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Laser Cleaning of Bronzes at the Shanghai Museum in the Lab and in Practice: Lessons from a Decade of Successes and Setbacks

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Abstract

This study examines a decade of laboratory investigation and bronze conservation practice at the Shanghai Museum using a 1064 nm Nd:YAG laser (El.En. S.p.A., Calenzano, Italy). Preliminary irradiation tests on heterogeneous archaeological fragments explored effective-cleaning fluence ranges and adverse-alteration limits under dry and wet LQS and SFR irradiation; reflectance measurements assessed optical response at 1064 nm. Despite recurring tendencies, operational ranges overlapped substantially and remained case-specific, limiting the predictive value of nominal fluence and reflectance. Eight historical artefact cases highlighted situations with greater practical potential for laser treatment, including well-preserved gold-bearing surfaces and selected aged restoration residues, whereas sensitive patinas and degraded metallic decorative layers offered narrower treatment margins. For certain restoration residues, useful removal was achieved even when their major constituents were weak absorbers at 1064 nm. In selected chloride pits, high-frequency SFR was associated with delayed and reduced visible recurrence but was accompanied by surface modification and the continued need for conventional corrosion-control measures. These successes and setbacks inform a practice-oriented decision framework integrating pre-treatment assessment, preliminary testing, observed response and conservation judgement to determine whether laser treatment should serve as a primary method, make an auxiliary contribution or be avoided, with its role reassessed as treatment progresses.

Keywords: laser cleaning; bronze conservation; Nd:YAG laser; copper-alloy artefacts; conservation practice; corrosion products

1. Introduction

A central challenge in bronze artefact cleaning is the removal of unwanted materials from complex surface structures while preserving the original or historicized appearance. This challenge is particularly evident in many ancient Chinese bronzes, which often combine intricate decoration with sub-millimetric cavities, and well-preserved patinas of both protective and aesthetic value, reflecting refined metallurgical technologies and long histories of burial, cleaning, polishing and use. Therefore, highly precise, efficient and selective methods are required.

The Shanghai Museum houses one of the most important bronze collections in China and the world, covering both archaeological findings and transmitted objects with complicated but unclear conservation histories. As one of the country's leading conservation institutions, it also undertakes treatments for numerous external collections. Faced with highly diverse cleaning challenges, conservators frequently encounter the limitations of

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conventional approaches: mechanical cleaning can be labour-intensive and highly dependent on operator skill, whereas chemical treatments may offer limited selectivity and can leave potentially harmful residues. These limitations have long motivated the search for alternative cleaning technologies.

Pulsed laser cleaning has emerged as a promising non-contact conservation technology, valued for its high spatial precision and potential selectivity arising from differences in optical and material properties between substrate and unwanted deposits [1]. It therefore appears well suited to many of the challenges posed by bronze artefacts. However, compared with the extensive literature on laser cleaning for stone conservation, studies focusing on metal artefacts, particularly bronze objects, are still relatively limited [2]. Notable successes have been reported for both gilt and non-gilt bronze artefacts [3–10], demonstrating the considerable potential of this technique under appropriate conditions. At the same time, previous work has shown that laser ablation on metallic substrates is not inherently self-terminating or selective and may involve significant photothermal or photomechanical risks [11–14]. Studies on non-gilt copper-alloy surfaces remain largely confined to laboratory-scale experiments and small specimens [15–20], while the macroscopic aesthetic consequences of laser treatment have received comparatively less attention. Whether threshold-based approaches and optical characterisation protocols, widely adopted for stone cleaning, can provide comparable guidance for bronzes remains uncertain. Taken together, the available evidence suggests that treatment outcomes are highly case-dependent. Overall, laser cleaning of bronzes remains a field where considerable promise coexists with substantial operational challenges.

Motivated by these opportunities and challenges, the Shanghai Museum acquired an EOS Combo Nd:YAG 1064 nm laser cleaning system from El.En. (Italy) in 2015. The system was introduced to systematically explore application scenarios and optimise methodologies for Chinese bronzes. Alongside laboratory investigation of laser–material interactions, the present study places particular emphasis on the professional assessment of conservators during practical treatment, where surface appearance, preservation of the original surface, and achievable cleaning efficiency are critical criteria for evaluating treatment suitability. The central objective was therefore to identify the types of unwanted materials and bronze surface conditions for which laser cleaning offers practical advantages, and to provide practice-oriented guidance for its operation, optimization, and integration with complementary conservation methods.

2. Materials and Methods

2.1. Laser Cleaning Setup

The EOS Combo Nd:YAG 1064 nm system operates in two modes: Long Q-Switched (LQS; 100 ns), with selectable energy levels of 150, 300, and 450 mJ, and Short Free Running (SFR; 30–110 µs), with adjustable energy levels from 200 to 2000 mJ. Optical attenuators, interchangeable with the handpiece lens, further reduce output energy to 50% or 25% of the nominal value for highly sensitive surfaces. Throughout this study, the reported pulse number refers to the number of laser deliveries to a given treatment area, as recorded during treatment. Although the 300 and 450 mJ LQS settings comprised two and three closely spaced 100 ns sub-pulses, respectively, each delivery was counted as one pulse in the reported pulse number. Both modes allow adjustable pulse repetition frequencies from single-shot to 30 Hz.

Designed for high precision and operational adaptability, the beam diameter is adjustable through the focal length knob. Accurate determination of laser spot size is not straightforward and may require dedicated beam-characterisation methods beyond simple visual inspection of the irradiated surface [21]. In conservation laser cleaning, spot size has

also been defined inconsistently across studies, using burn-paper marks, visibly affected areas or manufacturer information [2].

For the EOS Combo used here, the manufacturer specifies a treatment spot range of 2.5–6 mm and provides a separate visible aiming beam for positioning and focusing. No manufacturer-provided calibration relating the diameter of the visible aiming spot to that of the 1064 nm treatment beam was available, and the latter was not independently characterised during the historical treatments. In practice, focusing was established visually using the aiming beam, which could be reduced to approximately 1.5 mm under the tightest working conditions. Fluence values were therefore calculated from the pulse-energy indicated by the laser system and the diameter of the visible aiming spot under the corresponding working conditions, assuming an approximately circular spot. Accordingly, all fluence values reported in this study should be interpreted as nominal operational fluences rather than calibrated incident fluences.

For wet irradiation, the surface was prewetted immediately before treatment. Preliminary tests on archaeological fragments used either water or a 1:1 (v/v) water–ethanol mixture, selected according to surface wetting behaviour, whereas wet treatments of historical artefacts used a 1:1 (v/v) water–ethanol mixture. The liquid was applied with a soft brush or cotton swab, with excess liquid removed where necessary so that the surface remained visibly moistened without a thick standing layer. The liquid was reapplied as needed when repeated irradiation caused visible evaporation during cleaning. Dry irradiation was performed without intentional prewetting.

During laser treatment, the generated plume was locally extracted using a portable ULT LAS 200.1 fume-extraction unit (ULT AG, Löbau, Germany) positioned close to the treatment area. Respiratory protection was also used where appropriate as part of routine operator protection.

2.2. Assessment and Analytical Methods

Given the multi-year nature of this research initiative, a range of analytical tools was employed, although only the most frequently used instruments are described below according to their objectives. Methods were selected case-by-case according to conservation needs rather than applied uniformly, with instrumental analyses used to address specific material- or treatment-related questions.

- Morphological and aesthetic assessment: expert visual examination was prioritised as the primary method for macroscopic evaluation, particularly for defining the necessity and boundaries of laser intervention and judging treatment acceptability. Most laser treatments and first-line visual assessments were undertaken or supervised by the first author, a practising bronze conservator trained in traditional bronze restoration. For treatments on historical artefacts, treatment outcomes were also discussed with the responsible conservation team and, where applicable, senior conservators experienced in traditional bronze restoration. No universal numerical acceptance scale was used. Before irradiation, the material intended for removal, the intended degree of removal, and the surface intended for preservation were identified visually. Where available, a naturally patinated, relatively deposit-free area on the same object that did not require cleaning served as the primary visual reference; otherwise, comparable surfaces on similar objects or manually cleaned areas were used as contextual references. Treatment response was judged primarily from the extent of target removal and preservation of the pre-existing surface morphology, continuity, colour and gloss, where relevant. New discolouration, conspicuous treatment marks, melting or redeposition, roughening, or visible loss/disruption of patina or metallic decorative layers were treated as adverse responses. Microscopic characterisation was performed using a Dinolite AM73915MZT

handheld digital microscope (AnMo Electronics Corporation, New Taipei City, Taiwan, China), a desktop Hirox Hi-Scope KH-2400 digital microscope (HIROX Co., Ltd., Tokyo, Japan), or a desktop Keyence VHX-5000 3D digital microscope (KEYENCE Corporation, Osaka, Japan), depending on instrument availability and suitability for the object dimensions and surface morphology. Observations were typically made at magnifications up to 50× to retain a sufficiently broad field of view, with higher magnifications used selectively to examine localised alteration.

- Optical characterisation: Reflectance measurements employed a custom-built 15 cm integrating sphere (Labsphere Inc., North Sutton, NH, USA) with a barium sulfate diffuse-reflectance coating, operating in an 8°/hemispherical geometry and referenced to a calibrated gold reflectance standard (97% reflectance at 1064 nm). The system was coupled directly to the EOS handpiece, allowing the cleaning laser itself to serve as the diagnostic light source. Measurements were restricted to relatively flat specimens because the irregular geometry of most archaeological fragments was incompatible with reliable integrating-sphere measurements.
- Compositional analysis: Non-destructive analytical methods were preferred wherever practicable and selected according to the specific conservation question. The most frequently used techniques in the present study were portable X-ray fluorescence (pXRF; TRACER 5i, Bruker, Kennewick, WA, USA) for elemental characterisation and confocal Raman spectroscopy (inVia™ InSpect, Renishaw plc, Wotton-under-Edge, UK) for molecular and phase identification. pXRF measurements were typically performed without a filter using a variable-voltage acquisition protocol, with the excitation voltage reaching approximately 40–50 kV during the high-voltage stage and a total acquisition time of 60 s. Raman measurements generally employed 532 nm excitation and a 50× objective, with wavenumber calibration performed using a silicon reference. Spectra were typically collected over approximately 59–1837 cm^{-1}, with the range extended where required. Acquisition time, accumulations and laser power were adjusted according to sample response and signal quality.

Additional approaches, including fibre-optic spectroscopy, colour and small-aperture gloss measurements, in situ hyperspectral imaging, and multi-point Raman examination, were used selectively to address specific conservation questions. Because these methods were not applied systematically across the case series and were affected to varying degrees by surface irregularity and material heterogeneity, they are not presented as separate analytical datasets in this study.

2.3. Specimens and Artefacts

The initial stage focused on determining laser operational cleaning fluence windows and adverse-alteration limits using numerous unattributed bronze fragments from archaeological excavations. As these fragments were not intended for reassembly or restoration, they served as dedicated experimental samples. The documented dataset comprised approximately 50 fragments. The surviving records and observable typological characteristics indicate a broad chronological range from around 13th century BCE to late 19th century, although precise dating was generally unavailable. The fragments were selected primarily according to the presence of representative surface conditions and removal targets rather than archaeological chronology or alloy composition. Where sufficiently comparable areas were available on the same fragment, the surface was subdivided into small test zones so that different irradiation conditions could be examined on closely similar target materials. Most of the fragments therefore accommodated multiple small test zones, so the total number of individual test areas substantially exceeded the number of fragments. Comparable target types were also examined across multiple fragments. Corrosion products on

a substantial subset of the fragments were characterised by Raman spectroscopy during associated research projects, although these analyses were not applied uniformly across the entire fragment set. Where available, pXRF measurements were generally consistent with commonly encountered Cu–Sn–Pb bronze compositions. However, because corrosion products, patinas, and surface deposits were intentionally retained, these measurements were treated only as indicative compositional information rather than as a basis for systematic bulk-alloy classification.

Instead of individual cataloguing, they are categorised by their representative removal targets and substrates typical of Chinese bronzes. These included malachite-dominated green corrosion products (from powdery to crystallised forms), chloride pitting associated with active bronze disease, and adherent earthen deposits. Beyond typical deep-green or brownish patinas, two particular bronze surface types were investigated: the so-called silver-coloured *shui-yin-qin* and lustrous black *hei-qi-gu* patinas. Both are exceptionally smooth, glossy, tin-rich surface types particularly well known from Chinese bronze mirrors, with tin oxides commonly reported as major constituents of the altered surface layer [22].

To supplement these heterogeneous archaeological fragments, reference materials were introduced. Synthetic compound powders corresponding to common bronze corrosion products were compressed into pellets using a Shimadzu MP-35 briquetting machine (30-ton load for 30 s). Powder volume and pressing conditions were kept broadly comparable between preparations, although the resulting pellet surfaces were not expected to be microscopically homogeneous. High-purity malachite was used as a natural mineral reference; other copper minerals were not included because sufficiently homogeneous natural specimens of suitable size were not available for these measurements. Reflectance was measured at multiple spatially separated positions, with up to six positions examined on an individual pellet or flat specimen. For materials of particular relevance to bronze conservation, such as malachite and cuprite, measurements were obtained from more than one separately prepared specimen, and the total number of measurements therefore varied among materials.

Authentic historical artefacts were subsequently examined. The eight cases summarised in Table 1 collectively cover the principal cleaning scenarios investigated in this study, including interventions on gilt and silvered surfaces.

Table 1. Historical artefacts providing significant empirical data.

Object	Source	Image	Cleaning Targets/Surface Intended for Preservation; Scope of Laser Treatment (Section)
Bronze bell Qing Dynasty (1644–1912)	Shanghai History Museum		Earthen deposits and localised green corrosion/smooth mixed patina; exploratory cleaning test (Section 3.1)
Mantelpiece Early 20th century	Shanghai History Museum		Thick coating with powdery corrosion/smooth brown patina; localised treatment (Section 3.1)

Table 1. *Cont.*

Object	Source	Image	Cleaning Targets/Surface Intended for Preservation; Scope of Laser Treatment (Section)
Gilt-silver filigree hair ornament Ming Dynasty (1368–1644)	Shanghai History Museum		Mixed deposits/amalgam-gilded silver surface; localised treatment (Section 3.2)
Silvered-copper filigree bracelet with ivory plates Qing Dynasty (1644–1912)	Shanghai History Museum		Earthen deposits and localised green corrosion/amalgam-silvered copper surface; exploratory cleaning test (Section 3.2)
Gilt-brass Buddhist statue * Qing Dynasty, Qianlong Reign (1736–1796)	Shanghai Museum		Mixed surface deposits/shell-gilded brass surface; large-area treatment (Section 3.2)
Bronze *gu* vessel ** Shang Dynasty (ca. 13th–11th century BCE)	Shanghai Museum		Aged restoration residues/heterogeneous patinated bronze surface; large-scale treatment (Section 3.3)
Single-winged bronze bell Western Zhou Dynasty (1046–771 BCE)	Shanghai Museum		Localised chloride pitting/thick corrosion layers and coarse brownish patina; targeted treatment of chloride pits (Section 3.4)

Table 1. *Cont.*

Object	Source	Image	Cleaning Targets/Surface Intended for Preservation; Scope of Laser Treatment (Section)
Bottom of incense burner Southern Dynasties (420–589 CE)	Nanjing Archaeological Institution		Localised chloride pitting/smooth mixed patina; targeted treatment of chloride pits (Section 3.4)

* The previous study reported in Ref. [23] focused primarily on the characterisation of the surface deposits and reported subsequent cleaning treatment only briefly; additional treatment records and comparative interpretation are included here. ** The laser cleaning treatment of this object was previously reported in detail in Ref. [24]; it is included here for comparative interpretation within the present cross-case synthesis.

3. Results and Discussion

The findings are presented as a progression from laboratory investigations to practical conservation treatments, beginning with attempts to define operational fluence windows and reflectance metrics, followed by assessments of application scenarios involving specific surface conditions and unwanted materials. The accumulated observations are then synthesized to reconsider, from a practical conservation perspective, the role that laser can play in the treatment of bronze artefacts. Unless otherwise specified, all fluence values reported below are nominal operational values as defined in Section 2.1. For historical artefact treatments, values preceded by "~" indicate approximate nominal fluences, reflecting minor working adjustments made in response to local surface conditions during hand-operated treatment. A concise summary of the principal irradiation configurations and observed responses for the experimental and conservation cases is provided in Supplementary Table S1.

3.1. Operational Fluence Windows and Reflectance: From Optical Properties to Structural Reality

As one of the earliest objectives of this research, we examined whether threshold-based approaches and optical characterisation methods developed largely for stone conservation could provide practical operational guidance for bronze artefacts, drawing particularly on the methodological framework of the European standard EN 16782:2016 for preliminary irradiation tests, working-fluence selection, and reflectance characterisation using an integrating sphere [25].

A series of irradiation tests was conducted on archaeological fragments bearing diverse corrosion products, patinas and earthen deposits under LQS and SFR modes. Adapting the general concept of EN 16782:2016 to bronze surfaces, the following terms are used here in an operational conservation sense rather than as analytical material thresholds. "Effective cleaning" denotes removal of the intended target to a practically meaningful extent within the limited test sequence without perceptible adverse alteration of the surface intended for preservation. The "effective-cleaning fluence" refers to the lowest nominal fluence at which this criterion was met under a given test condition. The "adverse-alteration limit" refers to the lowest nominal fluence at which a perceptible unacceptable response was first observed. Where both boundaries could be identified, the "operational fluence window" denotes the range between effective cleaning and the onset of perceptible adverse alteration. These judgements were based primarily on visual examination, supplemented

by microscopic examination where appropriate, using the conservation criteria described in Section 2.2. They therefore represent conservation-relevant perceptible limits and should not be interpreted as thresholds for the onset of sub-visible chemical or structural modification. For chloride-pitting tests, where the original surface within the pit was already disrupted by corrosion, removal fluence was recorded separately rather than interpreted as a conventional operational window; the surrounding preserved surface served as the principal reference for unacceptable lateral alteration.

Tests followed a broadly standardised protocol using 1–2 pulses at 1 Hz and visible aiming-spot diameters of approximately 3–5 mm according to the treatment target, with fluence progressively increased until either effective removal or the adverse-alteration limit was reached. The low repetition rate was deliberately chosen to minimise inter-pulse thermal accumulation and to permit visual assessment of the surface response between successive irradiations. Below the adverse-alteration limit, fluences producing greater removal within the same limited pulse sequence were considered operationally more efficient. Both dry and wet methods were used. For wet tests, the surface was prewetted as described in Section 2.1; because only 1–2 irradiation events were typically applied at each setting, rewetting between successive events was generally unnecessary.

Where sufficient comparable surface was available, the same irradiation condition was examined on more than one visually comparable test area within the same fragment. The number of such repeat areas varied according to the extent and heterogeneity of the surviving surface. Fluence and observed response were documented for each individual test area.

Laser responses varied significantly across the tested surface conditions, yet several recurring qualitative tendencies emerged. Among patinated surfaces, *shui-yin-qin* exhibited the greatest irradiation tolerance, whereas *hei-qi-gu* showed early visible alteration and provided no useful operational window under the conditions tested. Superficial powdery corrosion products associated with chloride pitting were readily removed, while compact, strongly adherent corrosion layers and earthen deposits generally required higher fluence for meaningful removal, often narrowing the margin before adverse alteration.

Substantial variation was observed both among fragments and among nominally similar target areas on the same fragment, with considerable dispersion in effective-cleaning and adverse-alteration fluences. Rather than discrete thresholds, the data revealed overlapping operational fluence windows whose boundaries varied from case to case. Figure 1 therefore summarises the observed ranges as descriptive envelopes compiled from individual test areas and, where comparable target materials occurred on more than one fragment, from multiple fragments. Effective-cleaning fluence ranges are shown for green corrosion products and earthen deposits, removal-fluence ranges for chloride pitting and adverse-alteration limits for *shui-yin-qin* and *hei-qi-gu* patinas without evident corrosion. For chloride pitting, the original surface within the pit had already been disrupted by corrosion, and the surrounding surface intended for preservation served as reference for unacceptable lateral alteration. Selected material responses are shown in Figure 2. The breadth and overlap of these ranges indicate that a single operational fluence criterion is unlikely to be transferable across bronze surfaces. Given differences in irradiation conditions and surface states among published studies [2,12,15,17,19], these ranges are more appropriately used as references for preliminary testing than as transferable cleaning thresholds.

LQS exhibited a somewhat broader operational window under dry conditions and was applicable to a wider range of unwanted materials, while SFR was more effective for thin and homogeneous corrosion layers on relatively intact patina. Irradiation under wet conditions often facilitated material removal and tended to broaden the operational window, but the effect was not sufficiently consistent to provide transferable guidance. For example, wet SFR

proved effective on powdery corrosion of the early 20th-century mantelpiece, whereas wet LQS enabled removal of compact earthen deposits from the Qing-dynasty bronze bell, albeit with concurrent alteration of the surface intended for preservation (see Figure 2e–h). These discrepancies indicated that nominal fluence and irradiation mode alone were insufficient to predict treatment behaviour across heterogeneous bronze surfaces; subsequent treatment parameters were therefore adjusted according to object-specific surface responses and conservation objectives rather than selected directly from the ranges shown in Figure 1.

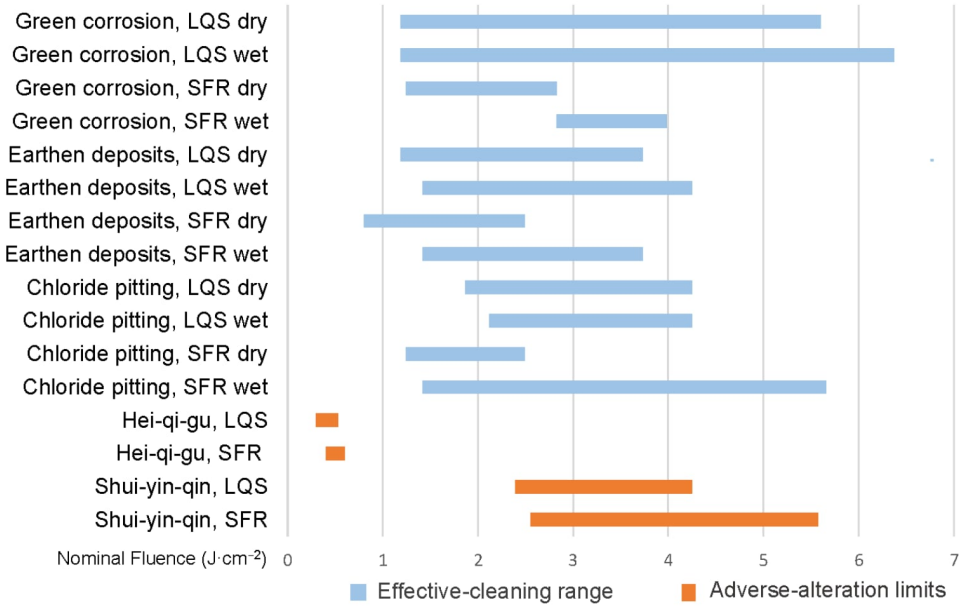


Figure 1. Selected nominal fluence ranges observed in preliminary tests across representative bronze surface and target conditions. Bars indicate effective-cleaning/removal ranges or adverse-alteration limits, as labelled.

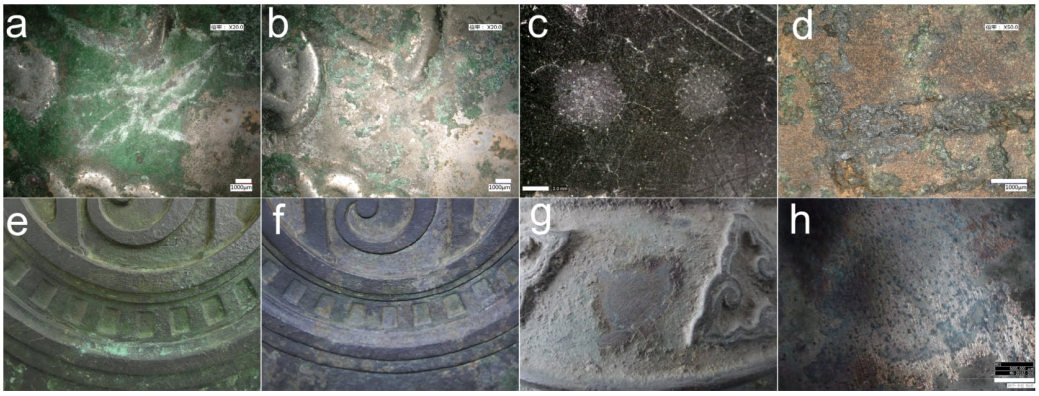


Figure 2. Representative surface responses during preliminary irradiation tests and conservation treatments. (**a**,**b**) *Shui-yin-qin* before and after wet LQS cleaning (~3.73 J·cm^{-2}); (**c**) irradiation marks on *hei-qi-gu* produced by wet LQS at 0.29 and 0.53 J·cm^{-2}; (**d**) melting and morphological modification of compact green corrosion after wet LQS irradiation (~2.12 J·cm^{-2}); (**e**,**f**) powdery green corrosion on the mantelpiece before and after wet SFR treatment (~4.25 J·cm^{-2}); (**g**,**h**) removal of compact earthen deposits from the bronze bell by wet LQS treatment (~2.39 J·cm^{-2}), with localised patina alteration shown at macroscopic and microscopic scales. Scale bars: (**a**,**b**,**d**) 1 mm; (**c**,**h**) 2 mm. Differences in colour between (**e**,**f**) reflect different imaging and illumination conditions and are not intended for colourimetric comparison. The Chinese label "倍率" in panels (a), (b), and (d) indicates magnification.

To examine whether optical absorption could provide predictive guidance, reflectance at 1064 nm was measured on compressed pellets of representative corrosion products and selected flat bronze fragments. Following the approach described in EN 16782:2016, reflectance was used as an experimentally accessible comparative measure of optical response at 1064 nm and as an indication of relative absorptance, which is difficult to quantify directly under practical conservation conditions [25]. Although the pellets appeared macroscopically homogeneous, appreciable variability remained among measurements (Figure 3). For the compressed materials, local differences in particle packing, surface roughness and scattering may have contributed to this dispersion; where more than one pellet was prepared, between specimen variation may also have contributed. Measured reflectance values differed from the existing literature [26], likely reflecting methodological and surface differences. Nevertheless, mean reflectance differed among corrosion types, although these differences were modest relative to the diversity in cleaning behaviour. More importantly, reflectance ranges of corrosion products overlapped substantially with those of stable archaeological patinas dominated by malachite and cuprite, indicating limited reflectance contrast at 1064 nm under the present measurement configuration. A new bronze plate likewise exhibited a reflectance of approximately 40%, showing that the metallic reference itself was not highly reflective under the present measurement configuration. Overall, reflectance provided useful comparative information on optical response but did not reliably predict cleaning behaviour across heterogeneous bronze surfaces examined. In this respect, most bronze corrosion-removal scenarios differ substantially from the canonical case of black-crust removal from white marble.

Comparison with the model specimens further highlighted the limitations of simplified sample systems. The malachite mineral slice showed higher reflectance than the corresponding pellets, indicating that optical response was sensitive to sample form and surface condition. More notably, material removal was generally achieved at lower fluence on the compressed pellets than on naturally formed corrosion layers under the tested conditions. Artificially compacted powders do not reproduce the cohesion and target–substrate interfacial characteristics of archaeological corrosion systems. Pellet data were therefore retained for comparative optical characterisation but excluded from the operational window evaluation.

These observations do not diminish the fundamental roles of material composition and wavelength-dependent absorptivity in laser–material interactions. Rather, they show that these properties, and measured reflectance in particular, are insufficient on their own to define practical operational windows for heterogeneous archaeological bronze surfaces. Physical and morphological characteristics of the surface–target configuration, including porosity, cohesion, stratigraphy, surface texture, and adhesion to the underlying surface, can substantially influence whether laser–material interaction is manifested as material removal, melting, or other thermal, morphological, and potentially chemical modification of the target material, and whether such effects extend to the surface intended for preservation. Loose and weakly adherent materials were generally the most favourable targets, whereas cohesive corrosion layers strongly anchored to the substrate were more resistant to removal. Smooth and compact underlying surfaces were often associated with a broader usable window, although *hei-qi-gu* represented a notable exception.

Consequently, operational fluence windows should be regarded as case-specific starting references rather than transferable prescriptions. For surfaces lacking clearly favourable or prohibitive features, preliminary testing on unobtrusive areas using appropriate ranges of fluence and irradiation modes, under dry or wet conditions where relevant, remains necessary. Close visual monitoring by experienced conservators is therefore essential for identifying the earliest unacceptable responses and determining when irradiation is

extending beyond the intended cleaning action. These preliminary tendencies provided a reference for interpreting the artefact cases that follow, including both situations in which laser treatment offered practical advantages and those in which object-specific surface conditions altered or constrained the expected response.

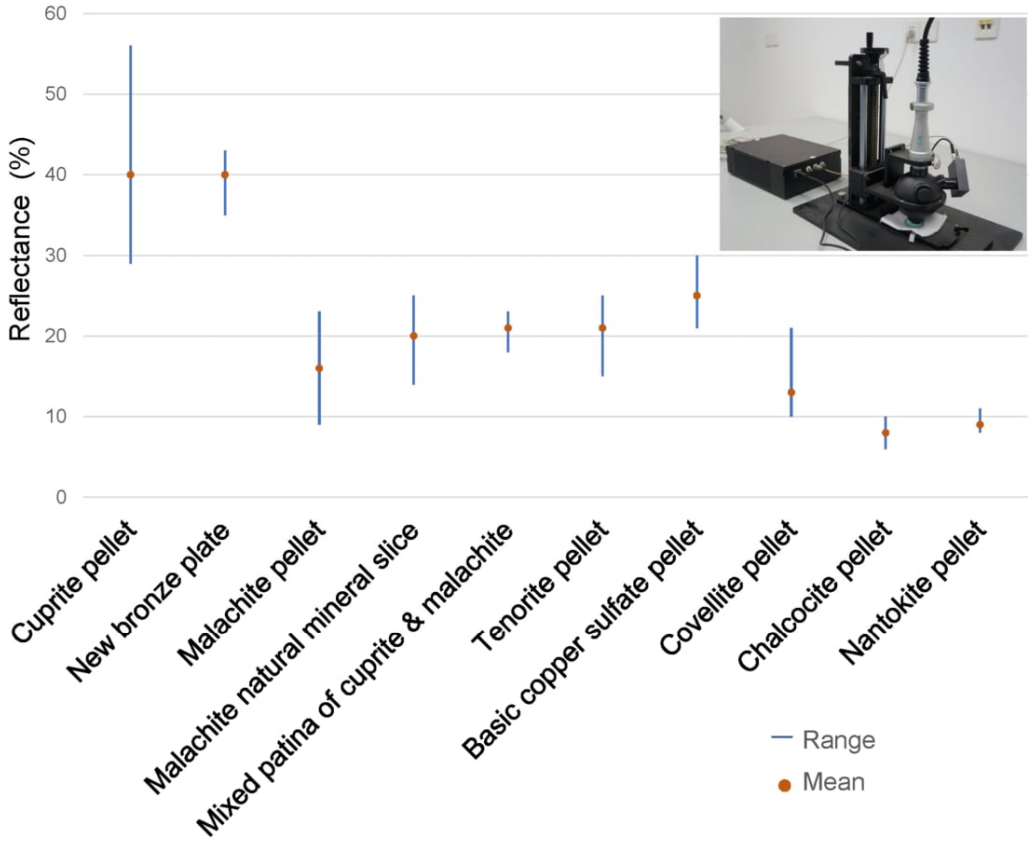


Figure 3. Reflectance characterisation of specimens at 1064 nm; inset shows the integrating-sphere setup coupled to the EOS laser handpiece. Plotted ranges represent the available measurements for each material. The numbers of measurements (n) were as follows: cuprite pellet ($n = 8$), new bronze plate ($n = 7$), malachite pellet ($n = 16$), malachite natural mineral slice ($n = 16$), mixed patina of cuprite and malachite ($n = 7$), tenorite pellet ($n = 7$), basic copper sulfate pellet ($n = 6$), covellite pellet ($n = 8$), chalcocite pellet ($n = 7$), and nantokite pellet ($n = 6$).

3.2. Cleaning Gilt and Silvered Surfaces: Beyond Expectation, Within Reason

The canonical treatment of Florence's "Gates of Paradise" demonstrated the considerable potential of laser cleaning on gilt surfaces [27]. The high infrared reflectance and low absorption of gold, together with favourable optical contrast between gilding and some surface deposits, can provide conditions for selective removal. However, previous studies have also shown that damage thresholds depend strongly on gilding systems, condition, and interfacial characteristics, and that laser treatment is not inherently self-terminating [28,29].

Despite this reference framework, our early trials on filigree objects from the Shanghai History Museum revealed responses less favourable than initially expected. XRF analysis detected mercury on both artefacts, consistent with mercury-based amalgam techniques used in their respective metallic surface treatments. On the gilt-silver filigree hair ornament, which bore mixed soil and oily deposits, SFR irradiation produced little useful removal, whereas LQS irradiation began to remove the deposits at ~0.53 J·cm^{-2}. At a low repetition rate of 2 Hz under wet conditions, the response depended markedly on deposit thickness. In thinly covered areas, as few as two pulses produced visible discolouration of the metallic surface, while lower tested fluences did not achieve effective cleaning. In contrast, areas

covered by thick deposits tolerated approximately 4–5 pulses at ~0.53 J·cm^{-2} without immediately visible alteration of the gilding, while increasing the fluence to ~1.06 J·cm^{-2} and reducing the number of pulses also produced substantial removal before alteration occurred (Figure 4).

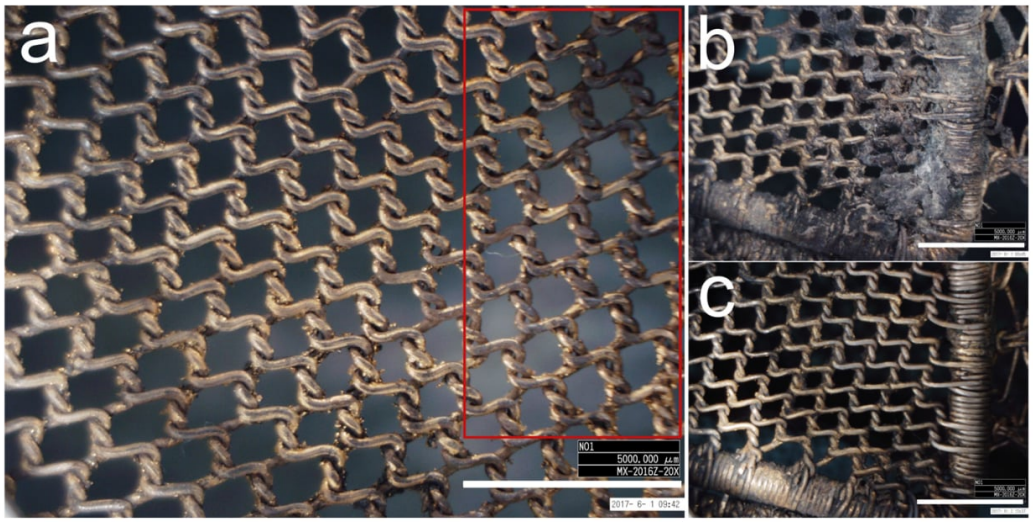


Figure 4. Representative responses of the gilt-silver filigree hair ornament during wet LQS treatment. (**a**) Localised discolouration observed in a thinly covered area (red box); (**b**,**c**) a relatively thick deposit before and after cleaning, showing substantial removal without immediately perceptible adverse alteration of the metallic surface. Scale bars: 5 mm.

These observations suggested a temporary shielding effect of the deposit layer. Previous work on amalgam-gilded bronze reported successful LQS cleaning at approximately 0.53 J·cm^{-2} using 1064 nm LQS irradiation with a pulse duration of 70–120 ns [30]. More recently, an operative range of 0.19–0.46 J·cm^{-2} at 2–7 Hz was reported for a 100 ns EOS1000 LQS system following preliminary steam and solvent-emulsion cleaning [6]. In the present filigree ornament, by contrast, ~0.53 J·cm^{-2} produced effective removal only where deposit was sufficiently thick. Although the reported fluences are numerically similar, these contrasting outcomes highlight the importance of considering surface preservation, deposit thickness and pre-treatment when judging the usable treatment margin.

The origin of the discolouration could not be analytically resolved during the original treatment campaign, and may have reflected local thinning or disruption of the gilded layer, changes in the exposed metallic surface, and/or morphological modification, but the relative contributions could not be distinguished. It was therefore treated in practice as a warning of unacceptable surface alteration.

Similarly, on the silvered copper bracelet, both laser modes showed limited effectiveness and substantial risk in removing the green corrosion, for which malachite was identified as the principal phase through Raman analysis. LQS irradiation again performed better than SFR, but appreciable removal was observed only when the fluence was increased to approximately 2.83 J·cm^{-2}. The first 1–2 pulses removed part of the relatively loose surficial corrosion; however, the more compact underlying layer proved markedly resistant. Further irradiation, whether by increasing the number of pulses, fluence, or repetition rate, produced little additional removal but increasingly visible discolouration of the remaining corrosion and/or alteration of the underlying silvered surface (Figure 5). Purple discolouration observed in some areas yielded no diagnostic Raman peaks; visually, it was consistent with possible thinning or partial loss of the silvered layer and increasing exposure of the copper substrate, although this interpretation could not be analytically confirmed.

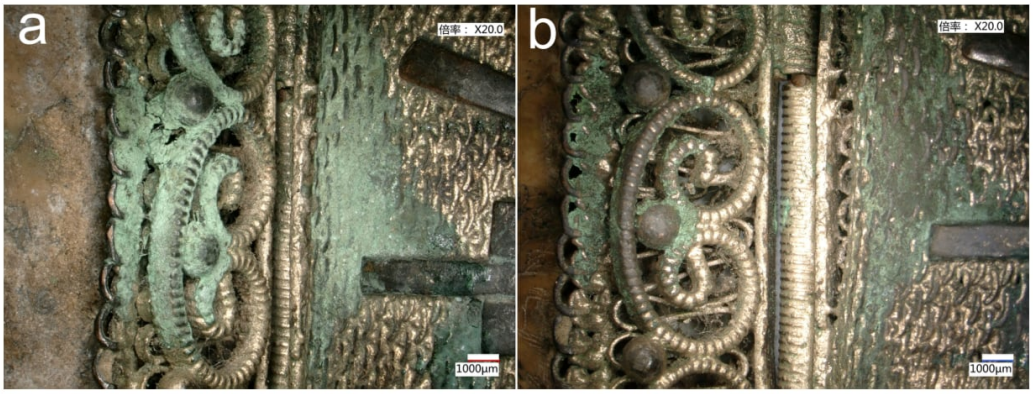


Figure 5. Representative area of the silvered copper filigree bracelet (**a**) before and (**b**) after laser treatment, showing partial removal of green corrosion accompanied by discolouration of the exposed metallic surface. Scale bars: 1 mm. The Chinese label "倍率" in the images indicates magnification.

The poor tolerance of these filigree surfaces probably reflects a combination of factors rather than a single material property. Amalgam-treated metallic layers are compositionally and structurally complex, commonly retaining residual mercury and exhibiting elemental interdiffusion across the metallic surface–substrate region [31]. Additional rapid heating during laser irradiation could therefore promote local mercury loss or redistribution and associated compositional or phase changes within the amalgam-derived layer, although no post-irradiation analysis was available here to determine whether such changes contributed to the observed discolouration. In the present objects, relatively thin metallic layers and intricate three-dimensional geometry may have introduced additional local heterogeneity in thickness, continuity, and laser response. In the bracelet, corrosion extending beneath the silvered layer, together with the compact and strongly adherent nature of the corrosion, further constrained selective removal.

By contrast, large-area laser cleaning was successfully applied to a Qing Dynasty Buddhist statue decorated using the shell gold (*ni-jin*), in which gold powder is mixed with a binder and applied as paint. Unlike amalgam gilding, which forms a metallic Au–Hg-derived layer directly associated with the substrate, shell gold consists of particulate gold dispersed in a binder, resulting in substantially different layer continuity and interfacial characteristics. The surface deposits and a brief account of cleaning were reported previously: the exposed gold layer was generally well preserved, while the thick dark deposits comprised degraded ritual tributes (cereal and oil substances), copper-corrosion products, dirt, and probably soot [23]. Wet LQS cleaning at a nominal fluence of ~0.6 J·cm^{-2} and 1–2 Hz was previously found to remove these deposits efficiently (Figure 6), with residual loosened material removed by ethanol swabbing [23]. Additional treatment records examined here showed that deposit thickness influenced the immediate treatment margin: most deposits were removed within 1–2 pulses in more thinly covered areas and approximately 3–4 pulses where the deposits were thicker. Continued irradiation after most of the overlying deposit had been removed produced darkening in some locally degraded areas and was therefore discontinued, showing that the treatment was not self-terminating in this case, despite the reflective gold-bearing surfaces.

The unpublished in situ reflectance measurements provided additional optical context for the observed treatment response. A diagnostic fluence of 0.2 J·cm^{-2} was used, approximately one third of the nominal fluence at which effective cleaning was achieved (~0.6 J·cm^{-2}); no visible cleaning or surface alteration was observed during the measurements. Reflectance ranged from 60% to 87% on the gilding, 40% to 65% on the dark deposit, and 19% to 34% on exposed brass. The overall ordering was consistent with the favourable

selective response of gilded areas and the poorer outcome observed on the exposed brass. However, the partial overlap between the gilding and deposit ranges indicates that reflectance contrast alone did not fully account for local treatment behaviour.



Figure 6. Corresponding areas of the *ni-jin* Buddhist statue (**a**) before and (**b**) after wet LQS cleaning, showing removal of the overlying deposits and exposure of the gold-bearing decorative surface.

Although the *ni-jin* technique of the Buddhist statue differs fundamentally from the gilding system of the "Gates of Paradise", both successful treatments shared two favourable features: a relatively well-preserved gold-bearing surface and a substantial overlying deposit. Conversely, the unsuccessful filigree trials indicate that, in the cases examined here, the presence of a reflective noble-metal surface alone was insufficient to ensure selective removal. In both the filigree and *ni-jin* cases, deposit thickness influenced the immediate treatment margin, but whether this margin was practically useful depended strongly on the condition and architecture of the underlying decorative layer. This interpretation is consistent with previous studies showing that gilding thickness and thermal contact with the substrate influence laser-induced temperature rise and damage thresholds [30], although no transient thermal measurements were available in the present treatments. Taken together, these cases suggest that preliminary assessment should consider not only optical contrast but also the condition and continuity of the metallic decorative layer, deposit thickness, and the stratigraphic relationship between corrosion and plating.

Retrospectively, an additional practical consideration concerns mercury exposure during treatment of amalgam-derived surfaces. Local fume extraction was used routinely, but mercury release was not specifically monitored. Hg-containing amalgam surfaces should therefore be regarded as a potential occupational-exposure concern, with local extraction and appropriate operator protection considered explicitly when planning laser treatment.

3.3. Removal of Aged Restoration Residues: From Abrupt Detachment to Practical Control

Aged restoration residues, typically composed of aged organic binders mixed with soil and corrosion products, can present particular cleaning difficulties on bronze artefacts. The organic matrices may become poorly soluble after ageing and prolonged interaction with dirt and corrosion products, while mechanical removal can be slow or difficult in recessed and highly decorated surfaces. Several successful applications of infrared laser cleaning to such materials have nevertheless been reported [7–10], despite the relatively low absorption of many synthetic resins at 1064 nm [32]. Their removal therefore cannot always be understood in terms of straightforward surface photoablation of the resin itself; the overall composition of the deposit, including the presence of more strongly absorbing constituents, together with its condition, thickness, and interfacial characteristics, may substantially influence the treatment response.

Preliminary tests on archaeological fragments illustrated this variability. On one fragment covered by a thin, aged and largely transparent polyacrylic coating, a single LQS pulse at ~0.6 J·cm^{-2} detached the resin but immediately produced visible discolouration of the underlying bronze surface. No useful treatment margin could therefore be identified. On another fragment, a substantially thicker resin-like restoration layer underwent extensive removal, accompanied by detachment of adjacent corrosion products, while the exposed cuprite-rich surface remained visually acceptable (Figure 7). In both cases, removal occurred abruptly rather than through progressive layer-by-layer ablation. Although direct discrimination of the relative mechanical, thermal, and interfacial contributions is experimentally demanding in practical conservation treatments, the abrupt flake-like morphology of detached material observed here, including associated lifting of adjacent deposit material in the thicker-layer case, was consistent with an interfacial contribution. Similar removal behaviour has been associated with photomechanical and interfacial processes in previous laser-cleaning studies [33,34]. Such behaviour was neither inherently controllable nor self-limiting; rather, the contrasting results suggest that a sufficiently substantial overlying layer may temporarily provide a practical margin before direct interaction with the surface intended for preservation becomes critical.

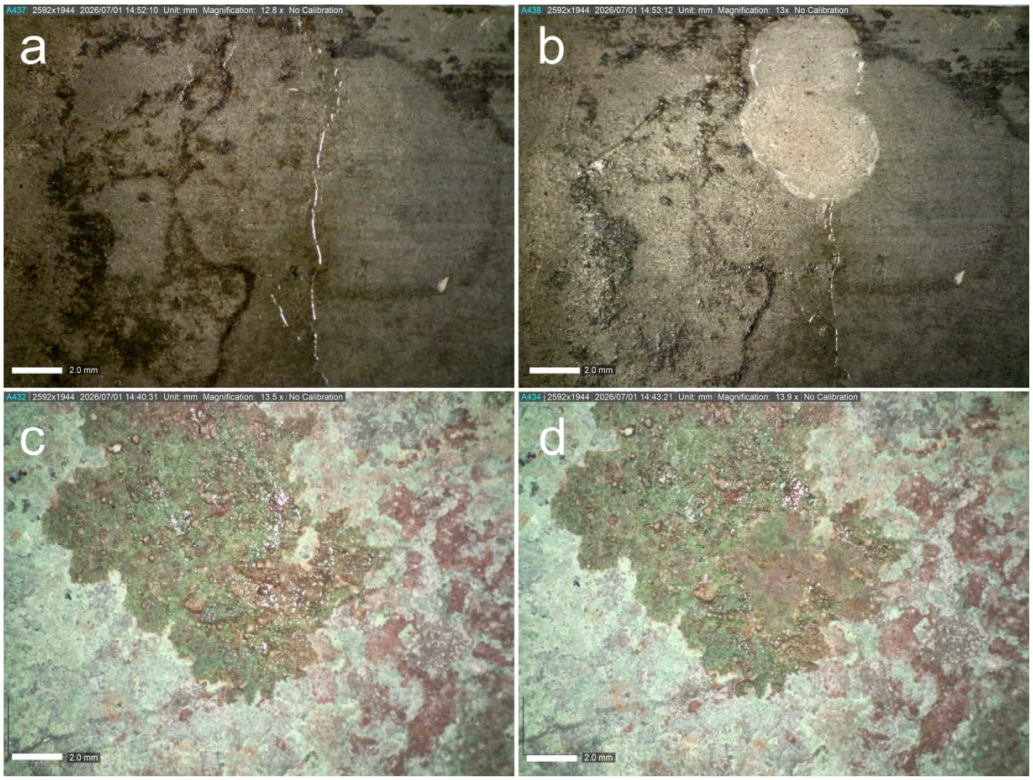


Figure 7. Contrasting responses of aged restoration residues to LQS irradiation. (**a**,**b**) Thin polyacrylic coating before and after treatment, showing detachment with surface discolouration; (**c**,**d**) thicker resin-like layer before and after treatment, showing abrupt bulk detachment with adjacent corrosion removal. Scale bars: 2 mm.

A previously reported treatment of the Shang-Dynasty bronze *gu* vessel [24] provides a large-area example in which this type of abrupt detachment could be exploited in practice. As reported previously, the tenacious restoration residue was a heterogeneous mixture dominated by an ethylene-based copolymer and corundum powder, with minor laser-responsive constituents. After prewetting with a 1:1 (v/v) water–ethanol mixture, LQS irradiation at a nominal fluence of ~2.1 J·cm^{-2} removed most of the material [24] (Figure 8). Model tests reported in the same study showed that small additions of lead- or copper-bearing phases

could markedly increase response of corundum-based mixtures [24]. Considered alongside the fragment tests and other artefact treatments, this case illustrates how deposit thickness, abrupt removal, and a changing treatment margin can affect practical control, and suggests that, under certain conditions, abrupt detachment can provide a useful treatment margin even when the major residue components are weak absorbers at 1064 nm.



Figure 8. Representative partially treated areas of the Shang Dynasty bronze *gu*, showing localised removal of restoration residues. The dashed lines indicate treatment boundaries; the treated area is on the left in (**a**) and on the right in (**b**). Treatment outcomes were also examined in situ using hyperspectral imaging and Raman spectroscopy at multiple positions [24].

The *gu* vessel shares an important feature with the *ni-jin* Buddhist statue discussed in Section 3.2: in both cases, the response of the heterogeneous deposit could not be predicted from its major identified components alone, and minor or dispersed absorbing constituents contributed to the overall interaction at 1064 nm. A substantial overlying deposit provided a useful treatment margin in both cases, but was particularly important for the *gu*. As shown in Section 3.1, archaeological patinas themselves may respond appreciably to 1064 nm irradiation and offer much less intrinsic optical selectivity than the reflective gold-bearing surface. Such situations may require moving beyond the idealized expectation of progressive, self-terminating layer-by-layer ablation and considering whether the response of the target–surface system can be exploited without unacceptable alteration. Comparable laser-assisted detachment of a weakly absorbing overlayer has been reported in polychrome conservation [35]. As with the *ni-jin* treatment, complete laser removal was not pursued once the remaining residue became thin or spatially smaller than the working spot; on the *gu*, the small amount remaining was readily removed with a mixed organic solvent that had been much less effective before laser treatment.

Across the present case series, exploiting a changing treatment margin depended heavily on adaptive hand-operated control. In the *gu* treatment, low repetition rates and slight defocusing were commonly used empirically to facilitate prompt adjustment and soften treatment boundaries. These practices were previously described for the *gu* treatment [24]. Similar use of defocused irradiation has also been reported in practical laser-cleaning studies of archaeological metals [36]. Handpiece position and irradiation delivery were likewise adjusted according to deposit thickness, surface geometry, and the treatment response observed as removal progressed. The practical significance of this adaptive control also depended on the visual characteristics of the surface itself. On the deeply modelled relief of the *gu*, minor variations in treatment boundaries were comparatively inconspicuous, whereas exploratory irradiation on the relatively smooth non-gilded brass areas of the *ni-jin* Buddhist statue, bearing a heat-coloured artificial patina that was more irradiation-sensitive than many of the archaeological patinas examined in Section 3.1, produced conspicuous spot marks, discolouration, and local gloss variation [23]. This contrast suggests that relatively smooth or planar surfaces may provide less visual tolerance to minor variation in spot place-

ment or overlap than strongly modelled relief, and illustrates why practical control involves both adapting irradiation conditions and judging whether the resulting surface response remains acceptable. The conservator's real-time visual judgement therefore complements, rather than replaces, parameter-based testing by translating preliminary test results into a changing treatment situation.

3.4. Localised Treatment of Chloride Pitting: Revisiting a Long-Neglected Parameter

Pitting corrosion associated with chlorides is among the most persistent and destructive forms of deterioration affecting bronze artefacts. Although loose superficial chloride-bearing corrosion products can often be removed relatively easily, the principal conservation difficulty lies in chloride-containing corrosion extending beneath the visible surface, particularly nantokite (CuCl), which may sustain recurrent corrosion under humid conditions [37,38]. Because such material may remain concealed beneath secondary cuprite, malachite, or other corrosion layers and may extend into the metal–corrosion interface, complete removal by conventional surface cleaning is difficult. Previous studies have shown that laser irradiation can efficiently remove superficial corrosion products and may also induce substantial thermal modification of copper-corrosion layers; however, its capacity to provide long-term control of active chloride corrosion remains uncertain, and complementary inhibition and protective measures are generally still required [2,3,6,14,39].

The conservation context of an active chloride pit differs from that of routine cleaning of a stable, preserved patina, because corrosion has already substantially disrupted the original surface stratigraphy within the pit. This changes the risk–benefit balance: limited modification within an actively deteriorating pit may in some cases be justified if continued chloride activity poses a greater threat to the surrounding preserved surface. In the present work, "localised" alteration is therefore used in a spatial rather than evaluative sense, referring to visible modification remaining primarily within the pre-existing corrosion pit and avoiding unnecessary extension into the surrounding preserved patina. The tightly focused working configuration used for these treatments, operationally estimated at approximately 1.5 mm, provided sufficient spatial control for treatment of many individual pits.

Initial trials on archaeological fragments and historical artefacts confirmed the broader tendency observed in Section 3.1: loose, powdery corrosion was readily removed, including superficial corrosion associated with active chloride pitting. Direct and microscopic examination, supplemented by in-situ Raman characterisation in selected areas, showed efficient cleaning of the visible superficial corrosion products. During irradiation, the fume extractor nozzle was positioned adjacent to the treatment area to collect ejected particles, followed by cleaning with ethanol-soaked cotton swabs. These trials nevertheless showed that superficial removal alone did not necessarily prevent recurrence. On the Western Zhou Dynasty single-winged bell, dry LQS treatment at ~2.83 J·cm^{-2} and 2 Hz efficiently cleaned the visible pitted corrosion. Small or less-corroded pits sometimes required only a single pulse, while up to five pulses were generally sufficient to remove most superficial corrosion from larger pits, although the cleaning response varied with pit condition (Figure 9). Powdery green corrosion reoccurred rapidly even in areas that had appeared well cleaned, indicating that the underlying source of active chloride corrosion had not been sufficiently affected by the treatment. Trials on other archaeological fragments similarly showed that increasing fluence alone did not resolve the problem: the surface response became more pronounced without preventing subsequent recurrence.

In previous conservation treatments, recurrent chloride pits were usually retreated and followed soon afterwards by corrosion-inhibitor measures, as in the single-winged bell and other previously treated objects. During treatment of a Southern Dynasties incense burner, approximately ten localised pit areas were identified, some containing more than

one individual corrosion pit. All were initially treated using the routine low-frequency approach of 3–5 Hz, which allowed continuous handpiece movement and rapid visual adjustment over complex surfaces; approximately half were treated predominantly with LQS at ~2.83 J·cm^{-2} and half with SFR at ~4.25 J·cm^{-2}. Most superficial pale-green corrosion was removed within 4–5 pulses per irradiated area, as assessed visually and microscopically. Visible recurrence was defined as the reappearance of pale-green corrosion within an area that had appeared free of such corrosion immediately after treatment. Recurrence was rapid, occurring in some areas within 2–3 days and generally within about one week, often approaching the pre-treatment visible extent. Several areas were retreated after recurrence using low-frequency LQS or SFR, but similarly limited persistence was observed. Increasing the pulse number alone did not materially alter this short-term behaviour, while further increases in fluence were avoided after tentative trials produced markedly stronger audible and mechanical responses that were considered potentially damaging.

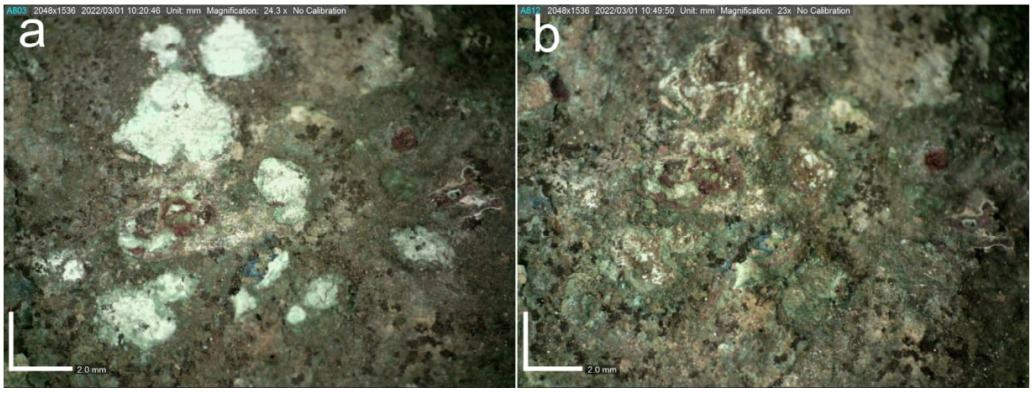


Figure 9. Typical response of active chloride pits on the single-winged bronze bell (**a**) before and (**b**) after localised dry LQS treatment. Most superficial powdery corrosion was removed, although the degree of clearing varied among individual pits according to their initial condition. Scale bars: 2 mm.

Higher-frequency treatment was explored only after rapid recurrence had been observed following the routine low-frequency interventions. An alternative approach reported previously provided a practical stimulus for considering whether a stronger localised thermal contribution might be useful in recurrent chloride pits [6]. Using a 1064 nm Smart Clean 2 laser in SFR mode, with the handpiece removed so that the optical fibre produced a highly localised thermal effect, they treated localised chloride-related corrosion at 200 mJ and 1 Hz, describing the effect as a form of "heat-sealing" [6]. Because this fibre-tip configuration differed substantially from the focused handpiece used here, the reported parameters cannot be translated into directly comparable fluence values, and the study did not establish a repetition-frequency effect. Nevertheless, it suggested that deliberately enhancing the thermal component of the interaction might merit exploration.

Because the active chloride pits on the incense burner were small, spatially fixed and located on a relatively flat surface, higher repetition frequencies could be explored with greater local control. At the time, one working hypothesis was that the shorter interval between successive SFR pulses might enhance cumulative heating and thereby promote thermal modification of chloride-bearing corrosion products, potentially facilitating more complete removal of the active corrosion. On this basis, SFR irradiation at 20 Hz was applied to selected recurrent pits at ~4.25 J·cm^{-2} for approximately 1–2 s, corresponding to about 20–40 pulses. In contrast to the preceding low-frequency treatments, these areas developed marked darkening, smoother surface morphology and localised spheroidal features, indicating substantial thermal modification. No visible pale-green recurrence

was observed during the first week, whereas recurrence had typically occurred within several days after the preceding low-frequency treatments (Figure 10). The same 20 Hz SFR conditions were subsequently applied to two additional recurrent pit areas, which showed a comparable short-term response.

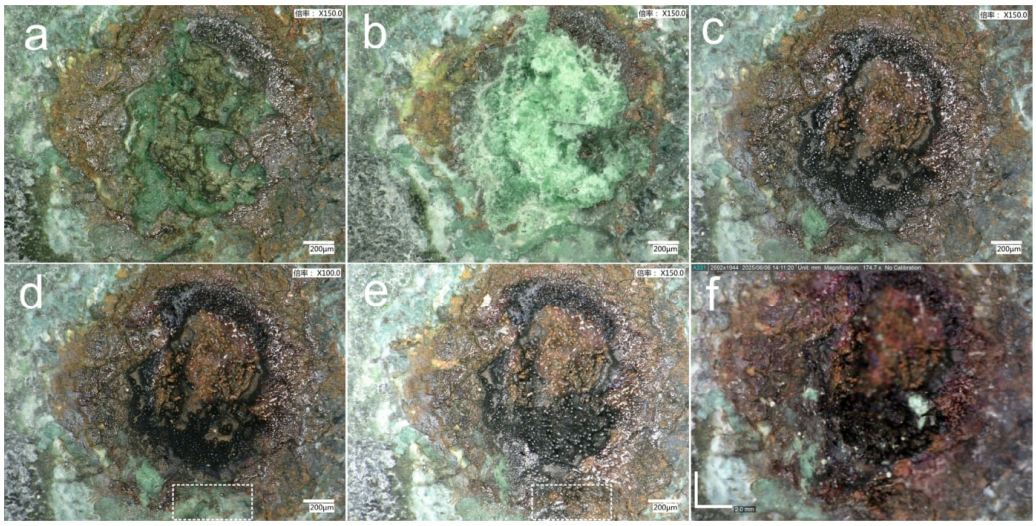


Figure 10. Time-dependent response of an active chloride pit on the incense burner. (**a**) After low-frequency SFR treatment (3–5 Hz); (**b**) recurrence one week later; (**c**) after subsequent 20 Hz SFR treatment; (**d**–**f**) follow-up at one week, three months, and seven months, respectively. The boxed lower-margin region in (**d**,**e**) was affected during subsequent treatment of an adjacent area and was excluded from longitudinal comparison. Scale bars: 200 µm (**a**–**e**) and 2 mm (**f**). The Chinese label "倍率" in panels (a–e) indicates magnification.

Following this observation, limited opportunistic comparison trials were undertaken using SFR at 10 Hz and LQS at 10 and 20 Hz, with approximately comparable pulse numbers where practicable. These conditions did not reproduce the same combination of pronounced thermal modification and delayed visible recurrence observed with 20 Hz SFR. Because the trials were not balanced across equivalent pits and were influenced by differing prior treatment histories, they were regarded as exploratory observations rather than as a systematic frequency-response experiment.

These observations prompted the extension of 20 Hz SFR treatment to the remaining pit areas. Follow-up observation took place in an indoor laboratory without dedicated temperature or relative-humidity regulation or continuous environmental logging. The object was exposed to ordinary seasonal fluctuations and routine ventilation, and no corrosion inhibitor or protective coating was applied during the observation period. At approximately three months, only isolated pinpoint recurrence of pale-green corrosion was observed. By seven months, localised recurrence had appeared in five individual pits across four pit areas, but remained limited in extent and differed markedly from the rapid and widespread regreening observed within days after the earlier low-frequency treatments. Figure 10 illustrates the progression in one representative area, from low-frequency treatment and follow-up after 20 Hz SFR at one week, three months and seven months.

A closer precedent for the accompanying surface modification is provided by Frank et al. [39], who used an optically modified 1064 nm Nd:YAG laser for localised treatment of active bronze-disease pits and reported micron- to sub-micron-scale micromelting on some treated samples. Although their irradiation conditions and optical configuration differ substantially from those used here and do not permit direct numerical comparison, their observations similarly show that localised removal of chloride-related corrosion can coexist

with surface modification. The present case extends this comparison by documenting the subsequent evolution of visible recurrence over more than seven months.

Raman analysis was used to examine whether the pronounced visual and morphological differences within the 20 Hz-treated areas corresponded to detectable differences in surface phase composition. Previous studies using 1064 nm lasers, although with irradiation regimes substantially different from the microsecond SFR treatment used here, have reported differing phase responses of copper-corrosion systems, including possible localised tenorite formation after nanosecond Q-switched treatment [15] and persistence of clinoatacamite after laser reduction of an artificial hydroxychloride layer [17]. In the present study, spectra acquired from three visually distinct subregions—a reddish area, a darkened area, and a spheroidal surface feature—were all attributable predominantly to cuprite despite their markedly different microscopic appearances (Figure 11). Raman signal intensity and spectral quality varied among the three surface morphologies and with acquisition conditions and were therefore not interpreted quantitatively. Within the surface region accessible to Raman examination, no distinct major phase corresponding to the pronounced morphological differences was identified. The condition of chloride-bearing corrosion at greater depth, however, remains unresolved.

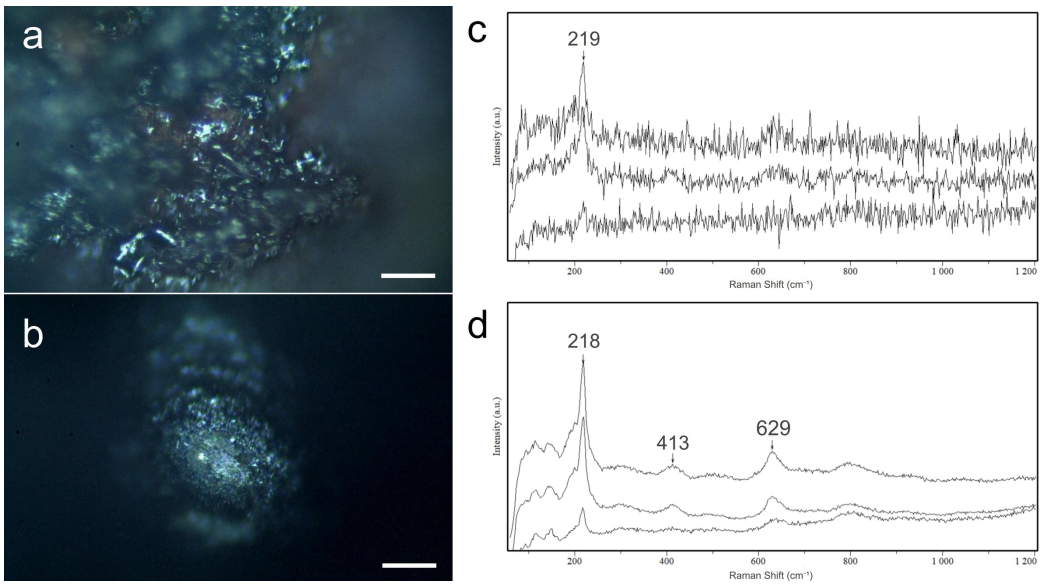


Figure 11. Microscopic and Raman characterisation of visually distinct subregions within a chloride pit treated at 20 Hz. (**a**) Intermixed reddish and darkened areas; (**b**) spheroidal feature; (**c**) short-acquisition (10% laser power, 1 s exposure, 1 accumulation) and (**d**) long-acquisition (10% laser power, 10 s exposure, 10 accumulations) Raman spectra. Spectra from top to bottom correspond to the reddish area, darkened area, and spheroidal feature. Scale bars: 20 µm.

The delayed and reduced visible recurrence following 20 Hz SFR treatment raises the possibility that repetition frequency contributed to the different response. Although repetition frequency has received comparatively limited attention as an independent treatment variable in conservation laser cleaning, it has been recognised as relevant to pulse delivery and to cumulative thermal and mechanical effects in laser–material interactions [40,41]. In the present exploratory trials, nominal fluence remained at approximately 4.25 J·cm^{-2}, but pulse number at 20 Hz was estimated from irradiation duration and was not tightly standardised, while preceding low-frequency treatment histories were not systematically examined. The observed response should therefore be regarded as suggestive of a frequency-related effect rather than as a controlled demonstration of one. At 20 Hz, successive pulses were separated by approximately 50 ms, which may have reduced the time available for thermal

relaxation within the heterogeneous corrosion layer–metal system and increased cumulative heating. Other processes may also have contributed, including transient vapour or plasma effects on energy coupling and progressive changes in surface morphology and composition that altered absorption from pulse to pulse. More extensive removal of chloride-bearing material and thermally induced modification of the residual corrosion structure are therefore plausible, non-exclusive contributors to the delayed and reduced visible recurrence, potentially also altering local pathways for moisture and oxygen transport within the pit. No transient temperature measurements or depth-sensitive chemical characterisation were performed, and the relative contributions of these processes therefore remain unresolved. Further cross-sectional analysis, complementary phase characterisation, and longer-term or accelerated-humidity monitoring would be required to test these possibilities.

The 20 Hz treatment also involved a clear conservation trade-off. Darkening, smoother surface morphology and localised spheroidal features were conspicuous under microscopic examination, and in some cases visible modification or patina loss extended approximately 0.1–0.3 mm beyond the original pit margin. The reasons for this uneven occurrence remain uncertain, but differences in local preservation state and heat-transfer conditions, as well as minor variations in spot placement during hand-operated irradiation, may have contributed. This lateral spread was particularly relevant because several pits were located close to surviving ink inscriptions; treatment was therefore confined as closely as possible to the individual areas. At normal viewing scale, these localised changes were less conspicuous against the heterogeneous and locally corroded surface of the incense burner (Figure 12). Following the observational period of more than seven months, small recurrent pale-green spots were retreated using 20 Hz SFR, with individual applications kept to approximately 1 s or less wherever practicable. Upon completion of the overall conservation treatment, all laser-treated pit areas received conventional corrosion-inhibition and protective measures.

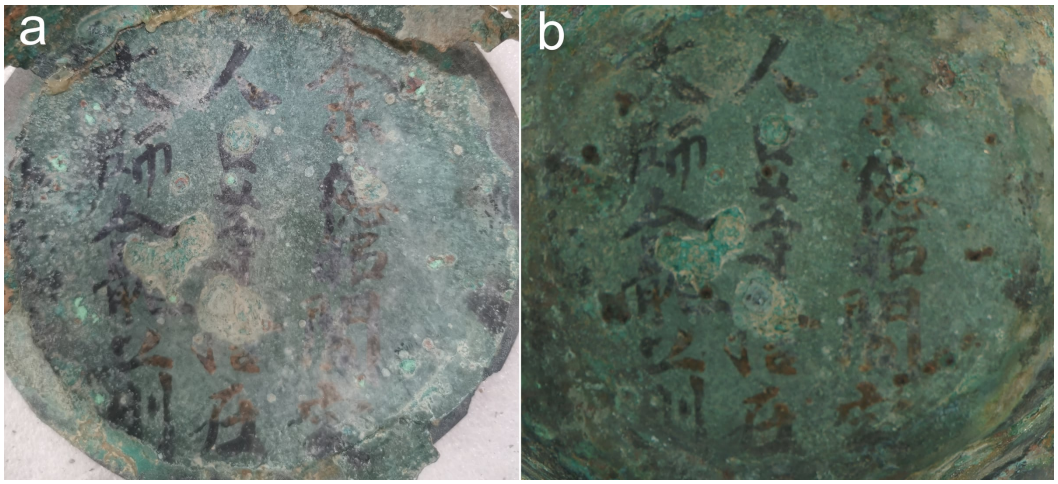


Figure 12. Overall appearance of the area affected by chloride pitting on the incense burner (**a**) before and (**b**) after conservation treatment.

Taken together, laser irradiation provided rapid and efficient removal of superficial corrosion associated with active chloride pits and, under the selected 20 Hz SFR conditions, was associated with a marked delay and reduction in visible recurrence. Whether the accompanying visual and surface alterations are acceptable depends on the balance between these practical benefits, the condition and significance of the surrounding surface, and the overall conservation objective.

3.5. Defining the Role of Laser Cleaning in Bronze Conservation: A Practical Framework

The observations presented above ultimately echo Asmus's longstanding view that laser cleaning is "not, and never was, a panacea" [42]. A decade of laboratory investigation and conservation practice suggests that the central question posed by practice is not simply to identify a fluence, pulse mode or optical contrast that produces removal, but to determine whether the resulting interaction offers a conservation advantage under the particular surface–target configuration encountered. Nominally similar irradiation conditions may lead to very different practical consequences when preservation state, surface morphology, target thickness, adhesion or stratigraphy differ. The problem therefore extends beyond parameter selection: preliminary testing must help establish whether a useful balance can be achieved between removal benefit, preservation of the historic surface and practical control of the intervention, within the intended scope and desired outcome of treatment. The framework proposed here was developed from this shift in emphasis, integrating pre-treatment assessment, experience-derived tendencies, preliminary testing, treatment-response observation and conservation judgement into a practice-oriented decision process.

Before irradiation, pre-treatment assessment is intended to assemble the information most relevant to that decision rather than to prescribe a fixed analytical sequence. Its central concern is relational: neither the surface intended for preservation nor the removal target can be judged in isolation, because practical selectivity depends on their contrast, interface, morphology and relative state of preservation. Where information on composition, manufacturing technique or previous analytical characterisation is available, it can sharpen expectations about laser–material response. Where such information is incomplete, directly observable features—including preservation state, surface morphology, target distribution, thickness, cohesion and the degree of adhesion or intergrowth—still provide a practical basis for identifying potential benefits and risks and for designing cautious preliminary tests. In some cases, assessment alone may identify surfaces so vulnerable, or surface–target relationships so unfavourable, that irradiation need not be used merely to confirm unsuitability. In this sense, the framework is intended to support structured conservation judgement under the uneven analytical access that often characterises practice. Its purpose is therefore not to provide a complete material description of every object but to identify, from the information realistically available, the features most likely to govern the feasibility and limits of intervention.

Viewed in relation to the three practical roles defined below, recurring combinations of these features tended to shift the treatment margin in characteristic directions. Where the preservation surface was laser-sensitive or poorly conserved, the target was densely intergrown with it, or target–surface differentiation and the interface itself were poorly defined, the margin tended to contract; *hei-qi-gu* patina and degraded gilding or silvering exemplify the tendency associated with Type I. By contrast, a relatively tolerant and well-preserved surface, loose or weakly adherent deposits, sufficient overlying target thickness and clearer target–surface differentiation could widen the usable margin, as observed with well-preserved *ni-jin* and *shui-yin-qin* surfaces and with compositionally distinct aged restoration materials. Surface morphology also influenced how minor variation in irradiation was expressed visually, with relief or coarsely textured surfaces generally providing greater tolerance than planar surfaces; these conditions underpin the tendency associated with Type II. A third group of situations was less well described by either a consistently narrow or broad margin: localised problems, heterogeneous or variably adherent targets, spatially changing target–surface differentiation, and weakly absorbing targets for which interfacial or mechanical effects may assist could make laser treatment useful only within restricted areas, over limited treatment stages, or in conjunction with subsequent conservation measures. Recurrent chloride pits and planar surfaces bearing relatively

irradiation-responsive patina exemplify this more conditional tendency associated with Type III.

These recurring tendencies provide a practical basis for anticipating where a useful treatment margin may be more or less likely to emerge, for identifying where caution should be concentrated, and for deciding what preliminary testing needs to resolve. They do not, however, assign a treatment Type in advance. The practical role of laser treatment emerges only after the observed response is considered together with conservation judgement, including removal benefit, surface preservation, controllability and the intended conservation objective. A tendency suggested by pre-treatment assessment may therefore be confirmed, modified or overturned during testing: a configuration that appears favourable may prove difficult to control, while an apparently unfavourable target may become useful if partial removal, structural weakening or localised intervention provides a meaningful conservation benefit. Conversely, repeated departures from an expected tendency add to the empirical basis of the framework and refine how those tendencies are understood. The framework is therefore inherently iterative and open: accumulated experience informs preliminary expectations, while each new treatment outcome can in turn modify the practical interpretation of those expectations.

Against this background, the three types describe practical roles that laser treatment may assume once the preliminary response has been interpreted in relation to the intended intervention. They are therefore best understood as outcomes of the decision process rather than as additional material categories.

- Type I: Laser generally unsuitable.

Type I is reached when preliminary testing does not establish a practically useful treatment margin for the intended intervention. This may occur because unacceptable alteration of the preservation surface precedes meaningful removal, or because irradiation transforms the target without providing sufficient conservation benefit to justify continued treatment. In some cases, this may reflect a particularly irradiation-sensitive surface, as observed for *hei-qi-gu* patina. More often, however, Type I reflects the combined effect of surface condition, the surface–target relationship and the conservation objective, such that laser treatment offers no defensible practical advantage over alternative approaches. Recognising this at an early stage is itself a useful outcome of the assessment process.

- Type II: Laser as a primary treatment.

Type II describes situations in which laser treatment can undertake the principal removal task with a sufficiently favourable and controllable balance between removal and preservation. In the present study, selected well-preserved *ni-jin* surfaces and certain aged restoration residues provided representative examples in which laser treatment could perform most or all of the intended removal within an acceptable treatment margin. This designation concerns the role of laser treatment rather than the permanence of a particular set of irradiation conditions: the response must be reassessed as treatment is extended, and broader application remains appropriate only while removal and surface preservation remain sufficiently acceptable and controllable.

- Type III: Laser as an auxiliary treatment.

Type III encompasses cases in which laser treatment makes a meaningful but deliberately limited contribution to the overall conservation process. The limitation may be spatial, because only isolated or selected areas benefit from irradiation; procedural, because laser treatment is most useful for partial removal, weakening or preparation before another method is applied; or strategic, because the laser addresses only one component of a broader conservation problem. In such cases, the value of treatment lies in improving the feasibility, safety or efficiency of the intervention without being expected to complete the conservation

task on its own. The treatment of recurrent chloride pits illustrates this localised role: laser irradiation was confined to individual corrosion sites and did not replace the subsequent corrosion-control and protective measures required for the object as a whole. Type III should not be regarded simply as an unsuccessful or weaker form of Type II: a deliberately localised or preparatory laser intervention may be the most appropriate use of the technique even when broader removal is technically possible.

In practice, however, the boundary between Type II and III is contextual rather than absolute. The same surface–target configuration may assume different practical roles depending on the treatment objective, the area under consideration, and the stage reached during treatment. The previously treated Shang Dynasty *gu* vessel illustrates this boundary particularly well. Laser irradiation was applied over a large area and accomplished most of the intended material removal, supporting a predominantly primary role; however, the abrupt detachment of the restoration residues required close visual control as the remaining layer became thinner, and complementary solvent finishing was still necessary. Broader application was facilitated by the substantial thickness of the overlying material, the compact, historically polished underlying surface, and the relief morphology, which made minor variation at treatment boundaries comparatively inconspicuous.

This case also illustrates why the removal mechanism itself does not define the treatment role. Progressive ablation, abrupt detachment, partial removal or structural weakening may each be useful under appropriate circumstances. What matters is how the observed response contributes to the intended intervention and how much complementary treatment remains necessary. Complete target removal is therefore not a prerequisite for a successful laser intervention: partial removal or weakening may constitute a meaningful outcome when it reduces the duration, intensity or risk of subsequent conventional treatment while avoiding unnecessary irradiation of the historic surface.

In practice, preliminary irradiation should begin with limited exposure so that the response to individual or small numbers of irradiation events can be assessed before repetition-frequency effects are deliberately introduced. The aim is not simply to identify an apparently effective setting, but to understand how the treatment margin changes as exposure increases and as the target is progressively altered. Reassessment becomes especially important during scale-up: a response that is acceptable in a small test area may become conspicuous or spatially variable when extended across differences in morphology, target thickness, adhesion or surface condition. Likewise, as an overlying target becomes thinner and the preservation surface is approached or exposed, the usable treatment margin may narrow even in an otherwise successful Type II intervention. Broader application is therefore appropriate only while the response remains acceptable and sufficiently uniform; otherwise, treatment should be restricted, modified, combined with complementary methods, or its practical role reconsidered. Treatment roles may consequently change during the course of an intervention rather than being fixed at the outset.

Figure 13 brings these relationships together as a practice-oriented decision framework. Pre-treatment assessment and experience-derived tendencies guide preliminary testing, while the observed response and conservation judgement determine the practical role assigned to laser treatment at that stage. Reassessment during scale-up allows that role to be maintained, restricted or revised as conditions change. This framework is intended to structure professional judgement and make the reasoning behind treatment choices more explicit, while remaining open to refinement as additional conservation experience accumulates.

3.6. Between Experimental Control and Conservation Reality: The Value and Limits of Practice-Based Evidence

The boundaries of the present study reflect both the diversity of bronze conservation problems and the conditions of practice-led investigation. Even when laboratory experiments and individual artefact cases reveal recurring tendencies, differences in preservation state, surface morphology and surface–target relationships make generally transferable treatment rules difficult to establish. The archaeological fragments examined here were obtained opportunistically, while the historical artefact cases likewise arose from available conservation assignments rather than systematic selection. Suitable matched specimens were not always available, and the resulting evidence could not cover the full range of relevant surface conditions.

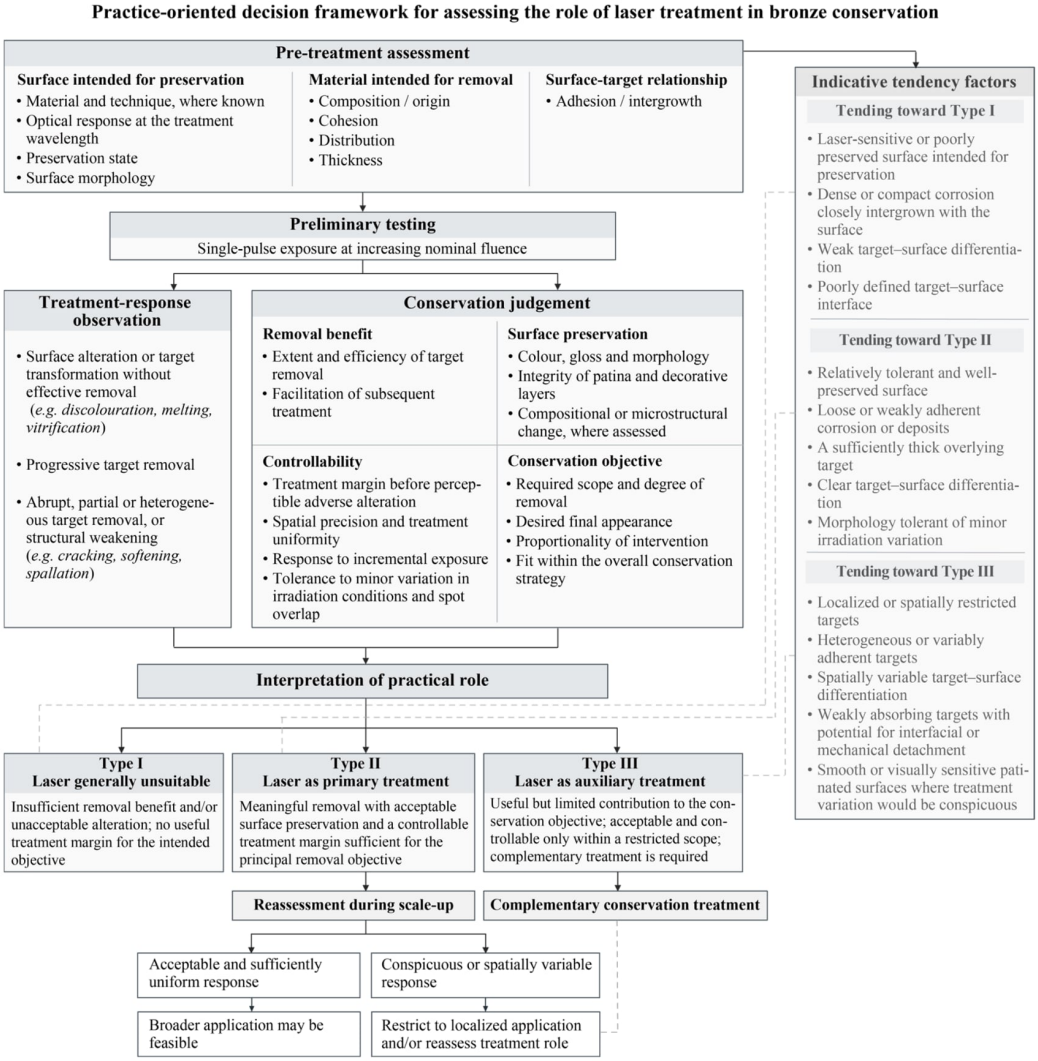


Figure 13. Practice-oriented decision framework for assessing the role of laser treatment in bronze conservation. Indicative tendency factors guide preliminary testing but do not determine the treatment Type; the practical role emerges from treatment response and conservation judgement and may be revised during scale-up.

Technical characterisation presents another challenge in conservation practice. Conservators whose expertise lies primarily in treatment may find it difficult to verify beam characteristics independently or investigate laser–material interaction mechanisms without specialist laser-physics support and diagnostic facilities. In the present work, the treatment beam was not independently characterised, and nominal fluence estimates relied on the

visible aiming spot. Treatment outcomes were assessed predominantly through visual and microscopic examination, with analytical methods applied selectively according to individual conservation needs. These observations provide a stronger basis for describing practical treatment responses than for establishing their underlying physical mechanisms. Several explanations proposed in this study therefore remain hypotheses, while alterations below the detection limits of the assessment methods cannot be excluded.

In the historical artefact cases, the scope for planned experimental comparisons was often shaped by the immediate demands of conservation treatment. Conditions were frequently adjusted as work progressed, and the control of comparison variables was not always sufficiently systematic. The sequential chloride-pitting trials illustrate this difficulty: although the treatment sequence and observed responses were documented, comparisons between repetition frequencies were exploratory, without fully controlling pulse number and preceding irradiation histories. More carefully planned comparisons, where compatible with conservation priorities, would strengthen the interpretation of similar cases in future.

A separate difficulty concerns comparison with published studies. Differences in laser systems, pulse regimes and beam-delivery configurations, together with incomplete reporting of some experimental parameters, often prevent meaningful numerical comparisons even between treatments addressing similar conservation problems. This limits the extent to which reported fluences can serve as transferable recommendations. The framework developed here instead provides a structure for using available evidence to guide case-specific testing and conservation judgement, while allowing its indicative tendencies to be refined as technical characterisation, reporting practices and comparative evidence improve.

4. Conclusions

Drawing on a decade of laboratory investigation and conservation practice at the Shanghai Museum, this study identified both practical opportunities and important boundaries for 1064 nm Nd:YAG laser cleaning of bronzes. Preliminary tests on archaeological fragments delineated effective-cleaning fluence ranges and adverse-alteration limits for representative surface conditions. Their substantial overlap and variability, together with the limited predictive value of reflectance at 1064 nm, showed why these values are better used as preliminary references than as transferable treatment thresholds. Beyond material composition and optical response, treatment margins were influenced by the preservation state of the underlying surface, target thickness and cohesion, interfacial adhesion and stratigraphy, and local morphology.

Despite the pronounced case specificity of bronze surfaces, recurring tendencies emerged across the fragment tests and artefact treatments. Well-preserved gold-bearing surfaces and certain aged restoration residues could provide useful margins for extensive laser treatment, whereas sensitive patinas, degraded metallic decorative layers and strongly intergrown corrosion often constrained selective removal. In selected active chloride pits, 20 Hz SFR treatment was associated with delayed and reduced visible recurrence, but also with local surface modification and the continued need for conventional corrosion-control measures. These contrasting outcomes showed that the practical value of irradiation depends not only on what can be removed, but also on what must be preserved and what further intervention is required.

The central lesson of these successes and setbacks is that laser cleaning should be judged by the role it can appropriately play within a conservation intervention. It may serve as the primary removal method, provide a limited contribution through localised treatment, partial removal or target weakening, or offer insufficient advantage to justify its use. Although the practice-led evidence leaves some interaction mechanisms unresolved and limits direct parameter comparisons, it provides a basis for the experience-derived,

adaptable decision framework proposed here. The ability to recognise when laser treatment should be restricted, supplemented or avoided is therefore as important as identifying conditions under which it can succeed.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage9110457/s1, Table S1: Principal irradiation configurations and observed responses in main experimental and conservation cases. All treatments used EOS Combo Nd laser at 1064 nm; LQS and SFR denote the 100 ns and 30–110 µs operating modes, respectively.

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Data Availability Statement: The data supporting the findings of this study are contained within the article and its figures. Additional underlying data generated and analysed during the study are not publicly available because they include conservation documentation and analytical records associated with cultural heritage objects that are subject to institutional access restrictions. These data may be made available from the corresponding author upon reasonable request and subject to permission from the Shanghai Museum.

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Abbreviations

The following abbreviations are used in this manuscript:

Nd:YAG	Neodymium-doped yttrium aluminium garnet
LQS	Long Q-switched
SFR	Short Free Running
pXRF	Portable X-ray fluorescence

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