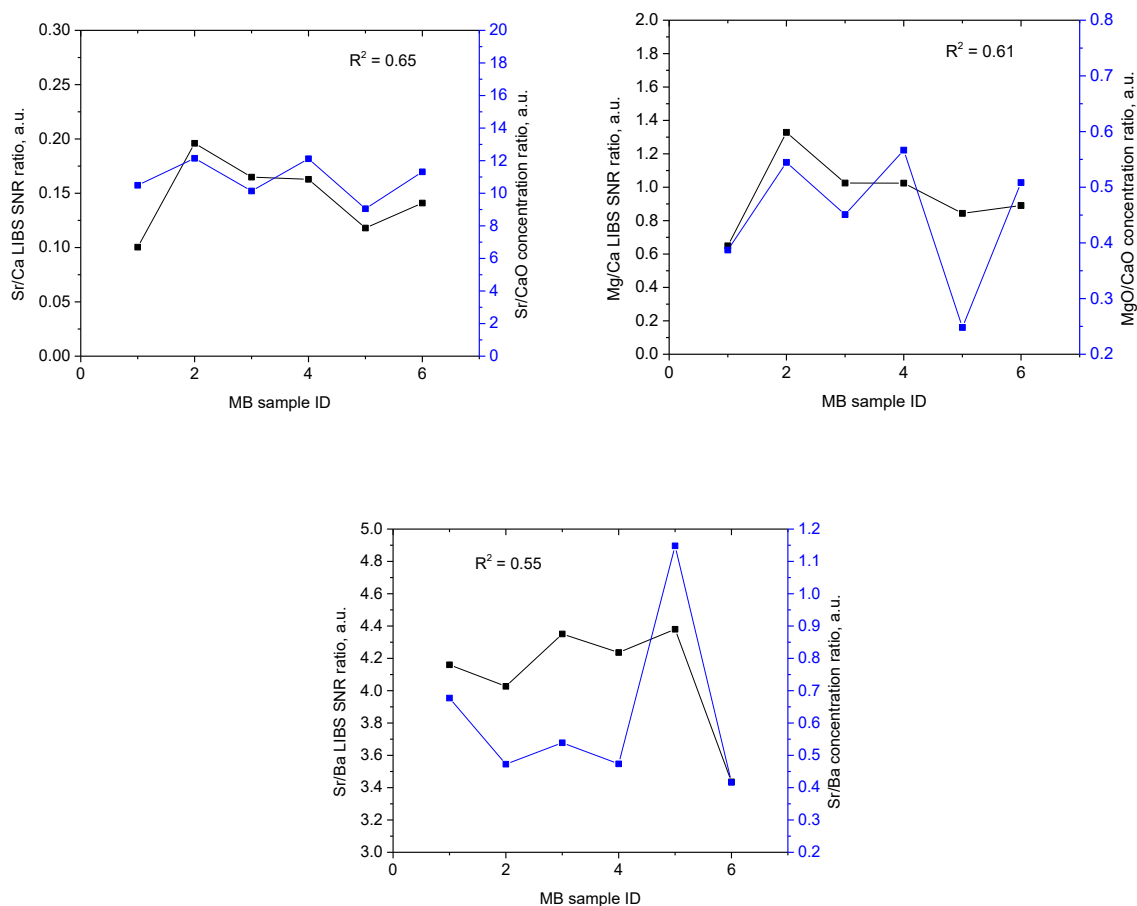


Fig. 24 DP-LIBS SNR ratio correlations to the LA-ICP-MS measured concentration values for MB sample series. LIBS spectra accumulations were done in 1000 mbar argon gas vicinity, 25/113 μ J pulse energy distribution, 375 ps double-pulse delay at 250 ns plasma gating time.

The obtained correlations between LIBS-derived SNR ratios and corresponding LA-ICP-MS elemental ratios ranged from approximately 0.55 to 0.78, with most values being close to 0.7. Considering the absence of calibration standards, complex geological matrix effects and the different physical principles of LIBS and LA-ICP-MS, these correlations indicate that ultrafast DP-LIBS measurements were capable of reproducing meaningful geochemical variations within the samples. The observed agreement suggests that the selected fs DP-LIBS conditions preserved relative paleoenvironmental trends rather than random fluctuations caused by plasma instability or surface heterogeneity. The highest correlation coefficient was obtained for the Sr/Ba ratio ($R^2 \approx 0.78$) in the Fröjel sample series. This may be related to the similar ionization behavior and spectral response of Sr and Ba lines located within a nearby visible spectral region, causing plasma fluctuations and matrix effects to partially compensate in ratio-based analysis.

Differences between the investigated series were also observed. The Fröjel dataset, which contained the largest number of samples ($n = 25$), consistently produced higher correlation coefficients than the smaller MB dataset ($n = 6$), while the BLA dataset ($n = 12$) showed intermediate behavior. This trend likely reflects a statistical sampling effect rather than limitations of the LIBS methodology itself, since larger datasets better preserve continuous stratigraphic variations and reduce the influence of local heterogeneity.

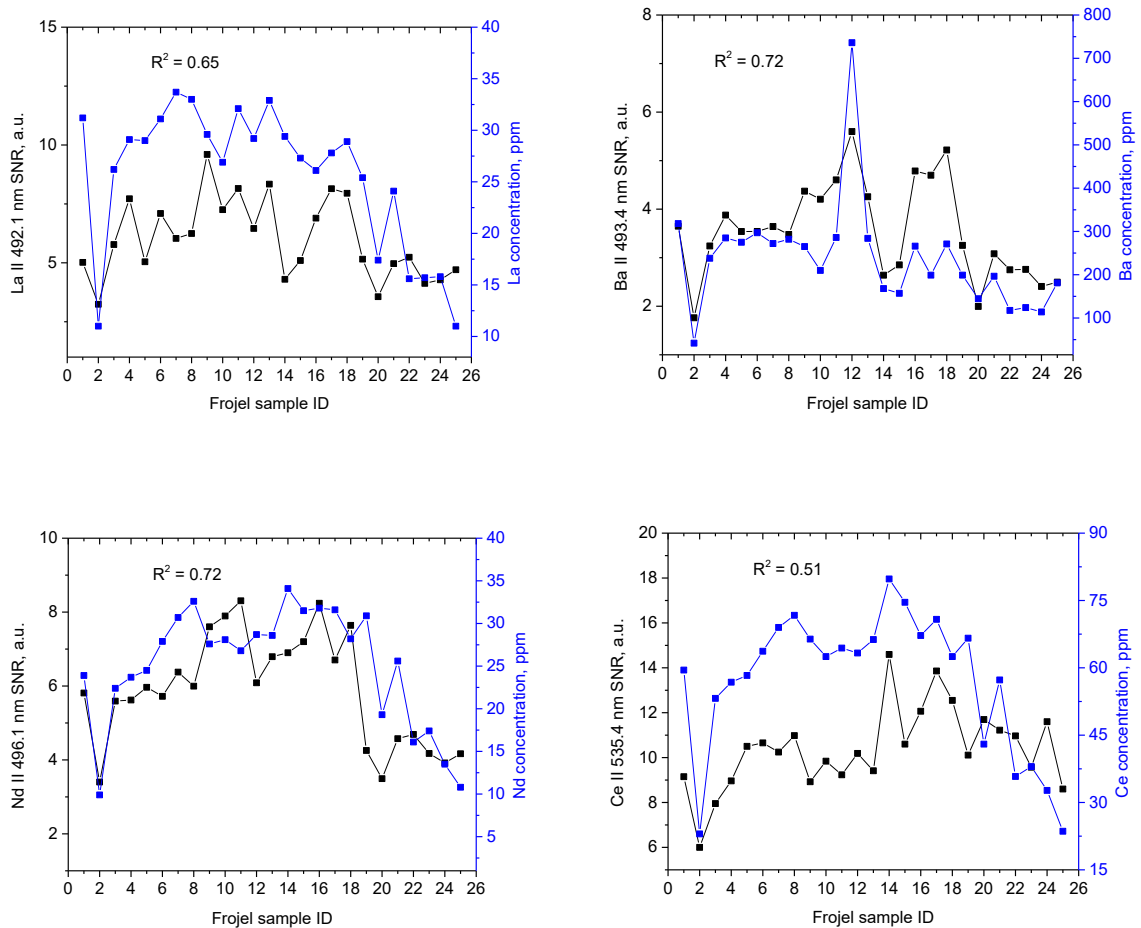


Fig. 25 DP-LIBS La, Ba, Nd, Ce correlations to the LA-ICP-MS measured concentration values for Fröjel sample series. LIBS spectra accumulations were done in 1000 mbar argon gas vicinity, 25/113 μJ pulse energy distribution, 375 ps double-pulse delay at 250 ns plasma gating time.

Despite concentrations being on the order of only a few tens of ppm, several ionized rare-element lines such as Ba II, Nd II, La II and Ce II exhibited clear spectral responses and preserved stratigraphic trends comparable to the LA-ICP-MS measurements. As shown in Figure 25, variations in LIBS spectral intensities followed similar tendencies to the corresponding reference concentrations. This is particularly important because ionized rare-earth emission lines generally require sufficiently energetic and stable plasma conditions. Their

successful detection under fs double-pulse excitation suggests that the reheating mechanism and selected double-pulse delays could sustain plasma excitation conditions favorable for low-level trace-element analysis. Importantly, these results were obtained using only univariate analysis without internal-standard normalization, lithology clustering, or multivariate chemometric approaches such as PLS, which are commonly required for reliable REE quantification in geological LIBS studies.

In several cases, these low-concentration ionized lines produced correlations comparable to ~ 0.7 or only slightly lower than those of stronger elemental signals. Furthermore, distinct spectral peaks corresponding to these species remained observable even at concentrations near ~ 20 ppm, demonstrating that the fs DP-LIBS configuration provided sufficient sensitivity for detecting weak emissions within a complex geological matrix. The agreement between LIBS and LA-ICP-MS trends indicates that the applied fs double-pulse regime was not only increasing overall signal intensity, but also improving analytical sensitivity for weak trace-element emissions relevant to paleoenvironmental interpretation.

To reduce the influence of pulse-to-pulse plasma fluctuations, variations in ablated mass and changes in overall plasma brightness, an additional internal normalization procedure was applied to the LIBS data. In this approach, integrated intensities of selected analytical emission lines were normalized to the total integrated emission intensity of the corresponding spectrum. Such normalization is commonly used in LIBS analysis to partially compensate for variations in plasma formation conditions and matrix-dependent effects, which are especially important in heterogeneous geological samples. The normalized intensity I_{norm} was calculated according to

$$I_{norm} = I_{line}/I_{total} \quad (4)$$

where I_{line} is the integrated intensity of selected spectral line and I_{total} is the total integrated emission intensity of corresponding LIBS spectra throughout the whole available spectrometer range - 400 to 800 nm. The obtained normalized values were subsequently used for recalculation of correlations with reference LA-ICP-MS elemental concentrations and elemental ratios. Results of correlation coefficient improvements are summarized in Table 10.

Table 10. Comparison of correlation coefficients (R^2) between LIBS-derived elemental ratios and corresponding LA-ICP-MS reference values obtained using univariate (Uni) and internally standardized (Int) approaches. Internal standardization was performed by normalizing spectral line intensities to the total integrated LIBS emission intensity of each spectrum. Results are presented separately for different series with varying sample numbers.

R^2	Fröjel Uni.	Fröjel Int.	BLA Uni.	BLA Int.	MB Uni.	MB Int.
Sr/Ca	0.66	0.75	0.55	0.57	0.65	0.63
Mg/Ca	0.68	0.74	0.75	0.74	0.61	0.63
Sr/Ba	0.78	0.86	0.71	0.74	0.55	0.85
La	0.65	0.74	-	-	-	-
Ba	0.72	0.88	-	-	-	-
Nd	0.72	0.81	-	-	-	-
Ce	0.51	0.75	-	-	-	-

The application of internal standardization produced systematic improvements in the obtained correlation coefficients for most investigated elemental signals and ratios. In several cases, R^2 values increased from approximately 0.55-0.7 in the univariate approach to around 0.70-0.80 after normalization, indicating that normalization to the total spectral emission successfully reduced the influence of plasma intensity fluctuations and matrix-dependent signal variability. The strongest agreement with LA-ICP-MS measurements was observed for the Fröjel dataset, where the Sr/Ba ratio reached the highest correlation coefficient of approximately $R^2 = 0.88$. This dataset also contained the largest number of samples ($n = 25$), such trends suggest that sample number and statistical representation of stratigraphic variability had a significant influence on the obtained correlations in addition to the LIBS methodology itself.

Normalization effects were particularly noticeable for weaker trace-element and ionized rare-element lines, where fluctuations in overall plasma brightness contribute more strongly to analytical uncertainty. Despite the absence of advanced chemometric processing, several elemental ratios and ionized rare-earth signals achieved correlation coefficients approaching the upper range commonly reported for LIBS analysis of heterogeneous geological materials. These results indicate that the applied fs DP-LIBS configuration together with simple internal standardization was capable of preserving meaningful paleoenvironmental geochemical trends across complex geological matrices.

Although internal standardization improved direct correlations between LIBS and LA-ICP-MS measurements, these correlations alone do not fully represent predictive capability of the correlation model, since the same dataset is used both for calibration and evaluation. Therefore, leave-one-out cross-validation (LOO-CV) was additionally employed in order to

assess robustness of the obtained relationships and estimate predictive performance for unseen samples[44]. In the LOO procedure, individual samples are sequentially removed from the dataset, calibration coefficients are recalculated using the remaining samples and the excluded sample concentration is predicted independently.

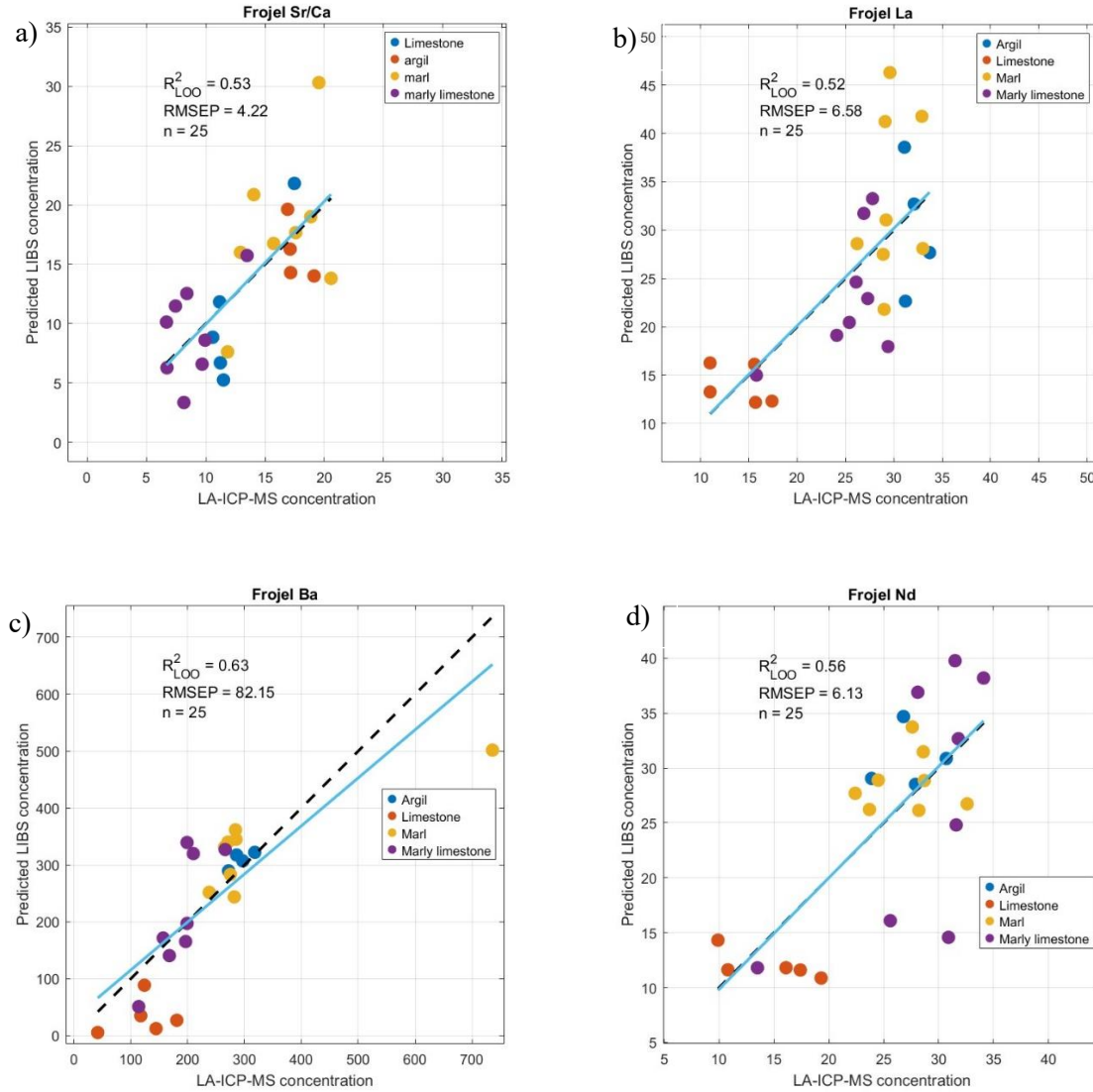


Figure 26. Leave-one-out cross-validation (LOO-CV) results for internally standardized fs DP-LIBS measurements compared with corresponding LA-ICP-MS reference data for (a) Sr/Ca, (b) La, (c) Ba and (d) Nd. The dashed y=x line represents ideal agreement between predicted and reference values, while the solid line shows linear regression of the predicted concentrations. Correlation coefficients obtained from LOO validation (R^2_{LOO}), root mean square prediction errors (RMSEP) and sample numbers (n) are indicated in each graph. Points are colored according to lithology in order to visualize possible matrix-dependent variations.

The leave-one-out cross-validation (LOO-CV) results shown in the Figure 26 represent the relationship between LIBS-predicted concentrations (y-axis) and reference LA-ICP-MS measurements (x-axis) for the investigated elemental ratios. The results showed lower correlation coefficients compared to the direct calibration relationships, with most R^2_{LOO} values decreasing by approximately 0.2 after validation. This reduction is expected, since LOO-CV evaluates true predictive performance by sequentially excluding individual samples from the calibration dataset and predicting them independently, rather than testing the model on the same data used for fitting. Despite this decrease, the obtained correlation values still indicate that internally standardized fs DP-LIBS measurements retain moderate predictive capability for the investigated elemental ratios and trace-element signals. Outlier influence was assessed by leave-one-out regression, and the removal of individual sample produced R^2 variations within ± 0.07 for the Fröjel series, indicating that the reported correlations are not driven by single high-leverage points.

The corresponding root mean square prediction error (RMSEP) values were approximately in the range of 10–20% of the measured maximum measured concentration in the dataset, indicating moderate prediction uncertainty for a univariate calibration approach without matrix-matched standards or advanced chemometric modelling. The reduction in predictive performance is partially attributed to the relatively limited sample number $n = 25$ and the heterogeneous geological matrix, which increase the sensitivity of the model to individual samples and lithological variability. In particular, samples originating from different lithological groups are likely have distinct ablation behavior and plasma characteristics, which introduce matrix-dependent deviations. This is further supported by the presence of several scattered or non-clustered points in the LOO validation plots, suggesting that lithology related effects are not fully compensated by the current univariate normalization approach.

These observations highlight that while a single global calibration captures the general geochemical trend across the dataset, lithology-dependent variability may still influence individual prediction accuracy. This indicates that future improvement of quantitative performance could benefit from lithological clustering or separate calibrations for distinct compositional groups, as commonly applied in LIBS studies of heterogeneous geological materials using chemometric approaches such as partial least squares (PLS) or clustering-based processing.

The final step of interpretation is therefore based on stratigraphic reconstruction, where the agreement between LIBS-predicted and LA-ICP-MS concentration depth profiles are

evaluated to assess whether the method reliably reproduces paleoenvironmental trends through the investigated section. As shown in the stratigraphic Figure 27, both datasets exhibit coherent variations with depth, including matching peaks and overall trend directions for elements and elemental ratios. Although absolute agreement is limited by residual matrix effects and predictive uncertainty, the preservation of these relative trends demonstrates that the applied internally standardized fs DP-LIBS approach can be considered semi-quantitative, providing reliable reconstruction of geochemical variability across heterogeneous geological sequences and showing real paleoenvironmental signal.

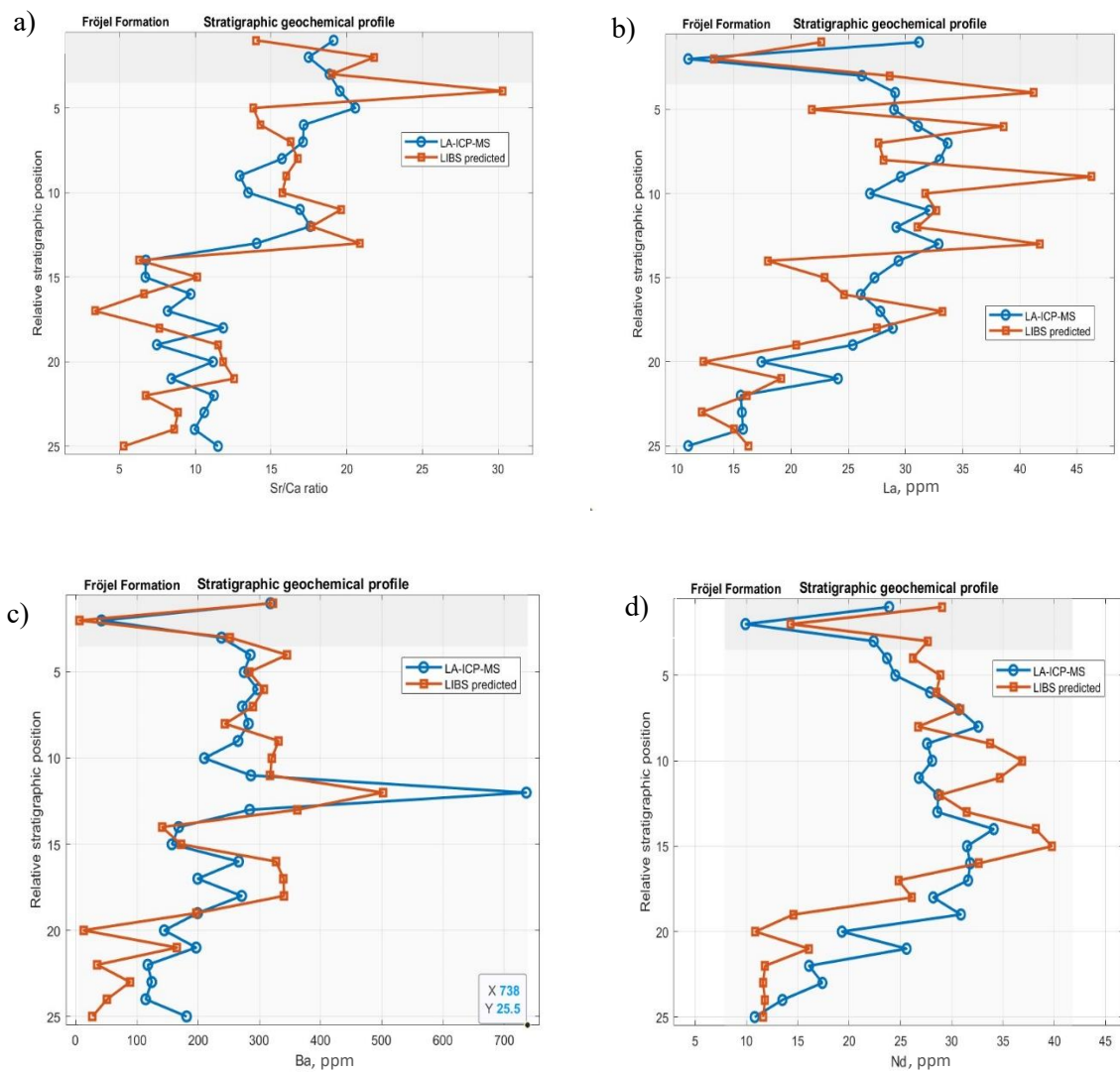


Figure 27. Stratigraphic comparison between internally standardized fs DP-LIBS measurements and reference LA-ICP-MS data for (a) Sr/Ca, (b) La, (c) Ba and (d) Nd. Profiles are plotted against relative stratigraphic position, with LA-ICP-MS values shown as reference and LIBS-predicted values obtained from the LOO cross-validation calibration model.

Estimated limits of detection (LoD) were additionally evaluated for representative major and trace-element emission lines in order to assess the practical sensitivity of the fs DP-LIBS configuration. The LoD values were estimated using the simplified relation:

$$LoD = 3\sigma_B/S \quad (5)$$

where σ_B represents the standard deviation of the local background signal near the analytical emission line and S is the slope of the corresponding LIBS versus LA-ICP-MS calibration relationship. Representative elements were selected to cover different concentration ranges and analytical significance - Sr and Ba as intermediate concentration and Nd as low-concentration rare-earth element. The LoD values for different elements are summarized in Table 11.

Table 11. Estimated limits of detection (LoD) for representative elements obtained under optimized fs DP-LIBS conditions using internally standardized LIBS signals and reference LA-ICP-MS concentrations. The slope values were determined from linear regression between LIBS signal intensity and corresponding LA-ICP-MS concentrations, while background noise (σ_B) was estimated from nearby spectral regions without emission peaks. Minimum concentrations measured in the investigated samples are also provided for comparison.

Element	Spectral line, nm	Slope, counts/ppm	σ_B	Lod, ppm	Min conc., ppm
Sr	460.7	95	725	23	141
Ba	493.5	98	631	19	41
Nd	495.9	5.5	599	327	11

The obtained LoD values demonstrate substantial differences in analytical sensitivity between the investigated elements. Sr and Ba exhibited comparatively low detection limits of approximately 20 ppm, reflecting strong ionic emission intensity and good correlation between LIBS and LA-ICP-MS data. In both cases, the estimated LoD values remained significantly below the minimum measured sample concentrations, confirming suitable sensitivity for semi-quantitative paleoenvironmental analysis. In contrast, Nd showed a substantially higher estimated LoD (~300 ppm), despite detectable spectral emission and observable sample correlations. It should be noted that the LoD values reported in Table 11 are based on the conservative univariate definition, where σ_B was estimated from the local background of the unnormalized spectra and S corresponds to the slope of the direct LIBS - LA-ICP-MS regression. This definition is well suited for major and moderately intense lines such as Sr II 460.7 nm and Ba II 493.5 nm, where it returns detection limits well below the minimum measured sample concentrations. For Nd, however, the same formula yields a LoD of ~300 ppm, which exceeds the minimum measured Nd concentration in the dataset (11 ppm) by more than an order of magnitude. This apparent contradiction with the clear Nd II 495.9 nm spectral response observed at tens of ppm (Figure 25) indicates that the unnormalized estimate

represents an upper-bound, worst-case detection limit rather than the practical sensitivity achieved after internal standardization. Such discrepancies between classical univariate LoD estimates and practical LIBS detectability have been discussed previously in the literature, particularly for heterogeneous matrices and non-ideal calibration conditions[43]. A more representative limit for Nd, recalculated from the residual standard deviation of the internally standardized LOO cross-validation model, is approximately 12 ppm (RMSEP-based), which is in better agreement with the experimentally observed LIBS response and with REE detection limits typically reported in the LIBS literature for heterogeneous geological matrices. Calculated using equation:

$$LoD_{LOO} = 3 \times RMSEP / S_{norm} \quad (6)$$

where RMSEP is the root mean square error of prediction obtained from LOO cross-validation model and S_{norm} is the slope of the internally standardized LIBS versus LA-ICP-MS regression.

Overall, the correlation analysis demonstrates that independently controlled fs double-pulse LIBS can preserve meaningful geochemical variability within complex geological samples while enhancing weak trace-element emissions. The detection of low-concentration ionized species, including Nd II and La II at levels of only a few tens of ppm, together with good agreement with LA-ICP-MS trends, supports the applicability of fs DP-LIBS for rapid paleoenvironmental investigations. The relatively broad optimum region of double-pulse delays and plasma gating conditions indicates that the configuration is robust against small experimental fluctuations and suitable for practical use rather than being highly parameter-sensitive. The leave-one-out cross-validation results confirm the semi-quantitative character of the method, showing reduced but still meaningful predictive performance under strict validation conditions. Despite this reduction, LIBS can still predict and reproduces stratigraphic geochemical trends observed in LA-ICP-MS data, confirming its applicability for paleoenvironmental reconstruction. Estimated limits of detection further showed that medium-concentration elements such as Sr and Ba can be quantified with comparatively good sensitivity, while low-concentration REEs exhibited substantially higher LoD values despite maintaining observable correlations between samples. This indicates that weak REE ionic emissions remain challenging for absolute quantitative analysis, although relative geochemical trends can still be reliably reproduced. These results further suggest that ultrashort double-pulse excitation improves not only signal intensity but also analytical sensitivity and operational stability for trace-element studies.

5 Main results and conclusions

In this work, geological speleothem samples from different stratigraphic depths were investigated using independently controlled femtosecond double-pulse LIBS with the focus on double-pulse delay, pulse energy distribution, plasma gating conditions, and ambient gas effects on trace-element detection relevant for paleoenvironmental research.

A relatively broad optimum region of approximately 300-450 ps double-pulse delays and 200-250 ns plasma gating delays was observed, indicating that fs DP-LIBS operation is comparatively robust against small experimental fluctuations.

Measurements performed in argon atmosphere increased SNR values by approximately 1.6 times compared to air due to stronger plasma confinement. Under equal total pulse energy conditions, independently controlled fs DP-LIBS achieved enhancement factors of approximately 2.5 relative to single-pulse excitation. The highest signal enhancement was further obtained when more energy was supplied in the second pulse, up to 3.5 times improvement in SNR, whereas crater morphology comparison proved additional plasma reheating - enhancement was beyond simple ablation increase.

The SNR enhancement using reheating pulse demonstrated that independently controlled fs double-pulse LIBS setup provides higher signal enhancement (~ 2.5 times) than commercial GHz burst excitation (~ 1.5 times), due to the possibility of asymmetric energy distribution between pulses under equal total pulse-energy conditions.

Correlation analysis between LIBS spectral intensities and corresponding LA-ICP-MS elemental profiles showed strong agreement, with most correlation coefficients being close to $R^2 \sim 0.7$ and reaching ~ 0.9 after internal standardization. Cross-validation reduced, but still left meaningful predictive capability and reproduced meaningful stratigraphic geochemical trends, demonstrating applicability of fs DP-LIBS for rapid paleoenvironmental investigations.

The investigated fs double-pulse regime enabled detection of low-concentration rare-element ionic lines, including Nd II and La II at concentrations with LoD on the order of several tens of ppm.

Overall, the obtained results show that independently controlled fs-fs DP-LIBS is not simply another parameter optimization approach, but a distinct ultrafast plasma excitation regime with advantages for spatially resolved trace-element analysis. The combination of broad

operating tolerances, signal enhancement and successful detection of weak ionic emissions suggests strong potential for future geological and paleoenvironmental applications.

6 References

- [1] R. S. Harmon, F. C. De Lucia, A. W. Miziolek, K. L. McNesby, R. A. Walters, and P. D. French, "Laser-induced breakdown spectroscopy (LIBS) – an emerging eld-portable sensor technology for real-time," *Geochemistry Explor. Environ. Anal.*, vol. 5, pp. 21–28, 2005.
- [2] S. Zhao, Y. Zhao, Y. Dai, Z. Liu, and X. Gao, "Spectrochimica Acta Part B : Atomic Spectroscopy Methods for optimization of the original signal in laser induced breakdown spectroscopy," *Spectrochim. Acta Part B At. Spectrosc.*, vol. 218, p. 106982, 2024.
- [3] A. Noor, E. Hasar, and P. Elahi, "Micro-laser-induced breakdown spectroscopy using GHz repetition rate pulses at nJ pulse energy," *J. Phys. Photonics*, vol. 8, no. 1, 2025.
- [4] N. Börner *et al.*, "Ostracod shell chemistry as proxy for paleoenvironmental change," *Quat. Int.*, vol. 313–314, pp. 17–37, 2013.
- [5] R. S. Harmon, R. E. Russo, and R. R. Hark, "Spectrochimica Acta Part B Applications of laser-induced breakdown spectroscopy for geochemical and environmental analysis : A comprehensive review," *Spectrochim. Acta Part B At. Spectrosc.*, vol. 87, pp. 11–26, 2013.
- [6] S. K. H. Shah *et al.*, "Laser induced breakdown spectroscopy methods and applications : A comprehensive review," *Radiat. Phys. Chem.*, vol. 170, p. 108666, 2020.
- [7] C. Alvarez-Llamas *et al.*, "Ultrafast μ LIBS imaging for the multiscale mineralogical characterization of pegmatite rocks," *J. Anal. At. Spectrom.*, vol. 39, no. 4, pp. 1077–1086, 2024.
- [8] K. Vig, A. Joe, and C. M. Barnett, "A Comparison of Libs for the Quantification of Au Nanoparticles using 1064 nm, 532 nm, and 266 nm Excitation," *Biophys. J.*, vol. 110, no. 3, p. 493a, 2016.
- [9] D. W. Hahn and N. Omenetto, "Laser-induced breakdown spectroscopy (LIBS), part II: Review of instrumental and methodological approaches to material analysis and applications to different fields," *Appl. Spectrosc.*, vol. 66, no. 4, pp. 347–419, 2012.
- [10] L. J. Lewis and D. Perez, "Laser ablation with short and ultrashort laser pulses: Basic mechanisms from molecular-dynamics simulations," *Appl. Surf. Sci.*, vol. 255, no. 10, pp. 5101–5106, 2009.
- [11] S. Vela, M. Morales, D. Munoz-Martin, and C. Molpeceres, "Numerical simulation of femtosecond laser ablation of Aluminium," *Results Phys.*, vol. 75, p. 108313, 2025.
- [12] A. De Giacomo, M. D. Aglio, A. Santagata, and R. Teghil, "Early stage emission spectroscopy study of metallic titanium plasma induced in air by femtosecond- and nanosecond-laser pulses B," vol. 60, pp. 935–947, 2005.
- [13] J. B. Sirven, B. Bousquet, L. Canioni, and L. Sarger, "Time-resolved and time-integrated single-shot laser-induced plasma experiments using nanosecond and femtosecond laser pulses," *Spectrochim. Acta - Part B At. Spectrosc.*, vol. 59, no. 7, pp. 1033–1039, 2004.
- [14] F. Alberto *et al.*, "Influence of working parameters on multi-shot femtosecond laser surface ablation of lithium niobate," *Opt. Laser Technol.*, vol. 177, p. 111067, 2024.

- [15] J. Zhan *et al.*, “Ablation enhancement and plasma shielding effects during multiple pulses irradiation with different femtosecond laser repetition rates,” *J. Manuf. Process.*, vol. 138, pp. 1–13, 2025.
- [16] J. A. M. van der Mullen, “On the atomic state distribution function in inductively coupled plasmas-I. Thermodynamic equilibrium considered on the elementary level,” *Spectrochim. Acta Part B At. Spectrosc.*, vol. 44, no. 11, pp. 1067–1080, 1989.
- [17] Z. Zhang, T. Li, and S. Huang, “Influence of the pressure and temperature on LIBS for gas concentration measurements,” *Spectrochim. Acta - Part B At. Spectrosc.*, vol. 155, pp. 34–43, 2019.
- [18] A. Nakimana, H. Tao, X. Gao, Z. Hao, and J. Lin, “Effects of ambient conditions on femtosecond laser-induced breakdown spectroscopy of Al,” *J. Phys. D: Appl. Phys.*, vol. 46, no. 28, 2013.
- [19] M. Rizwan, M. S. Afgan, S. Saleem, K. Kou, Z. Hou, and Z. Wang, “Double Pulse laser-induced breakdown spectroscopy (DP-LIBS): A Comprehensive technique Review,” *Spectrochim. Acta Part B At. Spectrosc.*, vol. 227, p. 107168, 2025.
- [20] V. Rai, F.-Y. Yueh, and J. Singh, “Theoretical model for double pulse laser-induced breakdown spectroscopy,” *Appl. Opt.*, vol. 47, pp. G30–G37, 2008.
- [21] C. M. Ahamer and J. D. Pedarnig, “Femtosecond double pulse laser-induced breakdown spectroscopy: Investigation of the intensity enhancement,” *Spectrochim. Acta Part B At. Spectrosc.*, vol. 148, pp. 23–30, 2018.
- [22] M. Gaidys, A. Selskis, P. Ge, and M. Gedvilas, “High-rate stainless steel laser colouring with GHz femtosecond bursts,” *Opt. Laser Technol.*, vol. 188, pp. 1–10, 2025.
- [23] H. U. Guang, J. I. N. Zhangdong, and Z. Fei, “Constraints of authigenic carbonates on trace elements (Sr, Mg) of lacustrine ostracod shells in paleoenvironment reconstruction and its mechanism,” *Sci. China Ser. D: Earth Sci.*, vol. 51, no. 5, pp. 654–664, 2008.
- [24] V. Balaram, “Current and emerging analytical techniques for geochemical and geochronological studies,” *Geol. J.*, vol. 56, no. 5, pp. 2300–2359, 2021.
- [25] C. Fabre and B. Lathuiliere, “Relationships between growth-bands and paleoenvironmental proxies Sr / Ca and Mg / Ca in hypercalcified sponge : A micro-laser induced breakdown spectroscopy approach ,” *Spectrochim. Acta B*, vol. 62, no. 12, pp. 1537–1545, 2007.
- [26] M. Martínez-Mincherro *et al.*, “Comparison of Mg/Ca concentration series from *Patella depressa* limpet shells using CF-LIBS and LA-ICP-MS,” *Talanta*, vol. 251, p. 123761, 2023.
- [27] J. Skruibis, O. Balachninaite, S. Butkus, V. Vaicaitis, and V. Sirutkaitis, “Multiple-pulse Laser-induced breakdown spectroscopy for monitoring the femtosecond laser micromachining process of glass,” *Opt. Laser Technol.*, vol. 111, pp. 295–302, 2019.
- [28] Y. Wang *et al.*, “Enhancement of optical emission generated from femtosecond double-pulse laser- induced glass plasma at different sample temperatures in air.” *Plasma Sci. Technol.*, vol. 21, no. 3, p. 034013, 2019.
- [29] Y. Wang *et al.*, “Enhancement of laser-induced Fe plasma spectroscopy with dual-

- wavelength femtosecond,” *J. Anal. At. Spectrom.*, vol. 31, no. 2, pp. 497–505, 2016.
- [30] T. A. Labutin, V. N. Lednev, A. A. Ilyin, and A. M. Popov, “Femtosecond laser-induced breakdown spectroscopy,” *J. Anal. At. Spectrom.*, vol. 31, no. 1, pp. 90–118, 2016.
 - [31] E. R. Ciobotea *et al.*, “Signal enhancement with double-pulse LIBS on biological samples and better discrimination of tissues through machine learning algorithms,” *Spectrochim. Acta Part B At. Spectrosc.*, vol. 222, p. 107063, 2024.
 - [32] Y. Meng, C. Gao, Z. Lin, W. Hang, and B. Huang, “Nanoscale laser-induced breakdown spectroscopy imaging reveals chemical distribution with subcellular resolution,” *Nanoscale Adv.*, vol. 2, no. 9, pp. 3983–3990, 2020.
 - [33] Q. L. Ma *et al.*, “Multi-elemental mapping of a speleothem using laser-induced breakdown spectroscopy,” *Spectrochim. Acta Part B At. Spectrosc.*, vol. 65, no. 8, pp. 707–714, 2010.
 - [34] S. Saha, J. Sanwal, P. Mahadik, P. Sengupta, and P. Mathi, “The analytical potential of Femtosecond Laser-Induced Breakdown Spectroscopy (fsLIBS) for determination of trace elements in speleothems,” *Microchem. J.*, vol. 207, p. 112215, 2024.
 - [35] F. Fontana *et al.*, “Laser Induced Breakdown Spectroscopy (LIBS) for whole rock geochemistry,” *J. Geochemical Explor.*, vol. 246, p. 107160, 2023.
 - [36] A. García-Escárcaga, S. Moncayo, I. Gutiérrez-Zugasti, M. R. González-Morales, J. Martín-Chivelet, and J. O. Cáceres, “Mg/Ca ratios measured by laser induced breakdown spectroscopy (LIBS): a new approach to decipher environmental conditions,” *J. Anal. At. Spectrom.*, vol. 30, no. 9, pp. 1913–1919, 2015.
 - [37] N. Rethfeldt *et al.*, “Detection of Rare Earth Elements in Minerals and Soils by Laser-Induced Breakdown Spectroscopy (LIBS) Using Interval PLS,” *Minerals*, vol. 11, no. 12, p. 1379, 2021 .
 - [38] X. Liu *et al.*, “Rapid quantitative analysis of rare earth elements Lu and Y in rare earth ores by laser induced breakdown spectroscopy combined with iPLS-VIP and partial least squares,” *RSC Adv.*, vol. 13, no. 22, pp. 15347–15355, 2023.
 - [39] H. Zhu, X. Dong, L. Feng, Y. Zhang, Z. Wu, and T. Lü, “Minimizing matrix effect in uranium polymetallic ores by orthogonal non-confocal femtosecond-nanosecond laser induced breakdown spectroscopy,” *Opt. Express*, vol. 32, pp. 44301–44312, 2024.
 - [40] J. M. Liu, “Simple technique for measurements of pulsed Gaussian-beam spot sizes,” *Opt. Lett.*, vol. 7, no. 5, pp. 196–198, 1982.
 - [41] P. Schober, C. Boer, and L. A. Schwarte, “Correlation Coefficients: Appropriate Use and Interpretation,” *Anesth. Analg.*, vol. 126, no. 5, pp. 1763-1768, 2018.
 - [42] S. Kucheryavskiy, S. Zhilin, O. Rodionova, and A. Pomerantsev, “Procrustes Cross-Validation—A Bridge between Cross-Validation and Independent Validation Sets,” *Anal. Chem.*, vol. 92, no. 17, pp. 11842–11850, 2020.
 - [43] F. Poggialini, S. Legnaioli, B. Campanella, B. Cocciaro, G. Lorenzetti, S. Raneri, and V. Palleschi, “Calculating the Limits of Detection in Laser-Induced Breakdown Spectroscopy: Not as Easy as It Might Seem,” *Applied Sciences*, vol. 13, no. 6, p. 3642, 2023.

7 Santrauka

Žygintas Dabulis

LAZERIU INDUKUOTOS PLAZMOS SPEKTROSKOPIJOS TAIKYMAS OSTRAKODŲ IR GEOLOGINIŲ BANDINIŲ ELEMENTINEI SUDĖČIAI NUSTATYTI PALEOAPLINKOS TYRIMUOSE

Lazerio indukuotos plazmos spektroskopija (LIPS) yra greitas daugiaelementis analizės metodas, reikalaujantis minimalaus mėginio paruošimo. Femtosekundinė LIBS metodika yra ypač patraukli geologiniams ir paleoaplinkos tyrimams dėl lokalizuotos, daugiausia neterminės abliacijos bei sumažintų matricos efektų. Tačiau mažų koncentracijų elementų aptikimas išlieka sudėtingas, nes ultratrumpų impulsų sukurta plazma yra trumpalaikė ir silpnesnė. Nors ultratrumpų impulsų dvigubo impulso LIPS jau parodė perspektyvias signalo sustiprinimo galimybes, GHz impulsų papliūpomis režimas LIPS tyrimuose vis dar yra mažai tirtas.

Šio darbo tikslas buvo optimizuoti femtosekundinės dvigubo impulso LIPS eksperimentines sąlygas ppm lygio elementų aptikimui geologiniuose, paleoaplinkai reikšminguose mėginiuose bei palyginti metodo veikimą su GHz impulsų papliūpomis režimu. Siekiant nustatyti sąlygas, palankias plazmos pakartotiniam kaitinimui, buvo tiriama dvigubo impulso užlaikymo, impulsų energijos pasiskirstymo, plazmos registravimo laiko bei aplinkinių dujų atmosferos įtaka LIPS signalo ir triukšmo santykiui. Taip pat metodo pritaikomumas paleoaplinkos tyrimams buvo vertinamas lyginant LIPS spektrinius pokyčius ir elementų santykius su etaloniniais LA-ICP-MS matavimais iš skirtingų stratigrafinių gylių.

Rezultatai parodė, kad nepriklausomai valdoma fs dvigubo impulso LIPS sistema pasiekė didesnę signalo sustiprinimą nei GHz impulsų papliūpomis režimas esant vienodai bendrai impulsų energijai. Geriausi rezultatai gauti daugiau energijos paskirsčius antrajam impulsui, taip patvirtinant plazmos pakartotinio kaitinimo svarbą. Fs dvigubo impulso LIPS pasiekė apie 2,5 karto didesnę signalo sustiprinimą, palyginti su vieno impulso režimu, o komerciniame GHz impulsų papliūpomis režime sustiprinimas siekė ~1,5 karto. Argono atmosfera papildomai padidino signalo ir triukšmo santykį maždaug 1,6 karto lyginant su oru. Nustatyta plati optimali veikimo sritis (300-450 ps dvigubo impulso užlaikymas ir 200-250 ns plazmos registravimo užlaikymas), rodanti stabilų fs dvigubo impulso LIPS veikimą. Koreliacija su LA-ICP-MS duomenimis parodė gerą sutapimą, kur didžiausios mėginių imties reikšmės artėjo prie $R^2 \sim 0,9$. Kryžminė validacija patvirtino realesnę pusiau kiekybinį metodo pobūdį, su sumažėjusiu, bet vis dar reikšmingu prognozavimo tikslumu.

8 Summary

Žygintas Dabulis

LASER INDUCED BREAKDOWN SPECTROSCOPY IN OSTRACODS AND GEOLOGICAL SAMPLES CHEMICAL ANALYSIS FOR PALEOENVIRONMENTAL STUDIES

Laser-induced breakdown spectroscopy (LIBS) is a rapid multi-element analysis technique requiring minimal sample preparation. Femtosecond LIBS is especially attractive for geological and paleoenvironmental investigations due to its localized, predominantly non-thermal ablation and reduced matrix effects. However, detection of low-level trace elements remains challenging because ultrafast laser-induced plasmas are short-lived and weakly emissive. While ultrafast double-pulse LIBS has already demonstrated promising signal enhancement capabilities, GHz burst excitation for LIBS remains comparatively less explored.

The aim of this work was to optimize femtosecond double-pulse LIBS experimental conditions for ppm-level trace-element detection in geological paleoenvironmentally significant samples and compare its performance with GHz burst excitation. The influence of double-pulse delay, pulse energy distribution, plasma gating conditions, and surrounding gas atmosphere on LIBS signal-to-noise ratio was investigated in order to determine conditions favorable for plasma reheating. Furthermore, the applicability of the developed setup for paleoenvironmental investigations was assessed by comparing LIBS spectral trends and elemental ratios with reference LA-ICP-MS measurements from different stratigraphic depths.

The results demonstrated that independently controlled fs DP-LIBS achieved higher signal enhancement than GHz burst excitation under equal total energy conditions, with best performance obtained when more energy was supplied in the second pulse, confirming efficient plasma reheating. Fs DP-LIBS achieved enhancement factors of ~ 2.5 , while commercial GHz burst excitation reached ~ 1.5 . Argon atmosphere further increased SNR by ~ 1.6 compared to air. A broad optimum region of 300-450 ps double-pulse delay and 200-250 ns gating delay indicated robust operation. Correlation with LA-ICP-MS showed strong agreement, reaching $R^2 \sim 0.9$. Cross-validation confirmed more realistic semi-quantitative performance with reduced, but still meaningful predictive capability.