



Original article

Influence of pulse duration on the effects induced by three Nd:YAG lasers operating at 1064 nm to tempera paintings mock-ups

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ABSTRACT

Laser cleaning of soiled wall paintings is a conservation practice that has been adopted for decades. However, the increasingly widespread availability of laser technology highlights the need to optimize the choice of laser systems and, consequently, the parameters used on a case-by-case basis. In this study, three Nd:YAG lasers (1064 nm) with different pulse durations were tested: a short free-running system (110 μs), long Q-switched system (100 ns), and Q-switched (8 ns). These lasers were tested on tempera painting mock-ups made of one pigment (i.e. malachite, azurite, lead white, orpiment, or cinnabar) mixed with an organic binder (i.e. egg yolk or rabbit glue) applied to a lime mortar. Each laser was also evaluated in tablets composed solely of one pigment. The reference and irradiated temperas were studied using stereomicroscopy, spectrophotometry, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX). The pigment tablets were also analyzed with micro X-ray diffraction (μXRD).

All samples suffered blackening after laser irradiation, the intensity of which depended on the nature of the pigment and the binder. Overall, pigment susceptibility was broadly comparable across the three pulse-duration lasers. Cinnabar exhibited the highest level of susceptibility, followed by copper carbonates and orpiment, while lead white proved to be the least affected pigment. The binders exhibited a protective effect on the pigments, although this effect was more intense in egg yolk paintings. Regarding pulse duration, it was found that at low fluences, the laser with the longest pulse duration generated the lowest color changes, while at high fluences, this same laser generated the greatest impact on the temperas. Physical effects were observed in the samples (mineral melting and binder loss), though these were not proportional to the intensity of the blackening.

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Introduction

Laser cleaning, particularly in the field of stone conservation, has been extensively investigated over the past three decades [1,2]. The use of lasers as a cleaning tool first gained attention in the 1970s when John Asmus successfully removed dark encrustations from Venetian marble surfaces using laser technology [3].

Traditional tempera paints consist of an inorganic pigment combined with a proteinaceous binder, as rabbit glue or egg yolk [4–6]. Soiling, biological colonization, and the formation of patinas are among the types of deterioration commonly observed in

pictorial heritage [7]. Since the introduction of laser cleaning in art conservation, the scientific community has thoroughly investigated the significant issue of intense blackening that arises when paintings are exposed to various lasers, such as KrF excimers and Nd:YAG [8–11]. Numerous studies have been addressed to understand the mechanisms underlying this color change phenomena [8,9]. Generally, laser irradiation leads to the formation of a greyish or blackened layer on the treated areas. When pigments were exposed to an Nd:YAG (1064 nm), vermilion and massicot underwent permanent blackening, whereas white and red lead pigments exhibited temporary darkening; various earth pigments and malachite darkened at different levels [12]. Initially, it was assumed that the heat generated by the laser pulse was the responsible for these color alterations, primarily due to oxidation. This pro-

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cess could lead, for example, to the transformation of red cinnabar into black metacinnabar or the conversion of yellowish massicot into globules of metallic lead [12]. Nevertheless, identifying the possible chemical and/or mineralogical effects induced by laser irradiation remains a considerable challenge, given that the laser generally affects the outermost micrometres of the treated surface. Regarding the influence of laser wavelength on paintings, in [13] used three specific wavelengths (213, 266 and 2940 nm) to remove aged varnishes from oil paintings. Their findings revealed that, when determining the damage threshold, the wavelength of 2940 nm caused greater damage than the other two wavelengths.

Studies focusing on pulse duration has also been considered in the literature. Pigments tablets made up of single pigments - namely vermilion, lead chromate and malachite- were irradiated using different Nd:YAG lasers emitting at 1064 nm (IR region) and 213 nm (UV region) with pulse durations of 150 ps and 15 ns, respectively, as well as with an XeCl excimer laser (248 nm) and 500 fs [14]. Vermilion underwent an allotropic transformation, while lead chromate and malachite suffered discoloration due to reduction processes [14]. Furthermore, these authors reported that employing lasers operating in the UV region with shorter pulse durations (ps and fs) mitigated the extent of induced modifications. In other investigation, Nd:YAG lasers operating in short free running (SFR) and Long Q-Switched (LQS) modes allowed for a broader range of operative fluences than Q-Switched (QS) laser when cleaning black carbon, dark limewash, dark Paraloid and white-wash on fresco wall paintings [15]. This aligns with findings from a comparative study of different pulse duration lasers (QS, LQS and SFR modes), which determined that the QS laser was the least effective in removing artificial crusts from tempera paintings on ceramics, due to its comparatively low damage threshold in comparison to the other modes [15]. Furthermore, in [16], the influence of the wavelength and pulse duration of an Nd:YAG laser was evaluated for the removal of unwanted substances from egg yolk-based tempera paints containing vermilion, lead chromate, or zinc white. Authors used lasers of diverse pulse duration and wavelength: 150 ps (at 1064 nm and 213 nm) and 15 ns (at 213 nm). The cleaning condition using UV wavelength combined with the shortest pulse duration was found to best preserve the original color. Discoloration and chemical changes were observed irrespective of the wavelength employed. Additionally, authors noted that lasers operating in the UV region with ultrashort pulses tend to be less aggressive than those operating at IR wavelengths. Other authors used three different Nd:YAG laser (1064 nm) working with varying pulse durations (250 μ s, 20 ns and 500 ps) for the removal of surface encrustations from fragments of genuine wall paintings. They concluded that each pulse regime offers specific optimal conditions: ultra-short pulses (ps) provide enhanced control, while longer pulses (μ s) are particularly effective for certain contaminants such as molten lead [17]. Additionally, experiments reported in [18] employing a Ti:Sapphire laser in fs domain demonstrated substantially higher damage thresholds compared to those obtained under ns irradiation.

Research aim

The main aim of this study is to investigate the influence of the pulse duration on the effects induced by three Nd:YAG lasers (1064 nm) with different pulse duration: SFR (110 μ s), LQS (100 ns), and QS (8 ns). Lasers were applied at increasing fluences to two types of mock-ups: pigments-only tablets and tempera painting mock-ups composed of a single pigment combined with a proteinaceous binder, either egg yolk or rabbit glue. To deepen the understanding of the effects of laser overexposure on tempera paintings, samples subjected to the highest fluences

were analyzed using a combination of complementary microscopic and spectroscopy techniques, including ATR-FTIR, SEM-EDX and μ XRD.

Materials and methods

Raw materials

Five pigments of different composition were selected as raw materials: two copper carbonates (azurite - $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ -, identified as AZ and malachite - $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ -, identified as MA), lead carbonate (PbCO_3), identified as WK (from White Kremser) and two sulphides: (orpiment - As_2S_3 - identified as OR and cinnabar - HgS -, identified as CI). These pigments were among the most frequently used in tempera wall paintings [19]. Regarding binders, egg yolk (EY) and rabbit glue (RG) were selected for this study. All raw materials were supplied by Kremer Pigments GmbH & co (Germany), with the exception of eggs, which were purchased in a local market. Mortar is composed by lime paste and silicate aggregates. A calcitic slaked lime, aged for over two decades, was provided by the Department of Mineralogy and Petrology of the University of Granada (Spain). Coarse (1–2 mm) and fine (0.4–0.8 mm) silica aggregates were purchased from hardware store also in Granada, while marble powder (<0.7 mm) from CTS S.L. Madrid (Spain).

Painted mock-ups preparation

Two types of mock-ups were prepared and examined in this study. Firstly, pigment-only tablets were created by placing the pigment powder into circular aluminum containers measuring 4 cm in diameter and 1 cm in height. The powder was then compressed using a 30 ton hydraulic press to obtain a measurable area for analysis upon irradiation. Secondly, to replicate ancient wall paintings, painting mock-ups were elaborated using a two-layer mortar substrate: 1) the innermost layer (*arriccio*) was composed of calcitic slaked lime with coarse and fine sand in a 1:3 (v/v) ratio; 2) the outermost layer (*intonaco*) was prepared by mixing lime with fine silica and marble powder in a 1:2 (v/v) ratio.

Mortar mock-ups, measuring 5 cm x 4 cm x 3 cm, were then stored under laboratory conditions (18 ± 5 °C and 70 ± 10 %RH) for 1 month to ensure the carbonation of the portlandite ($\text{Ca}(\text{OH})_2$) before the application of paint using the tempera technique.

Two binders were selected for tempera technique: egg yolk (EY) or rabbit glue (RG). For the EY-based paints, the yolk was poured back and forth in the half shells to separate it from the white. To get rid of any remaining egg white, the yolk was then rolled out onto a paper tissue. Finally, a needle was used to puncture the yolk's skin, and then the resulting liquid was transferred into a glass jar. For the RG-based paints, the preparation protocol followed can be consulted in [20]. Eight grams of rabbit glue were soaked in 100 mL of deionized water for 24 hours, with periodic stirring. Mixture was subsequently heated in a water bath below 50 °C with continuous stirring until a homogeneous solution was obtained. The rabbit glue was then left to cool to room temperature (18 ± 5 °C) until it reached a gel-like consistency. Each binder was then mixed with a powdered pigment up to get an adequate consistency (note that the paints' consistency was found adequate when droplets forming at the brush tip would not fall off easily). The prepared paints were applied in several layers onto the mortar mock-ups using a paintbrush. After application, tempera mock-ups were kept under laboratory conditions (18 ± 5 °C and 70 ± 10 %RH) for 1 month.

Laser methodology

The following three Nd:YAG lasers (1064 nm), with a constant repetition frequency of 1 Hz, were used, each one emitting pulses of different duration:

- An El.En group system Smart Clean II in Short Free Running mode (hereinafter SFR) and with a pulse duration of 50–110 μ s. The utilized pulse energies were 100, 200 and 400 mJ.
- An El.En group system EOS 1000 laser in Long Q-Switched mode (hereinafter LQS) and with a pulse duration of 100 ns. The utilized pulse energies were 32.5, 65 and 130 mJ.
- A Quanta system laser Thunder Art operated in Q-Switched mode (hereinafter QS) with a pulse duration of 8 ns. The utilized pulse energies were 40, 83 and 162 mJ.

The samples were irradiated by varying two laser parameters: the emitted energy (E) and the spot size. Following exploratory tests, a constant value of 25 % of the maximum emitted energy (E) was selected, as no noticeable color change was observed. This condition (designated as 25 %E) was considered to represent a no apparent damage situation, except for CI, which exhibited clearly visible color changes. To assess the effects of increasing fluences, two additional areas were irradiated using 50 % and 100 % of the maximum laser energy (E), while maintaining a constant the spot size. These two conditions were designated as 50 %E and 100 %E, respectively. Although no specific value for overlap was defined, irradiation was carried out with the lowest possible overlap to obtain a homogeneously irradiated area. The response of both pigment tablets and tempera mock-ups to laser irradiation is crucial for determining whether the presence of a binder plays a protective role, assessed in terms of *susceptibility*, which is defined as the propensity to undergo visible color changes under laser irradiation [21]. The diameter of the laser spot was measured using unplasticized polyvinyl chloride (UPVC) for each pulse duration.

Analytical techniques

The next complementary analytical techniques were used in this research:

- Laser diffraction using a Mastersizer 2000LF (Malvern Instruments, UK) with a Hydro 2000 G accessory was used to measure the granulometry of each powdered pigment. Samples were dispersed in ethanol. Data are based on 3 measures each acquired during 30 s. Results consider the distribution of the particle sizes based on volume (%) assuming a uniform distribution.
- Micro X-ray diffraction (μ XRD) (X'Pert PRO PANalytical B.V., the Netherlands) was used to determine the mineralogical characterization of the tablets before and after laser irradiation. Measurements were taken using a Bruker D8 DISCOVER diffractometer coupled with a detector DECTRIS PILATUS3R 11K-A. Working parameters included Cu-K α radiation, 50 kV voltage, 1 mA intensity, a 5–85° 2θ and speed of 0.02° 2θ with 40s/step. One millimeter was the diameter of the X-ray beam. Using X'Pert HighScore Plus program in conjunction with the *Crystallography Open database*, crystalline phases were identified.
- Stereomicroscopy using an Olympus SZX10 stereomicroscope equipped with an Olympus Color View I digital camera was used to check the superficial features (including color) of the pigment tablets and painting mock-ups before and after laser irradiation.
- Color spectrophotometry applying a Minolta CM-700d spectrophotometer was used for measuring the color of tablets and painting mock-ups before and after irradiation using the CIELAB and CIELCH color spaces, where L^* is the lightness, a^* is the

color coordinate between red (positive) and green (negative) and b^* is the color coordinate between yellow (positive) and blue (negative). In CIELCH space, C^*_{ab} is the chroma and h represents the hue [22]. A total of five measurement were made in specular component excluded (SCE) mode, using a D65 illuminant, a spot diameter of 3 mm and an observer angle of 10°. Then, the ΔL^* , Δa^* , Δb^* , ΔC^*_{ab} , ΔH^* and the color difference (ΔE^*_{ab}) were calculated taking the data color of the mock-ups (pigment tablet and tempera mock-up) before irradiation as reference [22].

- Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) with a Thermo Nicolet 6700 (Thermo Fisher Scientific, USA) was applied to evaluate the molecular composition of the mortar, the raw painting materials and the irradiated and unirradiated areas in the painting mock-ups. In the latter, ATR-FTIR was used to determine the possible molecular transformation occurred upon irradiation that could explain the color changes of the samples. Each mid-infrared region spectrum was recorded at 2 cm^{-1} resolution over 32 scans from 400 cm^{-1} to 4000 cm^{-1} .
- Scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDX using a Zeiss EVO60 scanning electron microscope equipped with a lanthanum hexaboride (LaB6) cathode and a silicon drift detector (SDD) and coupled with a 40 mm^2 Oxford Ultim Max EDS microprobe for semi-quantitative elemental analysis. Observations of the tablets and tempera mock-ups were carried out in secondary electron (SE) and backscattered electron (BSE) modes for the characterization of the micromorphological and compositional analysis of the irradiated and unirradiated areas. Samples were analyzed without any pretreatment in variable pressure mode, using an accelerating voltage of 20 kV and a pressure of 20 Pa.

Results

Characterization of raw materials: pigments, binders, and mortar

Details regarding the mineralogical and chemical composition of the pigments, obtained through XRD analysis, as well as their grain size distribution determined by laser diffraction, were reported in a previous study of the authors [21]. However, these data are included in Table 1 to facilitate a more comprehensive understanding of the materials used. FTIR characterization results are likewise presented in Table 1. In some cases, as happened for copper carbonates, the presence of impurities namely quartz (SiO_2) was not reported by the supplier, but it was determined via XRD analysis. Moreover, barite (BaSO_4) was also detected in the AZ pigment. Considering FTIR results, it should be mentioned that sulphide pigments (OR- As_2S_3 - and CI-HgS-) do not present spectral features in the mid-infrared region. Thus, only bands associated to pigments of carbonates are shown in this Table 1 and Table 2.

The mortar is primarily composed of calcite and quartz. This composition was confirmed by FTIR analysis through the identification of characteristic absorption bands attributed to calcite: 1484–1400 cm^{-1} (CO_3^{2-} asymmetric stretching), 870 cm^{-1} (CO_3^{2-} out-of-plane bending) and 712 cm^{-1} (CO_3^{2-} bending) [28,36–39]. The latter band is particularly indicative of crystalline calcium carbonate phases. A strong absorption band observed at $\sim 3640 \text{ cm}^{-1}$ (O–H stretching vibration) is associated with the presence of portlandite [38,40]. A band at 1794 cm^{-1} has been assigned to a contribution of asymmetric stretching (C–O) and in-plane symmetric bending (C–O) [41,42]. Several characteristic Si–O bonds were also identified: bands at 1175–1080 cm^{-1} related to asymmetrical stretching, 800–780 cm^{-1} (symmetrical stretching), $\sim 695 \text{ cm}^{-1}$ (symmetrical bending) and $\sim 450 \text{ cm}^{-1}$ (asymmetrical bending) [30,36,43]. The presence of symmetrical bending vibrations of the Si–O group at

Table 1
Mineralogical composition, particle size and molecular composition of the pigments.

Azurite (AZ) (Ref. 10,207)				Malachite (MA) (Ref. 10,345)				White Kremser (WK) (Ref. 4600)				Orpiment (OR) (Ref. 10,700)	Cinnabar (CI) (Ref. 10,624)
Mineralogical composition	Azurite (Cu ₃ (CO ₃) ₂ (OH) ₂), quartz (SiO ₂), malachite (Cu ₂ CO ₃ (OH) ₂) and barite (BaSO ₄)			Malachite (Cu ₂ CO ₃ (OH) ₂) and quartz (SiO ₂)				Cerussite (PbCO ₃)				Orpiment (As ₂ S ₃), realgar (As ₄ S ₄)	Cinnabar (HgS)
Pigment size (µm) ^a	R: 0.2–30 Mm: 15			R: 0.2–90 Mm: 35 (0.45)				R: 0.15–15 Mm: 4.5 (0.45)				R: 0.15–182; Mm: 40 (2.5)	R: 0.15–35; Mm: 6 (0.35)
FTIR assignment ^b	Wavenumber (cm ⁻¹) and intensity ^c	Related to:	Ref.	Wavenumber (cm ⁻¹) and intensity ^c	Related to:	Ref.		Wavenumber (cm ⁻¹) and intensity ^c	Related to:	Ref.		OR and CI (both sulphides) do not absorb infrared light between 4000 and 400 cm ⁻¹	
ν(O–H)	3434(vs)	Az	[23]	3395(s)	Ma	[24–26]		3441(w)	Cer	[27]			
ν(O–H)	3358(sh)	Az	[9,24]	3307(s)	Ma	[24–26]							
	2556–2489(vw)	Az	[28]					2410(w)	Cer	[28,29]			
ν _S (C–O) + ν _{AS} (C–O)													
ν _S (C–O) + in-plane δ(C–O)	1832(vw)	Az	[28,29]	1796(vw)	Ma	[24–26]		1729(w)	Cer	[27]			
ν _{AS} (C–O)	1490, 1463(vs)	Az	[28]	1485(vs)	Ma	[24–26]							
ν _{AS} (C–O)	1405(vs)	Az	[28]	1377(vs)	Ma	[24–26]		1369(vs), 1300(sh)	Cer	[27]			
ν _{AS} (S–O)	1185(m)	Ba	[30,31]										
trace of SO ₄ ²⁻													
ν _S (C–O)	1090(m)	Az	[23,24]	1097(m)	Ma	[24–26]		1107(w)	Impurities	[27]			
out-of-plane δ(O–H)	1039(w), 950(s)	Az	[24,30]	1041(s)	Ma	[24–26]		1050(m)	Cer	[27]			
out-of-plane δ _{AS} (C–O)	831(s)	Az	[23,24]					835(s)	Cer	[27]			
out-of-plane δ _S (C–O)	815(m)	Az	[23,24]	864(m), 816(m)	Ma	[24–26]							
in-plane δ _{AS} (C–O)	768(w), 744(w)	Az	[23,24]	777(m), 745(w)	Ma	[24–26]		675(vs)	Cer	[27]			
δ(Pb(O–H))								730(vw)	Cer	[27]			
δ _S (Si–O)	696(w)	Qz	[30,32]	709(w)	Ma	[24–26]							
δ _{AS} (S–O)	638(m), 610(m)	Ba	[33,34]										
ν(Cu–O)				570(s)	Ma	[24–26]							
ν(Cu–OH) or δ _S (Si–O)	527(m)	Qz	[32]	521(s)	Ma or Qz	[23,25,32]							
ν(Cu–O)	494(m)	Az	[23,35]	501(m)	Ma	[25]							
ν(Cu–OH) or δ _{AS} (Si–O)	448(m)	Az or Qz	[23,30,32,35]										
ν(Cu–OH)				487(sh), 425(s)	Ma	[23,25]							

Note: az (azurite); qz (quartz); ba (barite); ma (malachite) and cer (cerussite).
^a R (particle size range) and Mm (main maximum particle size). Numbers in parenthesis: secondary maximum particle size.
^b ν (stretching); δ (bending); S (symmetric); AS (asymmetric).
^c vs (very strong); s (strong); m (medium); w (weak); vw (very weak); sh (shoulder).

Table 2
Molecular composition of the binders (EY: egg yolk and RG: rabbit glue) by FTIR.

FTIR assignment ^a	EY		RG	
	Wavenumber (cm ⁻¹) and intensity ^b	Ref.	Wavenumber (cm ⁻¹) and intensity ^b	Ref.
N-H stretching of peptide bonds in this row	3285(m)	[44]	~3300(s,br)*	[45]
Amide II overtone	3070(w)	[44]		
cis double-bond stretching vibration of olefinic groups of unsaturated fatty acids	3009(w)	[46]		
ν _{AS} (CH ₃) from long chain fatty acids	2955(w)	[44]	2936(m, br)	[47]
ν _{AS} (CH ₂) from long chain fatty acids	2922(vs)	[44]	2855 (w, sh)	[47]
ν _S (CH ₂) from long chain fatty acids	2852(s)	[44]		
C=O (ester) ascribable to triglyceride	1743(s)	[44,48]	1740	[44,48]
Amide I ν(C=O)	1652–1633(s)	[44]	1631	[44,48,49]
Amide II: ν(C–N) (~40 %) and δ(N–H) (~60 %)	1540(s)	[44,48]	1552(s)	[49]
δ _{AS} (CH ₃), CH ₂ scissoring	1464(m) and 1454(m)	[44]	1455(s)-1047	[47]
collagen absorption features attributed to CH ₂ wagging, CH ₃ deformation, ν(C–N) and ν(C–OH)			1455(s), 1404(m, sh), 1338(m), 1283(m), 1240(m), 1200(m), 1161(m), 1112, 1081(m),1032(m)	[45,50,51]
δ(CH ₂ and CH ₃) groups of amino acid side chain	1379(w)	[52]		
Amide III: ν(C–N) and δ(N–H) (~30 % each), ν(C–C) (~20 %) and δ(C–H) (~10 %)	1233(m)	[30,53]		
ν(C–C) group of glycerol	1160–1064(m)	[54]		
Triplet characteristic of fatty acids. C–O–C (ester) stretching	1233(m)	[55]		
	1163(m)			
Amide III: ν(C–N) and δ(N–H) (~30 % each), ν(C–C) (~20 %) and δ(C–H) (~10 %)	1085(m)			
out-of-plane δ(CH)	969(m)	[30,46]		
ν(C–O–C) stretching of glycerol	878(w)	[30,54]		
CH ₂ rocking	720(w)	[44]		
δ(C=O)			606(w)	[56]

*Amide A band in protein.
^a ν (stretching); δ (bending); S (symmetric); AS (asymmetric).
^b vs (very strong); s (strong); m (medium); w (weak); vw (very weak); sh (shoulder); br (broadening).

Table 3
Laser conditions applied to the pigment tablets (T) and temperas with two different binders (EY: egg yolk and RG: rabbit glue) for each laser type (SFR, LQS and QS).

Laser	% of maximum energy	Pigment tablets (T)			Tempera mock-ups (EY and RG)		
		Energy (mJ)	Spot size (mm)	Fluence (J/cm ²)	Energy (mJ)	Spot size (mm)	Fluence (J/cm ²)
SFR (110 μs)	25 %E	100	5	0.51	100	4	0.8
	50 %E	200	5	1.02	200	4	1.59
	100 %E	400	5	2.04	400	4	3.18
LQS (100 ns)	25 %E	32.5	5	0.17	32.5	4	0.26
	50 %E	65	5	0.33	65	4	0.52
	100 %E	130	5	0.66	130	4	1.03
QS (8 ns)	25 %E	40	5	0.20	40	5	0.20
	50 %E	83	5	0.42	83	5	0.42
	100 %E	162	5	0.82	162	5	0.82

692 cm⁻¹ and out-of-plane vibration at 667 cm⁻¹ further confirm that the quartz is presented in crystalline form [32].

Assessment of the effects produced by increasing the laser fluence on samples

Table 3 shows the fluences corresponding to the irradiation conditions applied to both pigment tablets and tempera mock-ups. Firstly, it should be noted that during exploratory testing, tempera samples exhibited greater resistance to laser exposure than tablets when irradiated with LQS and SFR lasers, as higher fluences were required to induce surface darkening in the former. Comparing lasers, both in pigments and tempera, irradiation using the ns regimes (LQS and QS) allowed lower fluences than the μs regime (SFR). In other words, the longer the pulse, the higher the fluences that could be applied without causing visible damage. Between the two ns regimes, differences were minimal.

Fig. 1 shows the effects of each laser on both types of samples (pigment tablets and tempera mock-ups) providing an overall view of their behaviour under different pulse durations tested. It should

be noted that the irradiated area located at the bottom left of each sample (Fig. 1) is not considered in this study. More representative micrographs of the irradiated surfaces are shown in Fig. 2. For pigment tablets, regardless of the pulse duration, AZ, MA and OR tablets showed a visible blackening as fluence increased. This blackening was more significant upon irradiation with SFR and QS lasers, compared to the area treated with the intermediate pulse duration laser, LQS (Fig. 1 and 2A). A particular case occurred in WK-based tablets, which showed no visible darkening; instead, a slightly mechanical effect was noted only in the area irradiated at the maximum energy-100 %E- (Fig. 1 and 2B). CI-based tablets represented another exceptional case, as they darkened under all conditions, irrespective of fluence or pulse duration (Fig. 1). In terms of pigment susceptibility, the general trend was consistent across all three lasers: CI was the most susceptible, followed by copper carbonates and OR, while WK was the least susceptible.

Regarding tempera mock-ups, in the case of SFR laser, the fluence values causing no apparent damage were higher than those applied to the corresponding tablets (Fig. 1A). This behaviour suggests that tablets are more susceptible to laser irradiation than

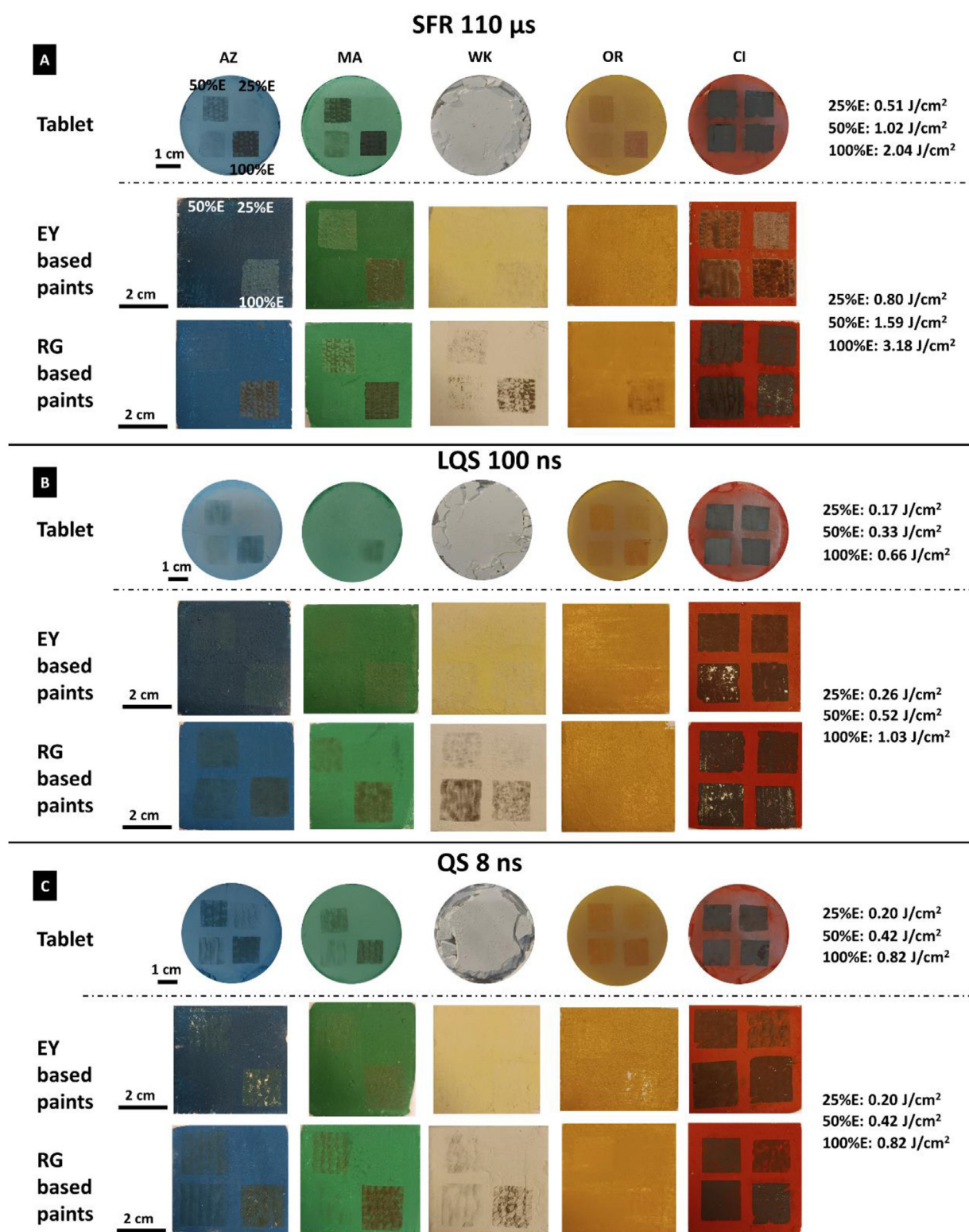


Fig. 1. AZ (azurite)-, MA (malachite)-, WK (lead white)-, OR (orpiment)- and CI (cinnabar)-based tablets and temperas with two different binders (EY: egg yolk and RG: rabbit glue) upon laser irradiation with three Nd:YAG lasers working at different pulse durations. A: SFR, B: LQS and C: QS. Values on the right indicate the fluence applied to each square of the mock-ups. Same scale for all samples. Irradiated area at the bottom left of each sample is not considered in this study.

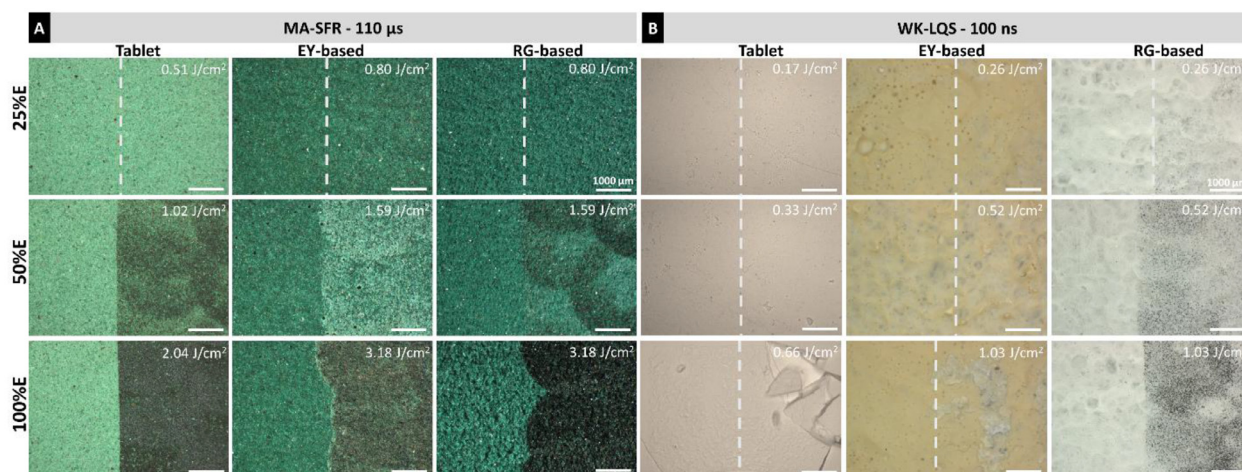


Fig. 2. Stereomicrographs showing the unirradiated areas (left half of each image) and the irradiated areas (right half of each image) with increasing fluences. A: MA-based tablets and temperas with two different binders (EY: egg yolk and RG: rabbit glue) irradiated with SFR laser and B: WK-based samples (pigment tablets and temperas) irradiated with LQS laser. Same scales for all samples. MA (malachite) and WK (lead white).

their tempera counterparts, as former exhibited a blackening more intense. These observations imply that the presence of a binder may exert a protective role on pigments. Following irradiation at the highest fluence (100 %E), AZ-, MA-, and CI-based temperas (both EY and RG-based temperas) did not show significant differences comparatively to the corresponding tablets. However, OR-RG and, most notably, WK-RG samples showed more intense darkening than their tablet counterparts. Additionally, whitening effects were detected in EY-based temperas made with AZ, MA and CI irradiated with SFR. This whitening was particularly noticeable in the 100 %E area of the AZ-EY tempera, in the 50 %E area of the MA-EY tempera, and in the 25 %E area of the CI-EY tempera.

As for the LQS irradiation tests (Fig. 1B), results were broadly consistent with those observed under SFR laser: fluences applied to the temperas were slightly higher than those used on the pigment tablets. This further supports the idea that the binder contributes to pigment protection, as greater fluences were required to induce detectable surface changes. Macroscopic examination (Fig. 1) confirmed that, for most samples treated with LQS laser, damages in tablets and temperas were similar, except for the WK-RG, which exhibited a clearly more intense darkening than its tablet counterpart. In the 100 %E areas of the CI-RG tempera, small areas of paint peeling were observed, revealing parts of the underlying substrate. A similar, though less intense, effect was also detected in the 100 % area of the OR-RG tempera.

Regarding samples treated with the QS laser (Fig. 1C), no major differences were observed between tablets and temperas, as fluences used in both type of samples were the same. In the 100 %E area, a noticeable darkening of the surface was evident in the WK-RG. Additionally, in the 100 % areas of AZ-EY and OR-EY, losses of pictorial material were once again observed.

Considering the influence of the binder, RG-based temperas showed more intense darkening than EY-based temperas (Fig. 1). The susceptibility of the paintings appeared to follow a similar pattern to that observed in the pigment tablets. However, the OR-based temperas displayed greater susceptibility to laser irradiation than the WK-based temperas.

Fig. 3 shows the evolution of color differences (ΔE^*_{ab}) for MA and OR pigment tablets, as well as for MA- and OR- based temperas as fluence increased. The evolution of ΔE^*_{ab} for all examined mock-ups is available in Fig. S1-Supplementary material. As expected, ΔE^*_{ab} values rose with increasing fluence for all tablets and temperas, except for CI-based samples, which already exhibited high ΔE^*_{ab} at the lowest fluences ($\Delta E^*_{ab} > 20$ CIELAB units).

AZ-, MA- and OR-based temperas showed comparable trends. A straight red line in Fig. 3 indicates the threshold of 3.5 CIELAB units, above which color changes become clearly perceptible to the human eye [57]. Generally, ΔE^*_{ab} values of the 25 %E areas remained below this threshold, except for the AZ tablet irradiated with LQS, the OR tablet irradiated with LQS and QS lasers, and the OR-based temperas with both binders following LQS. Notably, pigment tablets consistently suffered the highest ΔE^*_{ab} , followed by the RG-based temperas, while the EY-based temperas showed the lowest ΔE^*_{ab} . All values of color data are provided in Tables S1-S3 (Supplementary material).

Table 4 identifies the laser associated with the lowest ΔE^*_{ab} as fluence increased. In certain cases, such as AZ-based temperas irradiated at 25 %E, it was not evident whether one laser caused more visible changes than the others; these were noted as *No clear differences*. In other instances, such as the OR and CI tablets at 50 %E, the effects were comparable across all three lasers, labelled as *Similar damage by the 3 lasers*. Notably, at the lowest fluence (25 %E), the SFR laser caused the lowest ΔE^*_{ab} in the AZ- and OR-based tablets, as well as in OR-based temperas. For MA-EY and OR-based samples, the QS laser showed the lowest impact, comparable to LQS and SFR, respectively. Therefore, it suggests that, under low fluence, SFR laser was the most respectful with the original color.

As fluence increased, the LQS laser proved more effective at preserving original color. While SFR initially induced the least changes, its effect intensified more significantly than that of the other lasers at higher fluences. Although LQS still produced noticeable color changes (above 3.5 CIELAB units), these alterations remained below than those caused by SFR laser.

Pigment tablet susceptibility was generally similar under all three lasers, with CI being the most susceptible, followed by copper carbonates (AZ and MA), then OR and WK as the least affected. Overall, temperas were less susceptible to laser irradiation than tablets, except for both WK-based temperas, which were more vulnerable, especially the WK-RG. Thus, the least susceptible paintings were those containing OR, particularly, the OR-EY paintings.

Evaluation of the effects produced by an excessive irradiation (evaluating 100 %E areas)

Stereomicrographs of the 100 %E areas with ΔE^*_{ab} exceeding 15 CIELAB units are presented in Fig. 4. An exception was observed in the CI-based samples (both pigment tablets and temperas), where

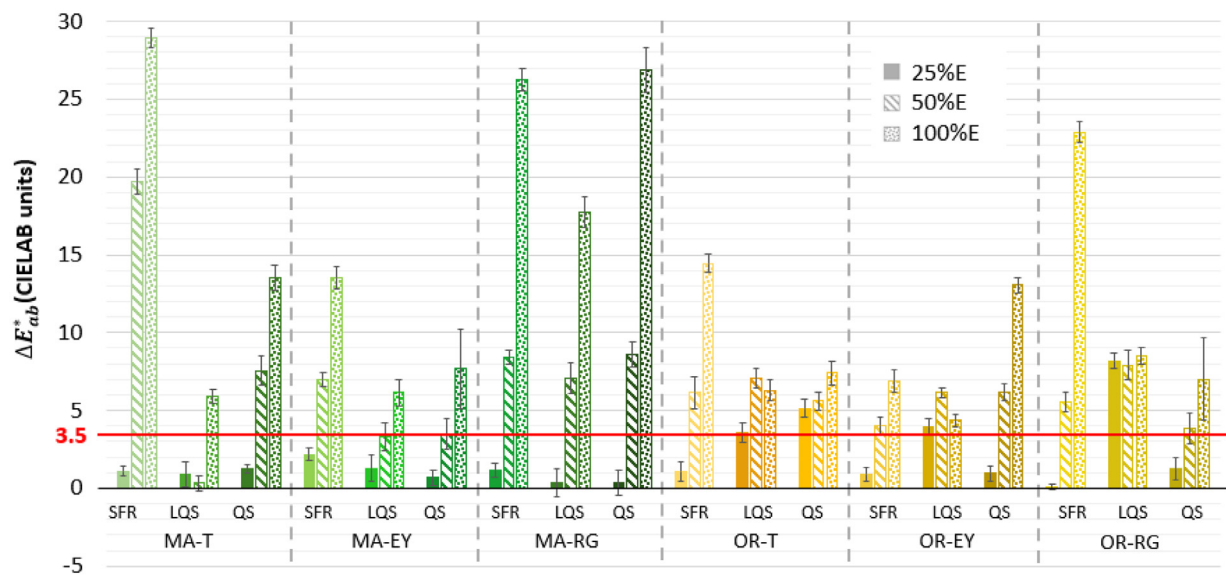


Fig. 3. Color differences (ΔE^*_{ab}) of MA- and OR- based samples, both pigment tablets (T) and temperas with two different binders (EY: egg yolk and RG: rabbit glue) irradiated with each laser at increasing fluence. MA (malachite) and OR (orpiment).

Table 4
Nd:YAG lasers that produced the lowest ΔE^*_{ab} with increased fluence (25 %E, 50 %E and 100 %E) in both pigment tablets (T) and temperas with two different binders (EY: egg yolk and RG: rabbit glue). AZ (azurite), MA (malachite), WK (lead white), OR (orpiment) and CI (cinnabar).

25 %E	T	EY-based paints	RG-based paints
AZ	SFR	No clear differences	No clear differences
MA	No clear differences	LQS and QS	No clear differences
WK	No changes	No changes	No changes
OR	SFR	SFR and QS	SFR and QS
CI	Similar damage by 3 lasers	QS	QS
50 %E	T	EY-based paints	RG-based paints
AZ	No clear differences	SFR and LQS	SFR
MA	LQS	LQS and QS	Similar damage by three lasers
WK	No changes	No changes	QS
OR	Similar damage by three lasers	SFR	SFR and QS
CI	Similar damage by three lasers	SFR	LQS and QS
100 %E	T	EY-based paints	RG-based paints
AZ	LQS and QS	LQS	LQS
MA	LQS	LQS	LQS
WK	Similar damage by three lasers	Similar damage by SRF, LQS, QS	LQS and QS
OR	LQS and QS	SFR	LQS and QS
CI	Similar damage by three lasers	SFR	LQS and QS

even the lowest fluence level (25 %E area) resulted in a clear color change (ΔE^*_{ab} =19.26 CIELAB units). Therefore, only a stereomicrograph of CI tablet upon SFR irradiation was included in Fig. 4G. The most intense blackening occurred under SFR exposure, in contrast to the darkening produced by the other two other lasers (Fig. 4A, B and D). AZ and MA tablets suffered the most significant color changes after SFR laser (Fig. 4A and B). Furthermore, RG-based temperas experienced greater ΔE^*_{ab} than their EY-based counterparts (Fig. 4B, D, E and F), as EY-based paints did not exceed 15 CIELAB units (Fig. S1- Supplementary material). Darkening was also evident in their respective temperas. Particularly, SFR irradiation of Cu carbonate-based paintings with RG (Fig. 4B and D) produced a more intense blackening (Fig. S1 in Supplementary material). It is important to highlight that the color measurements obtained for WK-based samples (Fig. S1-Supplementary material) reinforce the previous statement that no noticeable color alterations occurred in either the tablet or the WK-EY painting. In contrast, WK-RG samples suffered visible blackening. Color variations un-

der each laser condition is detailed in Tables S1-S3 (Supplementary material). The mineralogical composition of pigment tablets, both before and after laser irradiation, was determined by μ XRD and is summarized in Table S4 (Supplementary material). WK-based tablets were not analyzed by this technique, as no visible color changes were detected upon radiation. On the treated surfaces, tenorite (CuO) was identified in the AZ tablet (Fig. 4H) and in the MA tablet following SFR exposure (Fig. 4I). In CI tablets (Fig. 4J), a transformation from cinnabar (α -HgS, red hexagonal cinnabar) to metacinnabar (β -HgS, black cubic cinnabar) was detected across all lasers used in this study. FTIR spectra of unirradiated (reference) and irradiated areas of WK- and CI-based paintings are depicted in Fig. 5. In Tables 1 and 2, the main FTIR bands of the pigments and binders are shown with the assignments and the references. Attending to EY-based paints, the main features of this binder are located at 1745 cm^{-1} related to [$\nu(\text{C}=\text{O})$ ester], 1620 cm^{-1} associated to [$\nu(\text{C}=\text{O})$ from amide I], 1527 cm^{-1} attributed to the ab-

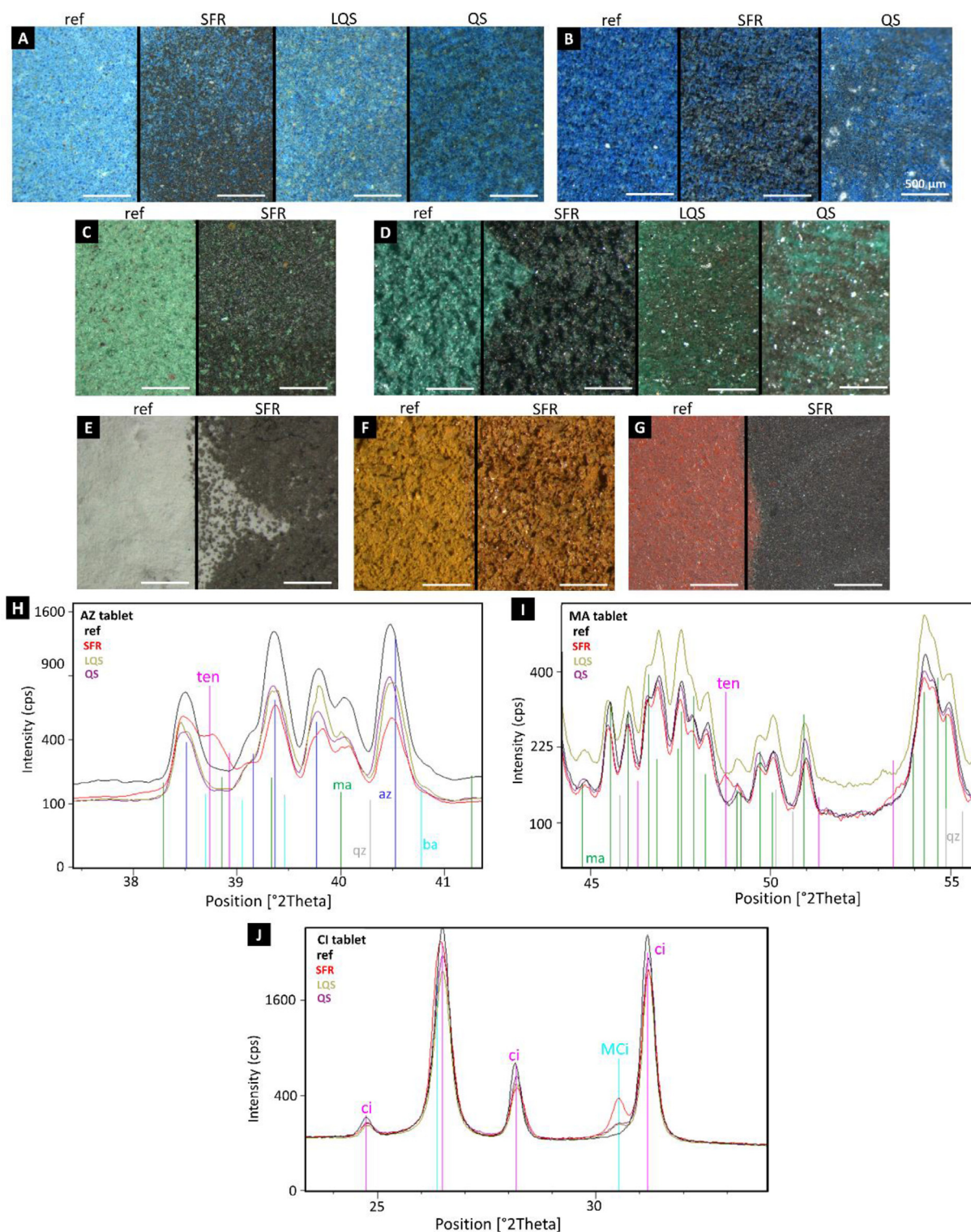


Fig. 4. A-G: Micrographs of the reference (left half) and 100 %E areas (right half). Same scale for all samples. H-J: μ XRD patterns of unirradiated and irradiated areas of A: AZ, B: AZ-RG, C: MA, D: MA-RG, E: WK-RG, F: OR-RG and G: CI. ten (tenorite), ci (cinnabar) and MCI (metacinnabar).

sorption of $\nu(\text{C-N})$ ($\sim 40\%$) and $\delta(\text{N-H})$ ($\sim 60\%$) from amide II] and 1235 cm^{-1} related to $\nu(\text{C-N})$ and $\delta(\text{N-H})$ ($\sim 30\%$ each), $\nu(\text{C-C})$ ($\sim 20\%$) and $\delta(\text{C-H})$ ($\sim 10\%$) from amide III]. When binder is combined with pigment, some spectral features are sometimes hidden under other bands, or they can suffer slight shifts. For RB-based mock-ups, the most important bands are located at: 1631 cm^{-1} which could be associated to $\nu(\text{C=O})$ from amide I], a band observed at 1552 cm^{-1} , that may be related to $\nu(\text{C-N})$ ($\sim 40\%$) and

$\delta(\text{N-H})$ ($\sim 60\%$) from amide II]. Finally, the region related to collagen absorption features ranging from 1400 to 1000 cm^{-1} .

Following the examination of the laser irradiated paintings (Fig. 5 and Figs. S2 and S3-Supplementary material), some possible signs of deterioration were identified:

- In most of the temperas, irrespectively of the binder used, a decrease in the intensity of the bands at 2926 and 2854 cm^{-1} (CH_2/CH_3) was observed. According to previous studies, this re-

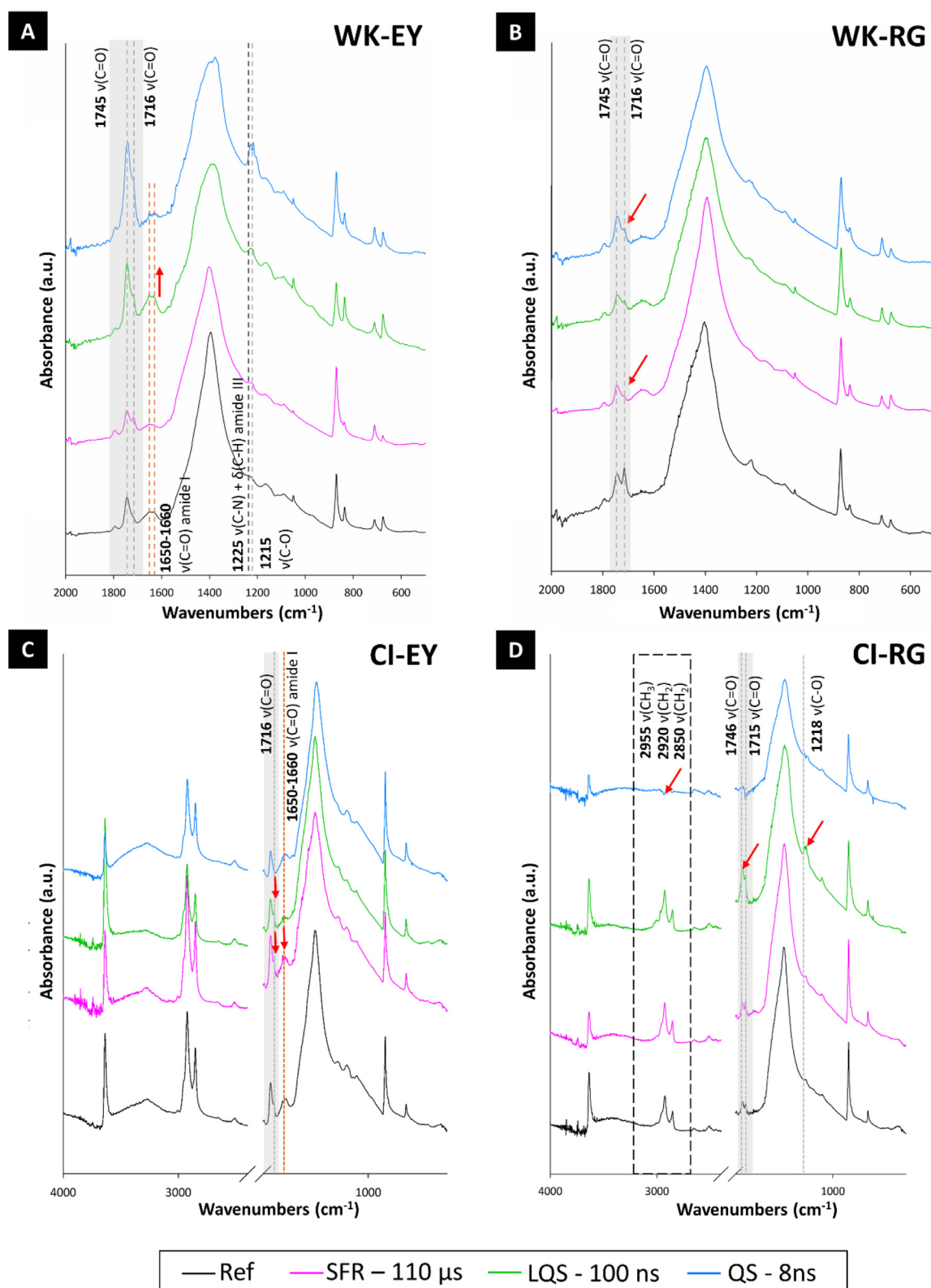


Fig. 5. FTIR (absorbance) spectra of paintings mock-ups before (ref) and after irradiation with the three Nd:YAG lasers (SFR, LQS and QS). A: WK-EY, B: WK-RG, C: CI-EY and D: CI-RG.

duction is related to oxidative chain cleavage (–C–H bond peroxidation), resulting in the formation of volatile oxidation products [58]. In this study, in the CI-RG tempera treated with QS laser, this band almost disappeared (Fig. 5D) indicating the possibility that such oxidation has occurred [59,60].

- An increase of the intensity of the band at $\sim 1745 \text{ cm}^{-1}$ after irradiation could suggest the formation of carbonyl moieties by oxidation of the proteins [61]. This feature is noticed in WK-EY and WK-RG paintings, mainly with QS and LQS lasers (Fig. 5A and B), and in the MA-RG after irradiation with the QS laser.

- Appearance of a new band at $\sim 1716\text{ cm}^{-1}$ is an indicative of free fatty acids generated upon hydrolysis of glycerol esters [62,63]. This feature occurred mainly in EY-based paints: in AZ-EY temperas upon the application of all three lasers, but especially after irradiation with the LQS and QS laser; in the WK after SFR laser (Fig. 5A), in the OR-EY after QS irradiation laser and in the CI-EY tempera when tested with SFR and LQS lasers (Fig. 5C). In addition, this feature also took place in the MA-RG painting after the use of all three lasers, but the increasing is especially intense upon QS laser and in painting WK-RG (Fig. 5B).
- Changes in the absorption bands at ~ 1660 and $\sim 1650\text{ cm}^{-1}$, assigned to amide I [$\nu(\text{C}=\text{O})$ ester] were detected. This region is the most informative about the secondary structure of proteins. The band at lower wavenumber (1650 cm^{-1}) is assigned to intermolecular β -sheet, whereas the band at 1660 cm^{-1} is usually assigned to α -helical and random-coil structures [59,64,65]. In [66], authors noted that changes in this region of the egg yolk spectrum could be associated with the increasing in temperature, since protein denaturation takes place above 60°C and, intensities related to β -sheet should increase slightly or remained constant. Elert et al., (2021) depicted the same features when they exposed to UV radiation a pure egg yolk [60]. However, they found that when the egg yolk is in presence of CI the band corresponding to amide I suffered a rapid decrease and β -sheet suffered a slight shift to lower wavenumbers, suggesting the presence of aggregated protein as a product of oxidation process [67]. A decrease of this band was observed in WK-EY with SFR (Fig. 5B), in OR-EY upon QS and CI-EY after LQS (Fig. 5C).
- Finally, some spectra revealed difference in the intensity of the band at $\sim 1218\text{ cm}^{-1}$ related to [$\nu(\text{C}-\text{O})$ ester]. Decreases or increases in these bands could suggest the oxidation of phospholipids [61]. These features took places especially in the RG-based paints, i.e. the AZ-RG after SFR and QS lasers, the MA-RG after QS, and in CI-RG after LQS laser (Fig. 7D); only WK-EY experienced an important increasing upon QS laser irradiation.

Concerning SEM observations, micrographs of irradiated and unirradiated samples are included in Fig. 6. AZ and MA tablets showed clear signs of mineral melting (Fig. 6A-1). This same phenomenon was observed in OR pigment, being more intense upon SFR laser irradiation, even though the appearance barely changed after irradiation with the three lasers. Voids of $5\text{ }\mu\text{m}$ in size were also observed in OR irradiated pigment with SFR laser (Fig. 6B-1, pointed out with arrows). CI tablets irradiated with LQS or QS lasers also experienced melting, while WK tablet did not undergo morphological changes.

In the unirradiated temperas, those prepared with EY exhibited a more homogenous distribution of pigment particles, resulting in a smoother surface appearance (Fig. 6A-2, 6-B2). In these samples, pigment grains appeared more embedded within the binder matrix compared to those prepared with RG (Fig. 6A-3, 6-B3). The RG-based temperas displayed rougher and more porous surfaces, with pigment grains protruding noticeably from the binder, making them more easily distinguishable (Fig. 6A-3, 6-B3).

Upon irradiation, the melting of the pigment particles was less severe than in the tablets, suggesting that they were protected by the binder. With respect to pigment composition, EY-based tempera containing both Cu carbonates suffered a binder loss, resulting in the formation of voids that increased pigment exposure. For instance, in the MA-EY irradiated with SFR, a void approximately $120\text{ }\mu\text{m}$ in diameter was observed (marked with asterisk in Fig. 6A-2). Similarly, the CI-EY sample after SFR laser also showed an increase in voids, whereas exposure to the other two lasers produced minimal changes. The OR-EY samples irradiated with LQS and QS lasers suffered a substantial binder loss, leaving pigment particle

exposed. By contrast, the OR-EY irradiated with SFR laser showed no apparent alteration (Fig. 6B-2). Furthermore, initial stages of pigment grain melting were observed at the particle edges in the OR-EY after QS laser (pointed out with an arrow in Fig. 6B-2).

Considering the RG-based temperas, the greater exposure of pigment particles may contribute to more intense damage upon laser irradiation. Following SFR and QS irradiation, tempera mock-ups showed slight localized disaggregation and melting at the edges of pigment particles (Fig. 6A-3, indicated by arrows). For the OR-RG after SFR, a barely increase in voids was observed, whereas LQS irradiation resulted in visible melting at the particles edges (Fig. 6B-3, marked with arrows). Regarding the CI-RG paints, both SFR and QS led to a slight loss of fine particles, while LQS exposure caused more evident melting. Contrary to expectations, CI-based temperas, regardless of the binder type or pulse duration, did not exhibit significant alterations despite severe color changes, even at the lowest fluences.

Discussion

Considering studied samples (tablets and temperas) treated with the lowest fluences (without apparently damages induced), the SFR laser (the longest pulse duration) provoked the minor color changes. Working with higher fluences, despite samples experimented ΔE^*_{ab} higher than 3.5 CIELAB units, which is the threshold value for a visible change detected by a human eye [57], the LQS laser affected the color of tablets and paintings to a lesser extent than the other two lasers.

After the irradiation of the pigment tablets with the three lasers, new mineral phases were formed: in AZ and MA tablets, tenorite (CuO) was detected after the irradiation with SFR laser, and in CI tablets, metacinnabar ($\beta\text{-HgS}$) was detected upon irradiation with the three lasers, while no neoformed minerals were detected in OR tablets. Transformation of azurite to cuprite takes place above 400°C in alkaline atmospheres [68]. Therefore, a thermal interaction may be occurring due to the interaction of the paint with the calcium carbonate in the mortar at a slightly basic pH. Moreover, some studies found that azurite can turn into black tenorite (CuO) when exposed to laser irradiation, depending on the size of the grains and, consequently, on the rise in temperature [23,69]. Further research will focus on the mechanism of tenorite formation in azurite and malachite tempera paintings on lime mortar. As malachite also appeared in the composition of the AZ pigment, their degradation had to be taken also in consideration. It is known that malachite is more stable than azurite, although its transformation to oxide compounds (cuprite and tenorite) is also possible upon radiation [14,70]. The significant blackening of the CI-based samples was associated to the transformation to metacinnabar (black cubic cinnabar) as it was reported in previous investigations [71,72] but without underestimating the melting of pigment particles upon LQS and QS lasers.

Considering color spectrophotometry and μXRD results and SEM observations, it was possible to distinguish different laser susceptibility of the pigments used, which is coincident for the three lasers: CI (the most susceptible), followed by copper carbonates and OR and WK (the least susceptible).

The mineralogical changes detected in the pigments can be associated with the deterioration features visualized by SEM, such as mineral fusion, which occurs in all pigments except for WK. These deterioration features may be responsible for the blackening; however, the degree of mineral fusion detected by SEM does not correlate with the intensity of the blackening. Thus, the blackening could result from the formation of darkened minerals at a micrometric scale on the surface, which is sufficient to produce this color. Consequently, additional analytical techniques, such as

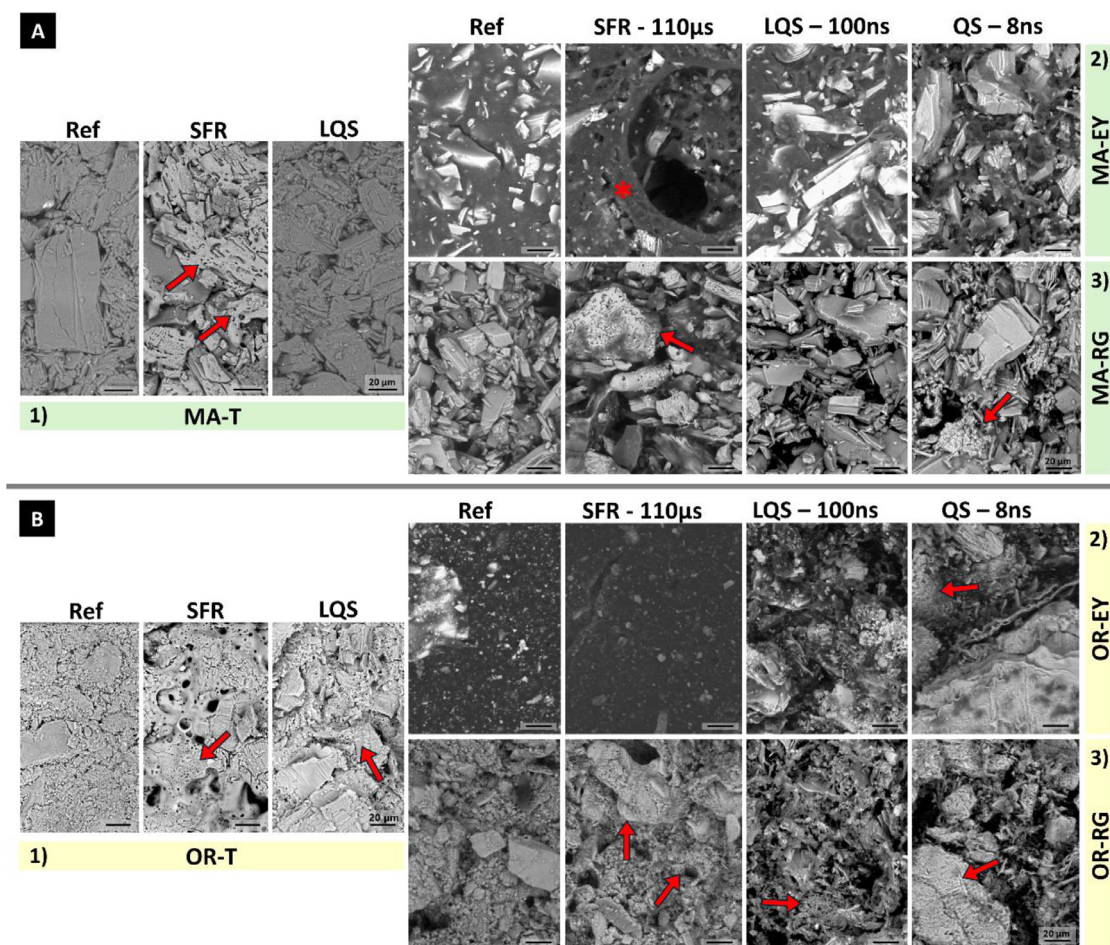


Fig. 6. SEM micrographs of the 100 %E areas of the A: MA- and B: OR-based pigment tablets (T) and temperas with two different binders (EY: egg yolk and RG: rabbit glue). Ref. indicates unirradiated area. Red arrows indicate melting signs and asterisk the presence of void in the binder after laser. Same scale for all samples. MA (malachite) and OR (orpiment).

Atomic Force Microscopy (AFM), should be employed for further investigation.

Blackening was also noted in tempera paintings. Deterioration of the binder was confirmed by both FTIR and SEM. The effects on the pigment and binder were not cumulative, as the blackening was not consistently more intense in the tempera samples compared to the tablets. Regarding the influence of pulse duration, SEM analysis confirmed the protective role of the binder, as more intense pigment melting was detected in the tablets than in their corresponding tempera mock-ups. SEM also allowed the identification of binder loss in the EY-based paints and melting at the edges of pigment grain in the RG-based temperas following laser application. These findings are consistent with the observation that pigment grains in RG-based temperas were less embedded in the binder matrix than in the EY-based ones. FTIR analysis identified chemical changes in the binders of some temperas, specifically protein and lipid oxidation; although, this technique could not clearly associate the extent of impact with a specific laser pulse regime. These results suggest that the visual appearance of tempera paintings upon laser treatment is influenced not only by changes in the inorganic pigments but also by degradation of the organic binder. A number of variables, including wavelength, fluence, pulse duration and optical properties of the irradiated materials, significantly impact the many processes that take place during laser processing [73]. In general, these mechanisms can be divided into two categories: non-thermal processes (for pulse durations less than 1 ps) and thermal processes (for pulse durations greater than 1 ps) [74]. For instance, in [75] authors reported successful removal of aged

varnish using an excimer laser with a pulse duration of 500 fs without thermal effects. In contrast, it was found that an Er:YAG laser with a pulse duration of 250 µs applied directly to paint layer could result in melted areas [76]. Authors have studied the relationship between temperature and surface oxidation, reporting that increased temperature promotes a thicker layer formation after irradiation of silicon oxide with a 355 nm laser [77]. Additionally, another research [78] indicated that longer pulse durations and higher repetition rates lead to greater heat accumulation, raising the oxygen content. In our study, evidence of oxidation is the transformation of copper carbonates into tenorite only after SFR laser (the longest pulse duration). Nevertheless, establishing relationship between temperature and surface oxidation is beyond the aim of this research. Furthermore, the possible impact of impurities present in the pigments should not be disregarded. Future research could focus on how different types and concentrations of impurities affect the interaction between laser irradiation and both pigment tablets and tempera paints. Such studies could clarify whether these impurities play a significant role in altering the physical or chemical responses during laser exposure.

When a real artwork is to be subjected to laser intervention, conducting pre-tests to define no apparent damage operating parameters becomes essential. These preliminary tests must be carried out in advance to ensure both safety and effectiveness of the procedure. Nevertheless, a key limitation is that the parameters determined during these trials are highly object-specific and cannot be directly applied to other laboratory mock-ups, artworks, or even laser systems. Consequently, these values should be con-

sidered as indicative rather than definitive. Notably, the damage thresholds observed in real artworks were significantly higher than those found in laboratory samples, a discrepancy likely attributed to the greater degree of carbonatation in the original pictorial layers [10].

Conclusions and future perspective

Regarding the susceptibility of the samples, regardless of the pulse duration used, both in tablets and temperas, cinnabar was the most susceptible followed by copper carbonates and finally, in terms of tablets, lead white was the most stable whereas in temperas was the orpiment regardless of the binder used. In addition, EY-based paints were less susceptible than their RG-counterparts. Binder presents a protective role on the pigments.

It is worth noting that SFR laser allowed higher fluences than the other two lasers without producing apparent damage. This property constitutes a clear advantage, as SFR laser can operate over a broader range of operation. Nevertheless, with increasing fluence, the impact of SFR laser became significantly more intense than that of the other two lasers. In contrast LQS proved to be the most effective in preserving the original color of the tempera at higher fluences.

In general terms, rabbit glue-based paints showed a less level of grain embedment comparatively to the egg yolk-based paintings. Consequently, pigment particles are more susceptible to the laser exposure: partially melting of the pigment grains were observed mainly in rabbit glue-based paints, especially in orpiment-based paints exposed to the LQS and QS lasers. The formation of voids in the binder (especially in EY-based paints) and pigment melting were the most commonly alteration patterns observed. Moreover, oxidation processes or/and changes in secondary structure proteins in the binders upon exposure will contribute to the color difference.

It is important to note that this is an experimental study based on laboratory-prepared samples. In contrast, historical wall paintings often present highly variable conservation states, which could significantly affect their response to laser irradiation. Additionally, any laser cleaning process must be carefully supervised by a qualified conservator, requiring a thorough understanding of the object's material properties and case-by-case assessment. The fluences identified as producing no apparent damage (25 % E) may serve as the starting point for subsequent cleaning tests on the same samples after artificial soiling and accelerated ageing.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2025.10.023.

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