

Dunhuang Murals at the Micron Scale: Pigment Identification and Layer Thickness Mapping by Micro-LIBS

Guoding Zhang

Northwest Normal University

Yaopeng Yin

Dunhuang Academy

Weiwei Han

Gansu University of Chinese Medicine

Marek Sikorski

Adam Mickiewicz University in Poznań

Xueshi Bai

Centre de Recherche et de Restauration des Musées de France (C2RMF)

Chenzhong Dong

Northwest Normal University

Duixiong Sun

sundx@nwnu.edu.cn

Northwest Normal University

Article

Keywords: Murals, micro-LIBS, parameter optimisation, pigments, pictorial layers

Posted Date: July 7th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10217141/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Version of Record: A version of this preprint was published at npj Heritage Science on September 10th, 2026. See the published version at <https://doi.org/10.1038/s40494-026-02981-y>.

Dunhuang Murals at the Micron Scale: Pigment Identification and Layer Thickness Mapping by Micro-LIBS

Guoding Zhang ^{1,2,4}, Yaopeng Yin ^{3,4}, Weiwei Han ⁵, Marek Sikorski ⁶, Xueshi Bai ^{7,8},
Chenzhong Dong ^{1,4*}, Duixiong Sun ^{1,4*}

1. Key Laboratory of Atomic and Molecular Physics and Functional Materials of Gansu Province, College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou, China

2. College of Engineering, Northwest Normal University, Lanzhou, China

3. National Research Center for Conservation of Ancient Wall Paintings and Earthen Sites, Dunhuang Academy, Dunhuang, China

4. Sino-French Joint Laboratory for Heritage Science (SFJL-HS), Dunhuang Academy, Dunhuang, China, Northwest Normal University, Lanzhou, China, Fondation Sciences du Patrimoine, Paris, France

5. School of Medical Information Engineering, Gansu University of Chinese Medicine, Lanzhou 730000, China

6. Faculty of Chemistry, Adam Mickiewicz University, Poznań, 61-614, Wielkopolskie, Poland

7. Centre de Recherche et de Restauration des Musées de France (C2RMF), Paris, France

8. SATIE, Systèmes et Applications des Technologies de l'Information et de l'Energie, CY Cergy-Paris Université, ENS Paris-Saclay, CNRS UMR 8029, Neuville sur Oise, France

Email: dongcz@nwnu.edu.cn; sundx@nwnu.edu.cn

Abstract

Murals are invaluable but fragile cultural heritage assets. Accurate characterisation of pictorial material composition and layer thickness is essential for conservation, yet conventional methods are either invasive or suffer from signal interference. Here, we show that micro-laser-induced breakdown spectroscopy (Micro-LIBS) – with optimised, nearly non-destructive – can precisely identify pigments and layer thickness in a detached fragment (MG-01) from the Dunhuang Mogao Grottoes. Using a 2.0 mJ laser pulse and 1.2 μ s acquisition delay, we identified atacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) for green, red lead (Pb_3O_4) for red, and anhydrite (CaSO_4) for the white ground layer, confirmed by Raman spectroscopy. By monitoring (Cu I, Pb I, Ca II) emission lines as a function of laser pulses, we reconstructed the painting sequence: ground—red—green, with individual layer thicknesses consistent with cross-sectional microscopy. These results

confirm that Micro-LIBS is a reliable, high-spatial-resolution, near-non-destructive tool for the stratigraphic analysis of ancient murals.

Keywords: Murals, micro-LIBS, parameter optimisation, pigments, pictorial layers

1. Introduction

Mural paintings constitute invaluable intuitive historical and cultural heritage that bears witness to human civilisation, but they have been so severely compromised by various forms of deterioration (chalking, flaking, smoke fouling, cracking, salt efflorescence) [1 – 6] that they impede the interpretation of their historical and cultural significance. During the conservation and intervention for such mural deterioration, precise characterisation is therefore required regarding pigment types, pigment particle-size distribution, salt species, and other key information within the painted layers. Conventional chemical analytical methods typically require invasive sampling, which inevitably causes irreversible harm to inherently fragile murals[6][7].

There is no doubt that non-invasive and fully non-destructive analytical techniques, including X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, and hyperspectral imaging (HSI), can provide partial elemental or molecular information [8]. Nevertheless, signals acquired during compositional detection are severely degraded by the complex substrate of murals and surface dust contamination, resulting in limited analytical performance, particularly in the stratigraphic analysis of pictorial layers. Therefore, minimally invasive analytical techniques that achieve high measurement accuracy without compromising the artistic integrity of murals have become a pragmatic alternative. Before truly in situ non-destructive analytical technologies reach full maturity, such minimally invasive approaches will play an indispensable role in the scientific analysis of mural relics and provide critical technical support for cultural heritage conservation. Laser-induced breakdown spectroscopy (LIBS) is a typical technique of this kind.

LIBS is a technique that focuses a laser beam on the sample surface to generate high-temperature plasma through ablation and excitation. The emitted atomic and ionic spectra from the plasma are then measured using an optical system, enabling qualitative and quantitative analysis of elemental composition and contents. With its distinct advantages of in situ microanalysis and the elimination of laborious sample pretreatment, LIBS has been widely applied in the characterisation and analysis of

cultural heritage and archaeological materials [12-14]. It has been successfully applied to the investigation of various heritage objects, including metal artefacts [15][16], stone relics [17], ceramics [18][19], murals [20][21], oil paintings [22], and bamboo, wood and lacquer wares [23]. It enables reliable qualitative, semi-quantitative and quantitative determination of deterioration-related substances [24][25], and is particularly suitable for compositional identification, differentiation of original materials, contaminants and restoration layers, provenance tracing, depth profile analysis, in situ mural evaluation, and stratigraphic dissection of multi-layered structures.

Nevertheless, conventional LIBS typically utilises laser focal spots on the order of hundreds of micrometres [20], and the ablation craters induced on cultural relic surfaces often result in macroscopically observable irreversible impairment. Accordingly, minimising the damage to cultural heritage specimens while preserving the analytical capability of LIBS poses a key scientific and technical challenge that must be urgently addressed in its application to cultural relic analysis.

Micro-LIBS [26] offers analytical capabilities similar to conventional LIBS but with significantly higher spatial resolution and lower sample damage, thanks to coaxial spectral signal collection that effectively suppresses surface unevenness-induced signal fluctuations. The laser spot, focused through a microscope objective, can be controlled to 10 μm or smaller [26-28], rendering it a nearly non-destructive technique increasingly applied in cultural relic material analysis. Corsi et al. [29] used Micro-LIBS for multi-element quantitative analysis of ancient bronzes to preliminarily discriminate their production origin. Bilal et al. [30] identified various pigments in ancient Roman murals with ablation craters $< 10 \mu\text{m}$, demonstrating excellent spatial resolution. Osticioli et al. [31] achieved precise identification of multi-layered structures and typical pigments (e.g., lead white, cinnabar) in Raphael school works and wooden icons via selective micron-scale analysis. Stefano et al. [32] combined Micro-LIBS with chemical mapping to obtain elemental distribution images of the underlying layers of murals for rapid mineral component analysis, and extended the method to cross-sectional analysis of pottery [33]. Richiero et al. [34] performed 22 μm high-resolution quantitative carbon analysis of archaeological iron alloys, overcoming conventional metallographic limitations to realise simultaneous spatially resolved multi-element (e.g., C, P, Mn) analysis, providing a novel tool for ancient iron and steel smelting research. Herreyre et al. [35] separated and quantified clay components in

archaeological ceramics using high-resolution multi-element imaging combined with partial least squares regression (PLSR) calibration, and applied this to provenance analysis of Augustan-period coarse pottery.

The aforementioned studies demonstrate that Micro-LIBS, by optimising laser energy and adjusting the optical focusing system, can maintain high signal-to-noise ratio (SNR) spectra while minimising sample damage to a nearly non-destructive, naked-eye-undetectable level, with ablation craters merely one-tenth the size of those from conventional LIBS. Furthermore, the shallower depth of field and higher spatial resolution of Micro-LIBS make it ideally suited for micron-scale stratigraphic analysis, particularly for layered cultural relics such as murals. Microstructurally, the chromatic presentation of mineral-pigment murals primarily stems from light scattering and reflection by micron-sized pigment particles [36]. Importantly, the micro-imaging capability of Micro-LIBS facilitates real-time visualisation and targeted analysis of fine mural details related to painting techniques, including definitive outline lines and hair strands.

To address the specific need for elucidating the fabrication procedures and painting techniques of Dunhuang Mogao Grottoes murals, simulated mural samples were employed in this study. Laser ablation morphologies on the mural surface were characterised via optical microscopy to optimise the low-damage experimental parameters for Micro-LIBS. Using the optimised parameters, an actual mural fragment with a three-layer pigment structure (approximately 3.5 cm × 2.5 cm) was selected as the research object. Pigment composition identification was achieved by integrating LIBS spectra with Raman spectroscopy. In addition, the depth distribution of multilayer paint layers was revealed, and the thickness of each individual pigment layer was quantitatively analysed.

2. Materials and methods

2.1 Experimental setup

A schematic of the Micro-LIBS experimental setup is shown in Fig 1. The system employs a 1064 nm Nd: YAG laser (Dawa-100, Beamtech Optronics) with an 8 ns pulse duration, a 4.5 mm beam diameter, and a maximum energy density of 0.63 J/cm². After passing through a beamsplitter cube, the laser pulses are collimated vertically and then focused onto the sample surface via a microscope objective (4×, working distance 18.5 mm, NA=0.10, depth of field 27.5 μm) to generate plasma. A movable CCD detector

images the ablation spot via a coaxial system, and the resulting data are used to form a 3D image of the ablation crater for position and depth determination, with a collimated LED light source (via 50% reflector) ensuring clear imaging. Plasma radiation is collected by a lens group (45° to incident laser) and coupled to an echelle spectrometer (Arylle200, Lct LTB Co.), while time-resolved spectral measurements are performed using an ICCD detector (PI Max-400, Princeton Instruments) with 10,000 resolving power and a 200 – 800 nm spectral range. A 3D electric translation stage controls the sample for point-by-point laser scanning, and a pulse timing generator (DG535, Princeton Instruments) synchronises the laser, spectrometer, and translation stage to ensure measurement accuracy.

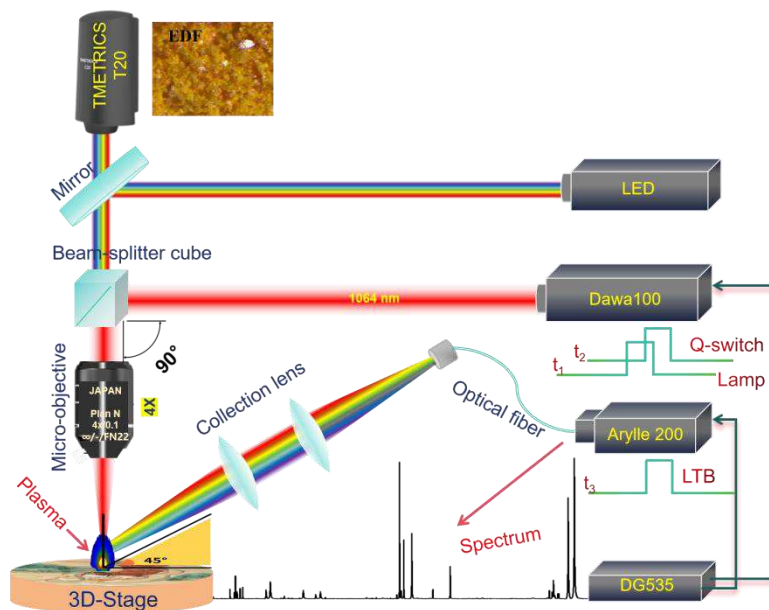


Fig 1 Schematic of the experimental setup

2.2 Samples

Two types of samples were employed in this experiment: simulated murals and actual mural fragments. The detailed preparation process of the simulated mural was elaborated in our previous work [37], and only a brief description is provided herein. Referring to the ancient mural production technique of the Mogao Grottoes, red lead (Pb_3O_4) powders were uniformly mixed with a 5% gelatin solution (serving as the adhesive between pigment particles and the mural substrate). The mixture was then applied to the simulated ground layer to form the pigment layer of the simulated mural, which was naturally air-dried for 72 hours before experimental measurement. The actual mural fragments used in this study were derived from the detached murals of the Mogao Grottoes in Dunhuang.

3. Results and Discussion

3.1 Experimental Condition Optimisation

3.1.1 Effect of Spectral Acquisition Delay on Spectral Signals

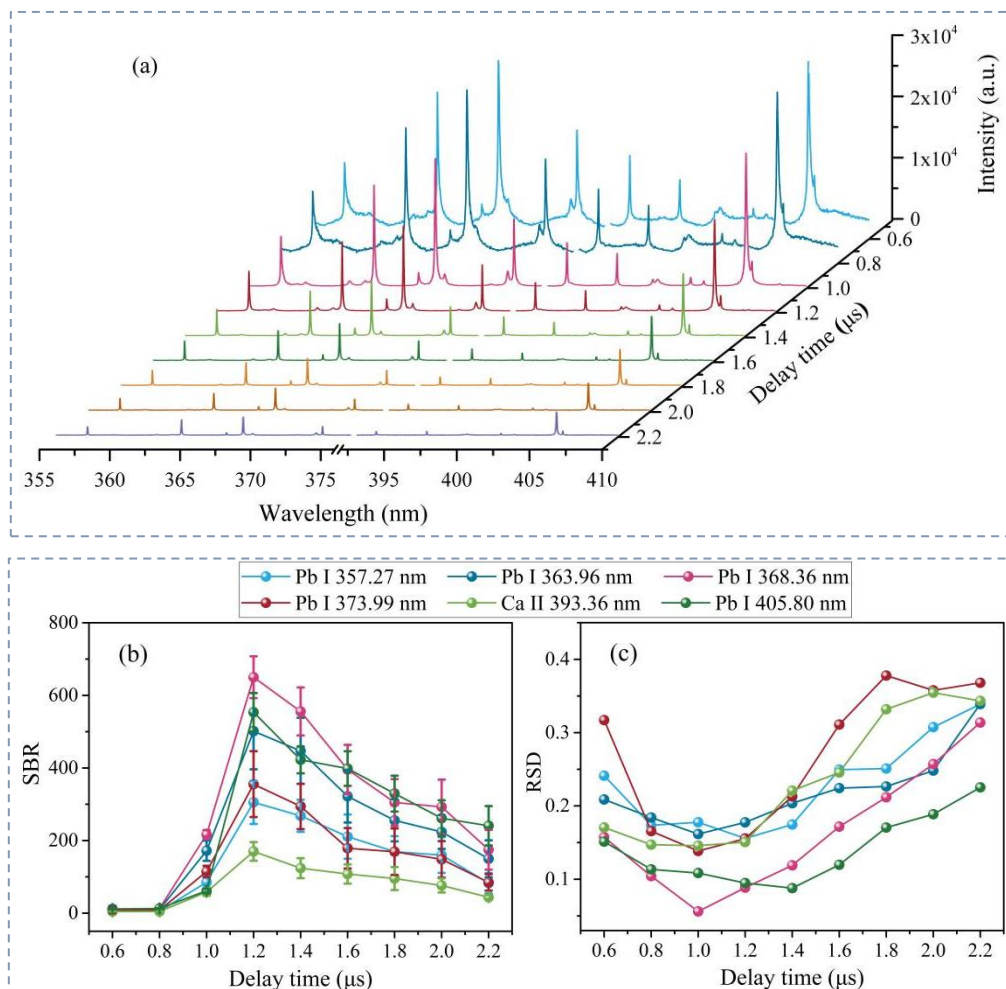


Fig 2. (a) LIBS spectra of red lead simulated mural at different delay times (0.6–2.2 μ s). (b) Signal-to-background ratio (SBR) and (c) relative standard deviation (RSD) for characteristic lines (Pb I 357.27, 363.96, 368.36, 373.99, 405.80 nm; Ca II 393.36 nm) as a function of delay time. Each spectrum is the average of 5 laser pulses at the same spot, and the final spectrum is the average of 20 such measurements.

In Micro-LIBS experiments, plasma is generated by laser ablation of a microscale area. Due to the shallow depth of field under microscopic conditions, laser energy is predominantly concentrated at the focal point, resulting in weaker plasma-laser interaction compared with conventional LIBS. This discrepancy causes differences in plasma radiation properties between Micro-LIBS and conventional LIBS, necessitating systematic delay time optimisation for spectral measurements. As shown in Fig 2, with

plasma evolution, bremsstrahlung-induced continuous background decreases rapidly, spectral line broadening is suppressed, and relative standard deviation (RSD) declines. The spectral signal-to-background ratio (SBR) peaks at 1.2 μ s, where spectral stability is also optimal (lowest RSD in 0.8–1.4 μ s). Further plasma evolution leads to rapid cooling and diffusion, causing synchronous reductions in signal intensity, SBR, and stability. Thus, the spectral measurement delay time was set to 1.2 μ s for reliable data acquisition.

3.1.2 Effect of Focal Position on Spectral Signals and Sample Ablation

When Micro-LIBS is used to analyse mural pigment layers, the microscopic focusing system possesses a much shallower depth of field than conventional LIBS. Without real-time adjustment of the microscopic objective-to-target distance as the ablation crater depth increases during continuous laser ablation at the same position, laser power density and focal spot size per pulse will change, which is equivalent to altering the distance between the laser focal point and the target surface (LTSD). To ensure analytical accuracy, the influence of LTSD on sample damage and spectra must be evaluated prior to detection of real samples.

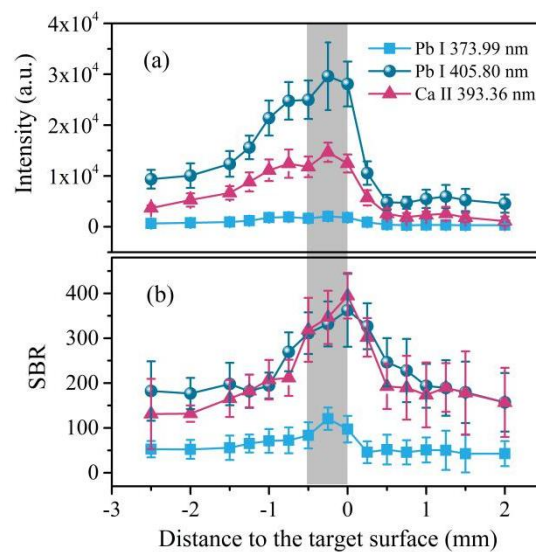


Fig 3. (a) Intensity and (b) signal-to-background ratio (SBR) of characteristic lines (Pb I 373.99 nm, Pb I 405.78 nm, Ca II 393.37 nm) as a function of laser focal position (LTSD, distance between laser focal point and target surface). Positive values indicate focal point above the surface.

Fig 3 shows the variations of intensities and SBR of characteristic lines (Pb I 373.99 nm, Pb I 405.78 nm, Ca II 393.37 nm) with LTSD. Both parameters reach their

peaks when the focal point is 0.25 mm below the target surface, which differs significantly from conventional LIBS experiments in which the focal point is 2 mm below the target surface [37][38][39]. Furthermore, spectral intensity variation is within 20% when the laser focal point is from the target surface down to 0.5 mm beneath the surface. Given the typical mural pigment layer thickness ($\leq 200 \mu\text{m}$), a fixed focal distance can be used for layer analysis, obviating the need for an autofocus system. Intensity variations from laser ablation point deviation from the focal point can be pre-calibrated by adjusting LTSD. Fig 4 shows that within this range, ablation crater diameter and discoloured area size are minimised, resulting in the lowest sample damage. Thus, the focal point was set to 0.25 mm below the target surface for subsequent real mural fragment pigment layer thickness analysis.

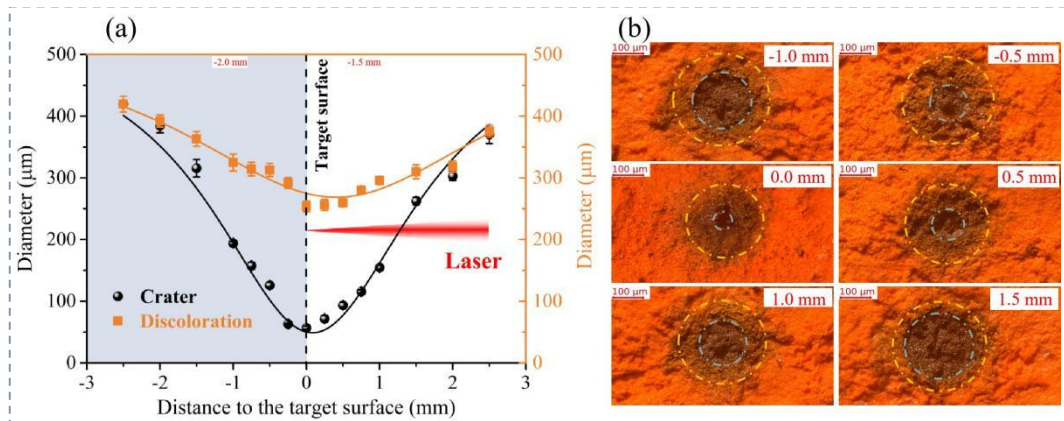


Fig 4. (a) Ablation crater diameter (black squares) and pigment discoloration areas diameter (red circles) at different laser focal positions. (b) Optical Microscope images of the red lead simulated mural surface after different 5 laser pulses at 3 mJ for each focal position. The craters and discoloration are minimal when the focal point is 0.25 mm below the surface.

3.1.3 Effect of Laser Pulse Energy on Spectral Signals and Sample Ablation

In Micro-LIBS experiments, a smaller laser focal spot results in higher power density at the focal point under the same incident laser energy. This makes the physical mechanism of sample laser ablation more closely related to incident laser energy, leading to a lower threshold incident laser energy for the transition from linear to nonlinear ablation [40]. For microscale granular mural samples, laser ablation spots deviate slightly above and below the focal point of the microscopic objective during sample movement. Thus, the incident laser energy must be within the linear ablation range, facilitating the elimination of instability caused by power density fluctuations

via normalisation or spectral line ratio methods during spectral data processing. Consequently, systematic optimisation of laser energy is required prior to experiments.

Fig 5 shows the variations of intensity, SBR, and RSD of characteristic lines (Pb I 357.27, 363.96, 368.35, 373.99, 405.78 nm and Ca II 393.37 nm) in LIBS spectra of simulated mural at different laser energies. Fig 5(a) shows that spectral intensity increases approximately linearly with incident laser energy, confirming a linear ablation process within this range. For mural surfaces with granular pigments (inset in Fig 5(a)), spectral intensity differences caused by focal point deviations due to uneven pigment particles can be eliminated via data processing. Fig 5(b) demonstrates that SBR increases with laser energy: it increases linearly when laser energy is below 2.5 mJ/pulse, but deviates from linearity above 2.5 mJ/pulse. Additionally, RSD decreases with increasing laser energy, indicating enhanced plasma stability. Thus, the spectral characteristics and quality suggest that the laser energy of the Micro-LIBS system should be below 2.5 mJ/pulse for measuring mural samples.

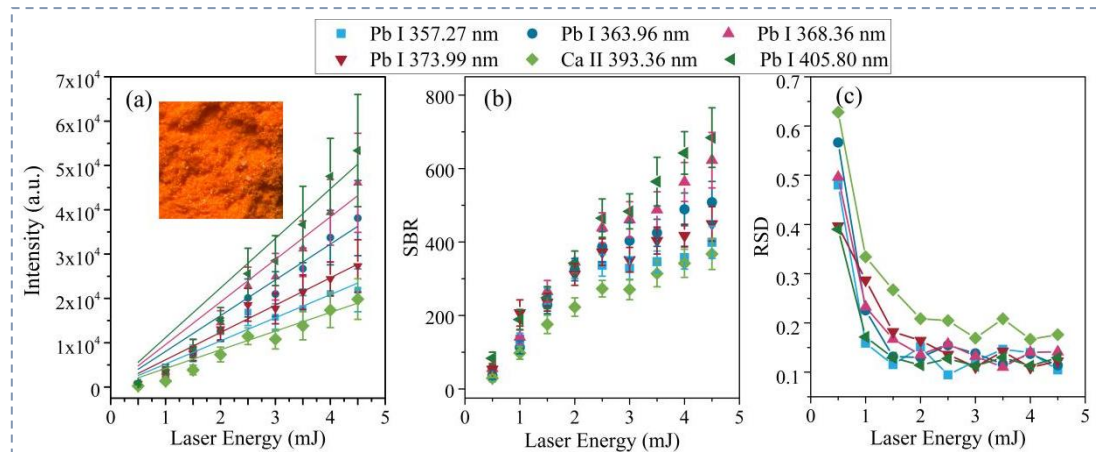


Fig 5. (a) Intensity, (b) signal-to-background ratio (SBR), and (c) relative standard deviation (RSD) of characteristic lines of (Pb I 357.27, 363.96, 368.35, 373.99, 405.78 nm; Ca II 393.37 nm) as a function of laser pulse energy (0.5 – 4.0 mJ). Inset: optical microscope image of the granular red lead simulated mural surface.

In addition to spectral quality, laser ablation-induced sample damage must be considered, as increasing laser energy increases the shock wave pressure during plasma generation and enlarges the ablation crater. Fig 6 presents the relationships between laser energy and ablation crater size, pigment discolouration area around craters induced by laser ablation, and the area ratio of discolouration region to ablation crater. Pigment discolouration is mainly caused by plasma thermal effects: red lead pigment

undergoes redox reactions due to decreased crystal structure stability at high temperatures, transforming from Pb_3O_4 to PbO_2 [41][42] and changing colour from red to brownish-black, a major cause of deterioration in red pigments in Mogao Grottoes murals [43]. It can be observed that the ablation crater diameter increases slowly with laser energy, while the discolouration area grows rapidly. At 0.5 mJ, almost no pigment discolouration occurs around the crater, which is attributed to weak shock waves and low plasma temperature at this energy. At 1.0 mJ, discolouration area increases significantly. However, combined with the spectral quality in Fig 5, spectral stability and SBR are poor when laser energy is below 2.0 mJ, which is unfavourable for LIBS spectral data analysis. Thus, considering both spectral quality and laser ablation-induced sample damage, a laser energy of 2.0 mJ was selected for measurements.

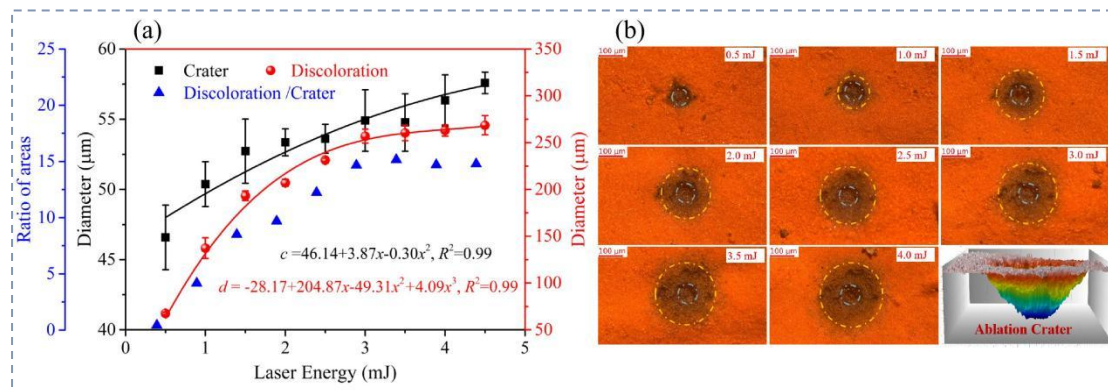


Fig 6. (a) Ablation crater diameter (black squares), pigment discolouration area diameter (red circles), and ratio of discolouration area to crater area (blue triangles) as a function of laser pulse energy, and c , d , h are polynomial fits of crater top diameter and discolouration area diameter vs. laser pulse energy (x). (b) Optical microscope images of craters after 5 pulses at each energy.

3.2. Micro-LIBS analysis

3.2.1 Pigment Characteristic Analysis of Actual Mural Fragments

Based on the optimised experimental parameters, the study analysed the pigment characteristics of the detached mural fragments of the Mogao Grottoes. Fig 7 shows the fragments and their detachment locations in the cave. Long-term natural exposure has altered the pigments' colour and tone, with a significant reduction in saturation. Micrographs of red, green, and exposed white ground-layer pigments reveal that the green pigment comprises particles no larger than $10\text{ }\mu\text{m}$, and the greyish-yellow areas may be inclusions resulting from low mineral purity or an uneven ground layer. Red

pigment consists of smaller particles mixed with black, brown, and other impurities of various particle sizes (which is attributed to mineral pigment processing), and the off-white ground-layer pigment is granular, with particles of other colours mixed in. These microstructural features confirm the mural fragment's pigments are mainly low-purity mineral pigments, because these minerals are often accompanied by associated ores in natural environments.

In mural restoration, detached fragments are usually re-fixed and the joint seams of spliced parts repaired, making it necessary to identify the main components of the various pigments on the fragments. Micrographs show ground layer particles mixed in both red and green pigments, indicating the pigment layer may be relatively thin. For accurate analysis, Micro-LIBS was employed under single-pulse conditions to analyze these three pigments. Fig 8 presents their LIBS spectra, with characteristic spectral lines identified and calibrated. The LIBS spectrum of green area P1 is mainly composed of the linear characteristic lines of Si, Fe, Pb, Mg, Al, Ca, and Cu. Based on the LIBS spectral database of common pigments, the green pigment is inferred to be atacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$), with other spectral lines originating primarily from impurities and associated minerals. The Pb characteristic lines may result from green pigment detachment at the focal point, causing partial laser irradiation of elements in the underlying red pigment—this is preliminarily confirmed by micrographs. A more accurate explanation will be elaborated in the next section, incorporating the morphological characteristics of post-ablation craters and pigment layer composition and structure. Similarly, the red pigment is inferred to be red lead from its LIBS spectrum, based on the LIBS spectral database of common pigments, and the white pigment is identified as gypsum based on its characteristic spectral lines.

To further verify the accuracy of the LIBS analysis results, Raman spectroscopy measurements were carried out on three regions (Fig 9), and the pigment compositions were matched in the RRUFFTM mineral Raman standard library. In Fig 9(a), characteristic peaks match the standard spectrum of $\text{Cu}_2(\text{OH})_3\text{Cl}$ [44]: the peak at 363 cm^{-1} corresponds to Cu-Cl stretching vibration, the peak at 514 cm^{-1} to Cu-O stretching vibration, the peaks at 815 cm^{-1} , 835 cm^{-1} , and 912 cm^{-1} to Cu-O-H bending or lattice vibrations, and the peaks at 121 cm^{-1} and 149 cm^{-1} to O-Cu-O bending or lattice vibrations. Fig 9(b) shows characteristic peaks at 480 cm^{-1} and 548 cm^{-1} , which are assigned to Pb^{4+} -O stretching vibrations in red lead[45][46], while the peak at 143 cm^{-1}

corresponds to lattice translation vibration. For Fig 9(c), the strongest peak at 1018 cm^{-1} corresponds to SO_4^{2-} symmetric stretching in anhydrite (CaSO_4), peaks at 416 cm^{-1} and 498 cm^{-1} correspond to symmetric bending vibrations, those at 608 cm^{-1} , 627 cm^{-1} , and 676 cm^{-1} to asymmetric bending vibrations, and those at 1128 cm^{-1} and 1160 cm^{-1} to asymmetric stretching vibrations [47].

Raman results confirm that pigment compositions can be accurately identified via LIBS characteristic lines combined with pigment colour systems, verifying LIBS analysis reliability.

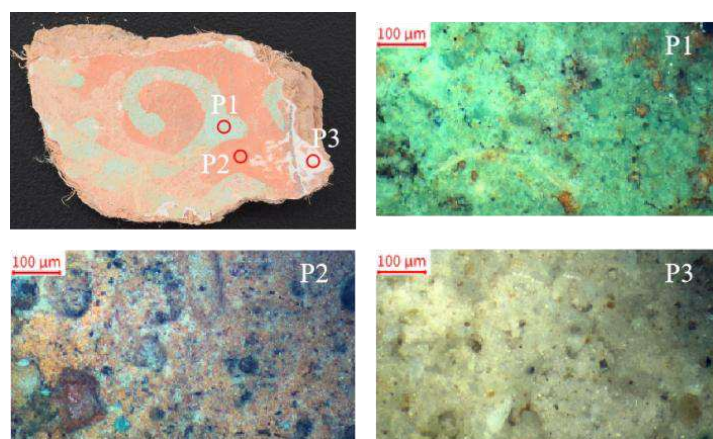


Fig 7. Optical microscope images of the actual mural fragment MG-01 (approximately $3.5\text{ cm} \times 2.5\text{ cm}$) detached from Dunhuang Mogao Grottoes Cave. P1 – green pigment area, P2 – red pigment area, P3 – exposed white ground layer. Scale bars indicate $100\text{ }\mu\text{m}$.

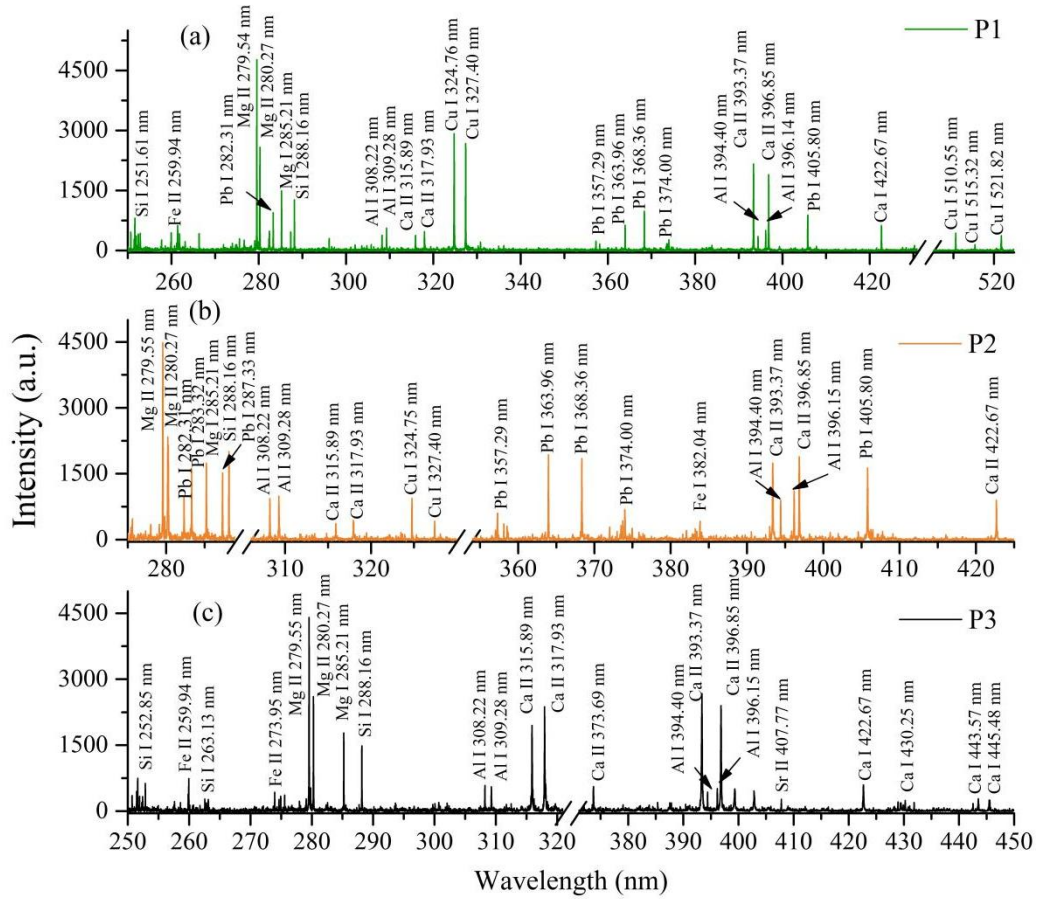


Fig 8. LIBS spectra of green (P1), red (P2), and white (P3) pigment areas from fragment MG-01. Characteristic lines: Cu I (green), Pb I (red), Ca II and Ca I (white ground layer).

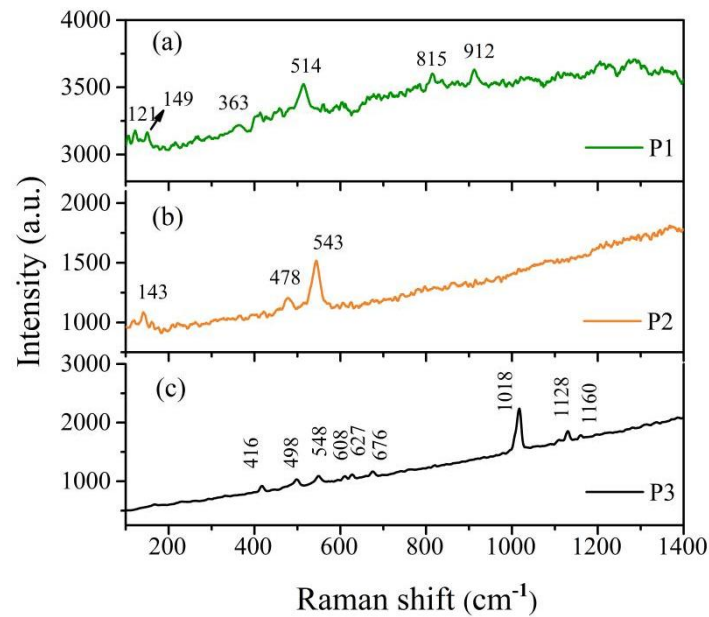


Fig 9. Raman spectra of (a) green pigment (atacamite, $\text{Cu}_2(\text{OH})_3\text{Cl}$), (b) red pigment (red lead, Pb_3O_4), and (c) white ground layer (anhydrite, CaSO_4).

Characteristic peak assignments are marked.

3.2.2 Pigment Layer Thickness Analysis

In mural restoration, precise pigment layer thickness measurement is as essential as identifying pigment compositions, because mineral pigment color also depends on layer thickness—even the same pigment exhibits distinct color differences with different thicknesses [48]. A calibration relationship between laser pulse count and ablation crater depth need be established to quickly estimate in-situ pigment layer thickness via laser pulse count and characteristic spectral lines.

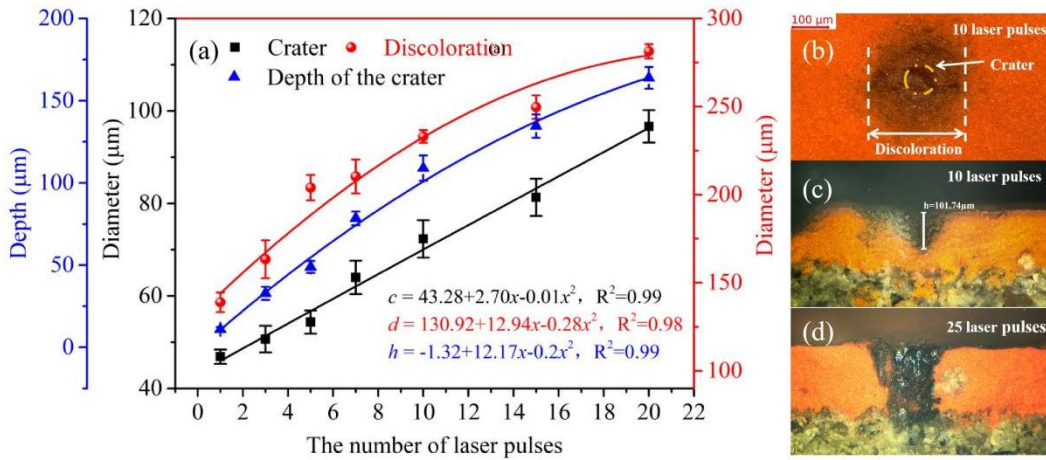


Fig 10. (a) Ablation crater top diameter (black squares), depth (blue triangle), and discolouration area diameter (red circles) as a function of the number of laser pulses (2 mJ, focal point 0.25 mm below surface), and c , d , and h are polynomial fits of crater top diameter, discolouration area diameter and depth vs. number of laser pulses (x). (b) Optical microscope images of craters after 10 pulses. (c, d) Cross-sectional optical microscope images of craters after 10 and 25 pulses.

Fig 10 shows ablation crater diameter, depth, and discolouration area variations with laser pulse count. All three parameters increase with the number of laser pulses. The ablation depth does not show a strict linear relationship with the cumulative number of laser pulses. Polynomial fitting shows that the increment in ablation depth gradually decreases with increasing pulse count. This phenomenon is attributed to the dynamic ablation mechanism during laser-material interaction. For pulse counts > 1 , the pigment at the laser-irradiated site is ablated layer by layer; the ablation crater diameter gradually increases under multiple shock waves, causing laser focus deviation and

changes in laser power density at the ablation point. In this experiment, the laser focus was set 0.25 mm below the sample surface, with power density at the crater bottom increasing with crater depth. For subsequent pulsed lasers, the existing ablation crater constrains the plasma, and part of the ablated material returns to the crater bottom during plasma expansion [49]. Thus, the increased laser power density does not significantly increase the ablation amount.

The competition between these two mechanisms results in a slow increase in ablation crater depth, showing a weak linear trend with laser pulse count. The average per-pulse ablation depth is $\sim 10.6 \mu\text{m}$, with a surface crater diameter of $\sim 46.86 \mu\text{m}$ and a discolouration area diameter of $\sim 138.89 \mu\text{m}$. After 5 laser pulses, the ablation crater diameter is $\sim 57.23 \mu\text{m}$, and the depth is $\sim 49.53 \mu\text{m}$, and the ablation depth reaches $\sim 134 \mu\text{m}$ after 15 laser pulses. Thus, polynomial fitting enables ablation crater depth estimation, and combined with changes in characteristic spectral lines, it aids in pigment layer thickness determination.

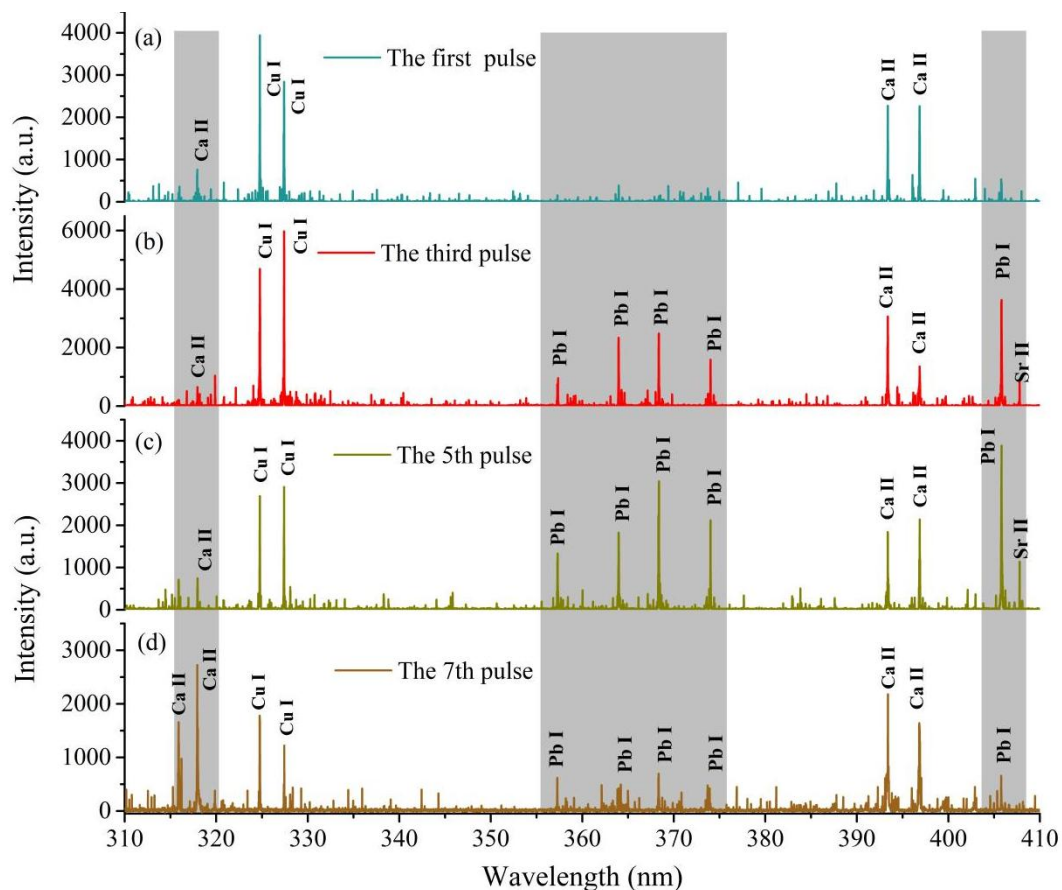


Fig 11. LIBS spectral evolution as a function of consecutive laser pulses at the green pigment area (P1). The Cu I line (green pigment) decreases after the 3rd pulse, while the Pb I line (underlying red pigment) appears and increases, indicating complete

ablation of the green layer.

Based on the relationship between laser pulse count and ablation crater depth, layer thickness analysis was performed on the red and green regions of actual mural fragments. Fig 11 and 12 show characteristic spectral line variations with consecutive laser pulses at positions P1 (green region) and P2 (red region), respectively.

At P1 (Fig 11), the Cu spectral line (green pigment characteristic element) was strong after the first laser pulse, with negligible Pb signal. As the pulse count increased, the green pigment layer was gradually ablated; after the 3rd pulse, the Pb spectral line intensity emerged and increased rapidly, while Cu signal weakened, indicating the green pigment layer was completely ablated. At P2 (Fig 12), the gypsum ground layer characteristic lines (Ca II 315.4 nm and Ca II 317.4 nm) appeared and strengthened with pulse count at the 3rd pulse, while Pb signal weakened, indicating laser interaction with the gypsum ground layer and the red pigment layer thickness at the measurement point was thus estimated to be 33.41 μm through the polynomial fitting formula. Since the laser spot mode adopted in the experiment was Gaussian, the laser simultaneously sampled the ablation crater sidewalls with increasing ablation times, so Cu and Pb spectral signals did not decrease to zero when the green and red pigment layers were ablated through.

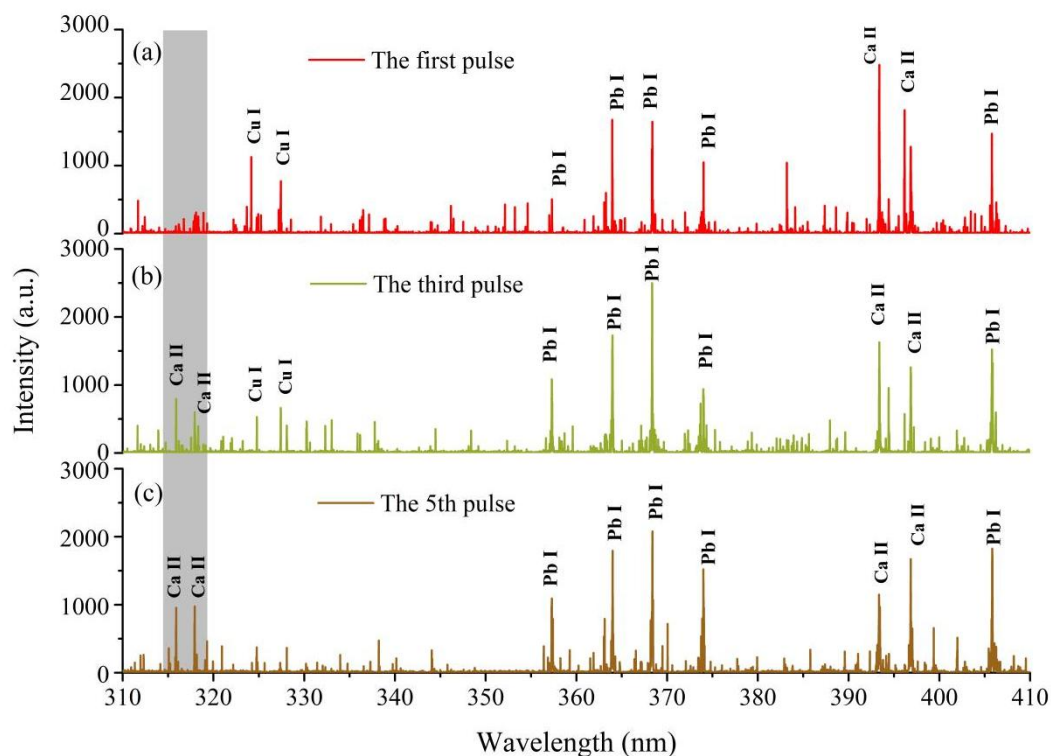


Fig 12. LIBS spectral evolution as a function of consecutive laser pulses at the red pigment area (P2). The Pb I line weakens after the 3rd pulse, while Ca II lines (ground layer) appear and strengthen, indicating ablation through the red layer.

To verify measurement accuracy, cross-sectional microscopic measurements were performed on samples. As shown in Fig 13, the thickness of the green pigment layer is $\sim 35.51 \pm 3.67 \mu\text{m}$, and the red pigment layer is $\sim 38.51 \pm 4.42 \mu\text{m}$ thick. These results are consistent with those from the calibration model established via simulated mural test blocks, enabling direct thickness estimation using the model. In addition, Fig 13 also shows the green pigment layer covers the red pigment layer, with significant thickness variation at different positions. This indicates the red layer was applied first, followed by the green layer, rather than using a single pigment along draft lines during mural painting. Based on these results, during restoration, the thickness of the applied pigment layer can be controlled by selecting pigments with a specific particle size, thereby making the restored appearance consistent with the original mural.

The dynamic evolution of Cu I and Pb I line intensities (Fig 11–12) directly visualises the layer-by-layer ablation process. Critically, the sudden rise of Pb signal after the 3rd pulse at the green area (P1) demonstrates that the green layer completely covers the underlying red layer, with an estimated thickness of $\sim 35 \mu\text{m}$. This finding—green over red—is not merely descriptive but reveals the painting sequence: the red pigment was applied first, followed by the green. Such stratigraphic information is essential for authentic restoration and is rarely obtainable without invasive cross-sectioning.

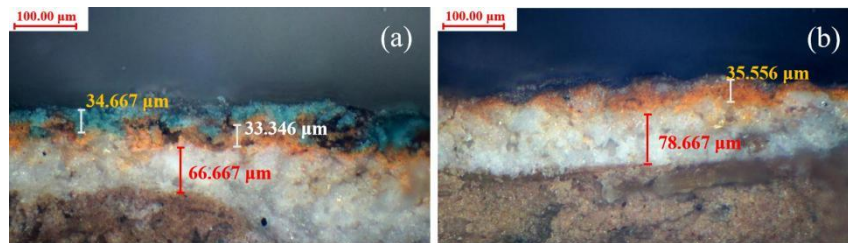


Fig 13. Cross-sectional optical microscope images of fragment MG-01. (a) Green pigment layer thickness = $35.51 \pm 3.67 \mu\text{m}$. (b) Red pigment layer thickness = $38.51 \pm 4.42 \mu\text{m}$. Arrows indicate measured layer boundaries. The green layer lies above the red layer, confirming the painting sequence: red first, then green.

4. Conclusion

We have demonstrated Micro-LIBS, with systematically optimised parameters, enables near-non-destructive, in-situ stratigraphic analysis of ancient murals. Using this approach on a Dunhuang Mogao Grottoes fragment, we identified the green pigment as atacamite, the red as red lead, and the ground layer as anhydrite—confirmed by Raman spectroscopy. More importantly, by monitoring characteristic emission lines during controlled laser ablation, we reconstructed the painting sequence (ground → red → green) and measured individual layer thicknesses with sub-5 μm accuracy, consistent with cross-sectional microscopy. These results challenge the assumption that non-invasive methods cannot resolve layer stratigraphy in polychrome murals. In contrast to conventional LIBS or XRF, Micro-LIBS resolves individual pigment layers without macroscopic damage. Micro-LIBS thus provides a powerful, minimally invasive tool for conservation science, and future work should extend this approach to in-situ profiling of salt efflorescence and deterioration products.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (12374384, 12474411), the Central Government-Guided Local Science and Technology Development Fund (23ZYQA293), the 2026 Gansu Province Industrial Technology Support Programme (2026CYZC-012), the Gansu Provincial Science and Technology Plan Project (22JR5RA151), the Gansu Province University Innovation Fund Project (2024A-007), the Lanzhou Youth Science and Technology Talents Project (2024-QN-102), the Special Project for Research on Unpopular & Unique Traditional Disciplines of the National Social Science Fund (23VJXT011).

References

- [1] Su, B. M., Zhang, H. B., Zhang, B. J., Jiang, D. Q., Zhang, R. & Tan, X. A scientific investigation of five polymeric materials used in the conservation of murals in Dunhuang Mogao Grottoes. *J. Cult. Herit.* **31**, 105-111 (2018).
- [2] Li, J. et al. Investigation of the renewed diseases on murals at Mogao Grottoes. *Herit. Sci.* **1**, 31-40 (2013).
- [3] Li, Y., Wang, F. P., Fu, X. Y., Sun, Z. J. & Xu, Y. Q. Analysis of the pigments for smoked mural by confocal micro-Raman spectroscopy. *J. Raman Spectrosc.* **48**, 1479-1486 (2017).
- [4] Al-Emam, E., Motawea, A. G., Caen, J. & Janssens, K. Soot removal from ancient

-
- Egyptian complex painted surfaces using a double network gel: empirical tests on the ceiling of the sanctuary of Osiris in the temple of Seti I—Abydos. *Herit. Sci.* **9**, 1-10 (2021).
- [5] Gil, M. et al. Microscopy and microanalysis of an extreme case of salt and biodegradation in 17th century wall paintings. *Microsc. Microanal.* **21**, 606-616 (2015).
- [6] Pereira - Pardo, L., Gil, M., Prieto, B. & Silva, B. Multi-analytical approach to the material characterization of 16th century wall paintings from Ribeira Sacra (Galicia, NW Spain): pictorial palette, technique and alterations. *Color Res. Appl.* **41**, 263-269 (2016).
- [7] Zhao, C., Zhang, Y. W., Wang, C. C., Hou, M. L. & Li, A. Q. Recent progress in instrumental techniques for architectural heritage materials. *Herit. Sci.* **7**, 36-85 (2019).
- [8] Daniilia, S. et al. An extensive non-destructive and micro-spectroscopic study of two post-Byzantine overpainted icons of the 16th century. *J. Raman Spectrosc.* **33**, 807-814 (2002).
- [9] Queiroz, A. L. et al. PLS-DA and data fusion of visible reflectance, XRF and FTIR spectroscopy in the classification of mixed historical pigments. *Spectrochim. Acta A.* **265**, 120384 (2022).
- [10] Yogurtcu, B., Cebi, N., Koçer, A. T. & Erarslan, A. A review of non-destructive Raman spectroscopy and chemometric techniques in the analysis of cultural heritage. *Molecules.* **29**, 5324 (2024).
- [11] Reichert, A. S. et al. Database of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and hyperspectral imaging (HSI) spectra of pigments and dyes for historical document analysis. *Anal. Bioanal. Chem.* **417**, 4351-4372 (2025).
- [12] Botto, A. et al. Applications of laser-induced breakdown spectroscopy in cultural heritage and archaeology: a critical review. *J. Anal. At. Spectrom.* **34**, 81-103 (2025).
- [13] Spizzichino, V. & Fantoni, R. Laser induced breakdown spectroscopy in archeometry: a review of its application and future perspectives. *Spectrochim. Acta B.* **99**, 201-209 (2014).
- [14] Lazic, V. et al. Applications of laser-induced breakdown spectroscopy for cultural heritage: a comparison with X-ray fluorescence and particle induced X-ray emission techniques. *Spectrochim. Acta B.* **149**, 1-14 (2018).
- [15] Fortes, F. J., Cabalín, L. M. & Laserna, J. J. Fast and in-situ identification of archaeometallurgical collections in the museum of Malaga using laser-induced breakdown spectroscopy and a new mathematical algorithm. *Heritage.* **3**, 1330-1343 (2020).
- [16] Mico, S. & Hidri, S. Laser-induced breakdown spectroscopy (LIBS) for coins analysis. *Eur. Phys. J. Plus.* **141**, 111-122 (2026).
- [17] Senesi, G. S., Carrara, I., Nicolodelli, G., Milori, D. M. B. P. & De Pascale, O. Laser cleaning and laser-induced breakdown spectroscopy applied in removing and characterizing black crusts

-
- from limestones of Castello Svevo, Bari, Italy: a case study. *Microchem. J.* **124**, 296-305 (2016).
- [18] Kuzmanovic, M. et al. Analysis of lead-based archaeological pottery glazes by laser-induced breakdown spectroscopy. *Opt. Laser Technol.* **134**, 106599 (2021).
- [19] Chen, Y. et al. Exploring the classification of painted pottery artifacts from different cultural sites in Northwest China by using LIBS technology combined with machine learning. *J. Cult. Herit.* **77**, 273-283 (2026).
- [20] Veneranda, M. et al. In-situ multianalytical approach to analyze and compare the degradation pathways jeopardizing two murals exposed to different environments (Ariadne House, Pompeii, Italy). *Spectrochim. Acta A.* **203**, 201-209 (2018).
- [21] Yin, Y. P. et al. In situ study of Cave 98 murals on Dunhuang Grottoes using portable laser-induced breakdown spectroscopy. *Front. Phys.* **10**, 847036 (2022).
- [22] Lazic, V. et al. Identification of materials in oil paintings through studies of correlations and ratios between the element line intensities during LIBS stratigraphy. *Spectrochim. Acta B.* **201**, 106601 (2023).
- [23] Poggialini, A. et al. Stratigraphic analysis of historical wooden samples from ancient bowed string instruments by laser-induced breakdown spectroscopy. *J. Cult. Herit.* **44**, 275-284 (2020).
- [24] Bassel, L. et al. Laser-induced breakdown spectroscopy for elemental characterization of calcitic alterations on cave walls. *Environ. Sci. Pollut. Res.* **24**, 2197-2204 (2016).
- [25] Pérez-Diez, S. et al. Chemometrics and elemental mapping by portable LIBS to identify the impact of volcanogenic and non-volcanogenic degradation sources on mural paintings of Pompeii. *Anal. Chim. Acta.* **1168**, 338565 (2021).
- [26] Menut, D. et al. Micro-laser-induced breakdown spectroscopy technique: a powerful method for performing quantitative surface mapping on conductive and nonconductive samples. *Appl. Opt.* **42**, 6063-6071 (2003).
- [27] Huang, W. H., He, C. J., Wang, Y., Zhao, W. Q. & Qiu, L. R. Confocal controlled LIBS microscopy with high spatial resolution and stability. *J. Anal. At. Spectrom.* **35**, 2530-2535 (2020).
- [28] Wang, X. et al. Portable confocal-controlled LIBS microscopy for topographic and LIBS mapping. *Spectrochim. Acta B* **207**, 106759 (2023).
- [29] Corsi, M. et al. Archaeometric analysis of ancient copper artefacts by laser-induced breakdown spectroscopy technique. *Microchim. Acta.* **152**, 105-111 (2005).
- [30] Ali, B. A. et al. μ -LIBS/ μ -Raman spectroscopic analysis of pigments in a Roman fresco. *Laser Techniques and Systems in Art Conservation. Proc. SPIE.* **4402**, (2001).
- [31] Osticioli, I., Wolf, M. & Anglos, D. An optimization of parameters for application of a laser-induced breakdown spectroscopy microprobe for the analysis of works of art. *Appl. Spectrosc.*

-
- 62**, 1242-1249 (2008).
- [32] Pagnotta, S. et al. Micro-laser-induced breakdown spectroscopy (micro-LIBS) study on ancient Roman mortars. *Appl. Spectrosc.* **71**, 721-727 (2017).
- [33] Pagnotta, S. et al. Micro-chemical evaluation of ancient potsherds by μ -LIBS scanning on thin section negatives. *Mediterr. Archaeol. Archaeom.* **18**, 171-178 (2018).
- [34] Richiero, S. et al. Laser-induced breakdown spectroscopy (LIBS) imaging for carbon quantification in archaeological ferrous alloys. *J. Anal. At. Spectrom.* **40**, 1746-1753 (2025).
- [35] Herreyre, N. et al. μ -LIBS imaging of archaeological ceramics: Quantification of clay fraction in provenance study. *Talanta* **303**, 129452 (2026).
- [36] Yang, X. & Wan, X. Analysis of the spectral reflectance and color of mineral pigments affected by their particle size. *Color Res. Appl.* **45**, 246-261 (2020).
- [37] Yin, Y. P. et al. Investigation of ancient wall paintings in Mogao Grottoes at Dunhuang using laser-induced breakdown spectroscopy. *Opt. Laser Technol.* **120**, 105689 (2019).
- [38] Fortes, F. J. Moros, J., Lucena, P., Cabalín, L. M. & Laserna, J. J. Laser-induced breakdown spectroscopy. *Anal. Chem.* **85**, 640-669 (2013).
- [39] Feng, S. J., Yang, Q., Mei, J. N., Qin, H. U. & Yao, S. C. Investigation of fiber laser-material interaction mechanisms governing ablation modes and plasma excitation in FL-LIBS. *At. Spectrosc.* **46**, 629-640 (2025).
- [40] Cremers, D. A. & Radziemski, L. J. *Handbook of Laser-Induced Breakdown Spectroscopy* (John Wiley & Sons, 2006).
- [41] Seauve, T. et al. Continuous wave laser thermal restoration of oxidized lead-based pigments in mural paintings. *Appl. Phys. B.* **127**, 162-173 (2021).
- [42] Aze, S. Vallet, A. B. & Olivier, G. Red lead darkening in wall paintings: natural ageing of experimental wall paintings versus artificial ageing tests. *Eur. J. Mineral.* **19**, 883-890 (2007).
- [43] Li, Z. X. A study on the red pigments used in the Mogao frescoes and the mechanism of their discolouration. *Dunhuang Res.* **3**, 41-54+128-129 (1992) .
- [44] Bouchard, M. & Smith, D. C. Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology, especially on corroded metals and coloured glass. *Spectrochim. Acta A.* **56**, 2247-2266 (2003).
- [45] Amat, A. et al. A combined theoretical and experimental investigation of the electronic and vibrational properties of red lead pigment. *J. Cult. Herit.* **46**, 374-381 (2020).
- [46] Burgio, L. & Clark, R. J. H. Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation. *Spectrochim. Acta A.* **57**, 1491-1521 (2001).

-
- [47] Yuan, X., Mayanovic, R. A., Zheng, H. F. Determination of pressure from measured Raman frequency shifts of anhydrite and its application in fluid inclusions and HDAC experiments. *Geochim. Cosmochim. Acta.* **194**, 253-265 (2016).
- [48] Pozo-Antonio, J. S., Cardell, C., Sánchez, S., & Rueda, J. M. Reflectance of oil paintings: influence of paint layer thickness and binder amount. *Coatings.* **12**, 601 (2022).
- [49] Corsi, M. et al. Effect of laser-induced crater depth in Laser-Induced Breakdown Spectroscopy emission features. *Appl. Spectrosc.* **59**, 7, 853-860 (2005).