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Research Article

Multianalytical Study of Laser Pulse Duration Effects in the IR Laser Cleaning of Wall Paintings from the Monumental Cemetery of Pisa

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The feasibility of laser cleaning for the removal of a variety of surface deposits from fragments of real wall paintings from the monumental cemetery of Pisa using Nd:YAG at 1064 nm at (μs), (ns), and (ps) regimes is presented. Multianalytical investigations of the samples from irradiated surfaces of fragments were carried out in order to characterize the original and added materials and to detect any laser-induced alterations; analysis included scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), laser-induced breakdown spectroscopy (LIBS), pyrolysis-gas chromatography-mass spectrometry (PY-GC-MS), and gas chromatography-mass spectrometry (GC-MS). The presence of nitrocellulose and pure lead contaminations on the surface of the samples has been identified. Assessment of the laser cleaning has highlighted the importance of the optimization of laser parameters, specifically pulse duration and fluence at the specified wavelength.

1. INTRODUCTION

The use of lasers to selectively remove unwanted materials from sensitive surfaces is well studied and has extensive applications [1], including the conservation of cultural heritage. Over the last decade, lasers have been used as a highly controllable cleaning tool for the removal of dirt and various layers; numerous successful case studies on the laser cleaning of a variety of materials have been reported and include stone, varnished icons and paintings, metals, and paper [2, 3]. Laser cleaning of paintings and polychromy requires a careful selection of laser parameters: wavelength, pulse duration, fluence, repetition rate, and number of pulses. Most importantly, the removal of dirt or other unwanted materials from the surface of a painting must not result in damage, chemical modifications, or otherwise compromise the integrity of the original material. Laser-induced pigment alterations have been indicated as problematic in various studies of the cleaning of wall paintings [4, 5] and this has led to a series of model investigations of the physiochemical parameters that may induce and influence alterations [6–8]. In addition, investigations of the photothermal reactions on polymer-based materials have been studied in a variety of model systems [9, 10] and on varnishes [11].

Particular advantages are associated with the use of ultrashort laser pulses where limited photochemical modifications and thermal diffusion occur at the laser-substrate interface. However, cleaning using ultra-short laser pulses is complicated and not yet well defined [12] and such sources are of limited availability.

Studies on the laser cleaning of both model systems [4, 13, 14] and real samples [5, 13, 14] of paintings have investigated various laser wavelengths (Er:YAG at 2.94 μm, Nd:YAG at 1064 nm) and different pulse durations (μs and ns, resp.). The aim of this work is to assess the feasibility of the use of laser cleaning for the removal of surface deposits from fragments of real wall paintings from the monumental cemetery of Pisa using Nd:YAG laser irradiation at 1064 nm with pulse durations of μs, ns, and ps.

The cycle, painted from the late medieval until early renaissance, is considered one of the finest Italian wall

(a) (b)

Figure 1: Images under visible radiation of (a) fragment 1 and (b) fragment 2.

paintings, executed by artists including Taddeo Gaddi, Benozzo Gozzoli, and Bonamico Buffalmacco. The exterior wall paintings were exposed to inevitable fluctuations in temperature and humidity; their condition is further complicated by restorations from the 19th and early 20th centuries during which various modern materials including nitrocellulose were applied to the surface of the paintings. Second World War damage led to fire, which caused further contamination of the surface of the paintings with ash, soot, and molten lead from the roof.

In order to evaluate the influence of pulse duration on cleaning of the wall paintings, tests were carried out on representative fragments of the paintings to remove different patterns of surface dirt. The fragments choosen for the laser cleaning investigations were systematically studied for a thorough characterization of the contaminant and original paint layer (binding media and pigments).

Moreover, to assess the long-term effects of laser action on the substrate, organic material was analyzed six months after laser irradiation tests.

2. EXPERIMENTAL

The precious fragments of the wall paintings from the monumental cemetery were examined in the following order. First, samples were photographed and their condition was recorded. Selected areas were sampled for transmission FTIR analysis (diamond cell) for the characterization of the surface coating. Further, samples were prepared in cross-section for examination using optical microscopy followed by scanning electron microscopy with energy-dispersive X-ray emission (SEM-EDX) for both elemental analysis and high-resolution imaging. Microdestructive analysis was carried out for elemental depth-profiling using laser-induced breakdown spectroscopy in selected points. Pyrolysis-silylation gas chromatography-mass spectrometry (Py-silylation/GC-MS) and GC-MS [15, 16] were used for the characterization of the organic material before the laser treatment; following laser cleaning, the ablated material was analyzed to assess possible photothermal modifications of surface coatings. Finally, laser-cleaned areas were subjected to colorimetric control under the microscope and samples were taken and prepared in cross-section for examination using optical and scanning electron microscopy.

3. METHODOLOGY AND METHODS

3.1. Samples

The study focused on two representative fragments from the monumental cemetery of Pisa for the assessment of the most suitable laser parameters for the removal of surface treatments (*patinas*) and encrustations. The fragments which are painted over a red background come from decorative sections of the painting and contain a floral motif and creeping vine leaf, as shown in Figure 1.

3.2. Laser instrumentation

The fundamental frequency (at 1064 nm) of the following Nd:YAG laser systems at various pulse durations has been used:

(1) a fibre-coupled short free-running laser system (El. En., EOS 1000) emitting pulses of 120–1000 mJ output energy and pulse duration in the range of 50–130 μs;

(2) a Q-switched laser system (SPECTRON, SL805) emitting pulses of 15 ns and maximum output energy of 450 mJ;

(3) a Q-switched laser system (EKSPLA, SL312) with pulses up to 120 mJ and 150 ps duration.

For a systematic study of the laser cleaning parameters, this investigation has been limited to laser cleaning at a single wavelength (1064 nm) with different pulse durations (μs, ns, and ps). Laser-assisted removal of the surface dirt, past treatments, and encrustations was carried out with different energy density values as well as a variable number of pulses. The pulse repetition was kept at slow values (2–4 Hz) in order to follow and control the removal process. The application of water as a wetting agent has also been considered. Selected tests are reported in Table 1. (See Section 4.2) for fragment 1 and fragment 2.

3.3. Analytical techniques

The following instrumental techniques have been used to analyze samples of the fragments, to characterize the original and added materials and to detect any laser-induced alterations:

(1) FT-IR spectrophotometer (Perkin Elmer, USA), mod. Spectrum GX I, interfaced with a FT-IR autoimage system microscope (Perkin Elmer USA);

(2) low-vacuum scanning electron microscope JSM 5600 (JEOL, Tokyo, Japan), equipped with energy-dispersive X-ray emission—system Oxford Link ISIS for spot analysis. Backscattered electron images of the cross-section were taken at 20 kV;

(3) a nanosecond Q switched Nd:YAG laser (pulse duration ca. 10 ns) using the third harmonic (355 nm) for laser induced breakdown spectroscopy (LIBS). The laser beam focused on the sample surface by means of a 50 mm focal length planoconvex quartz lens and a single laser pulse measurement was performed. Typical laser pulse energy values ranged from 2 to 4 mJ with a spot diameter on the sample of approximately 100–150 μm. The spectrum was recorded with an intensified CCD detector (Andor Technologies, DH520-18F-01 with an EEV30-11 sensor). The gating pulse applied to the intensifier was delayed 200–500 ns with respect to the laser pulse and has a temporal width of 500–1000 ns [17, 18];

(4) pyrolyser operating in constant temperature mode (Pyrojector II, SGE, Austin, Tex, USA), connected to the PTV injector of the GC system gas chromatograph. The pyrolyses were performed with "in situ" hexamethyldisilazane silanization [15];

(5) 5890 series II gas-chromatograph (Hewlett Packard, Palo Alto, Calif, USA) coupled with a quadrupole mass spectrometric detector mod. 5971A (electron impact 70 eV, ion source temperature 180°C, interface temperature 280°C).

4. RESULTS AND DISCUSSION

4.1. Characterization of the materials

The diagnosis of the constituents of works of art is of primary importance before starting the laser cleaning; the fragments of the wall painting were covered with surface deposits and encrustations of unknown origin, and hence it was necessary to identify the contaminant materials. Therefore, thorough analysis with different techniques were carried out, in order to plan the laser tests on the basis of the materials present in the selected areas of the fragments. A careful investigation of the inorganic materials was performed by cross-section analysis of the fragments under the microscope, SEM-EDX, and LIBS analysis, while the characterization of the organic material and their degradation products was carried out using FT-IR, PY-GC-MS, and GC-MS.

4.1.1. Inorganic material

A representative cross-section is shown in Figure 2. The complexity is evident, a deposit of a metal is visible on the surface

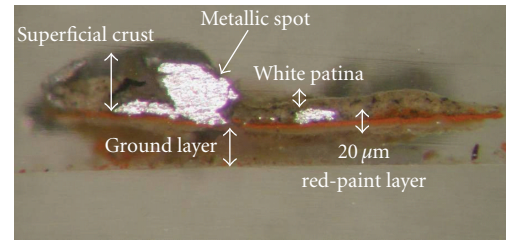


Figure 2: Cross-section from fragment 2.

of the red-paint layer of about 20 μm or less; moreover a thick grey layer is observed as a thick crust over the paint layer, and over it a very thin white layer is present. Below the red paint, the ground preparation of about 50 μm is present.

SEM-EDX analysis permitted the identification of the inorganic constituents of the different layers. Specifically, the metallic material deposited on the surface of different fragments is lead, as confirmed by the LIBS analysis; the presence of lead on the surface of the fragment is due to fires following Second War World bombing, during which the lead roof melted, and molten lead fell onto the surface of the wall paintings. The SEM-EDX analysis of the shiny metal spot, particularly apparent in the back scattered electron image is reported in Figure 3 together with the LIBS spectrum. The LIBS analysis was carried out on many metallic grey spots present on much of the surface of both the samples; the observed spots vary from small droplets to larger stains of metallic lead, with a diameter varying from about 0.5 cm to 8 cm.

The SEM-EDX analysis also highlighted the presence of iron oxide in the red-paint layer, identified as red ochre, which was further confirmed by LIBS analysis. In Figure 4, a spectrum of the red pigment in fragment 2 is presented. Moreover, LIBS provided elemental confirmation of red and yellow ochres, iron containing pigments in the different fragments, as well as the presence of a copper-based green pigment.

As a further example of the characterization of the inorganic materials found in the fragments, in Figure 5 the SEM-EDX analysis of the thick grey crust found on top of the red-ochre layer is given: it consists predominantly of calcium carbonate, carbon-black, and calcium sulphate, and in the electron image the needle-like shape of the calcium sulphate (gypsum) is clearly visible.

4.1.2. Organic material

The thin white layer observed as an opaque layer over the thick crust in the cross-section from fragment 2, but also widespread on the surface of fragment 1, was further identified using micro-FT-IR in the diamond cell. A comparison of the spectrum with that of the naturally aged reference material nitrocellulose, seen in Figure 6, indicates strong similarities between the compounds. The semitransparent adhesive nitrocellulose was likely applied to the painting in conservation treatments dating to 1947.

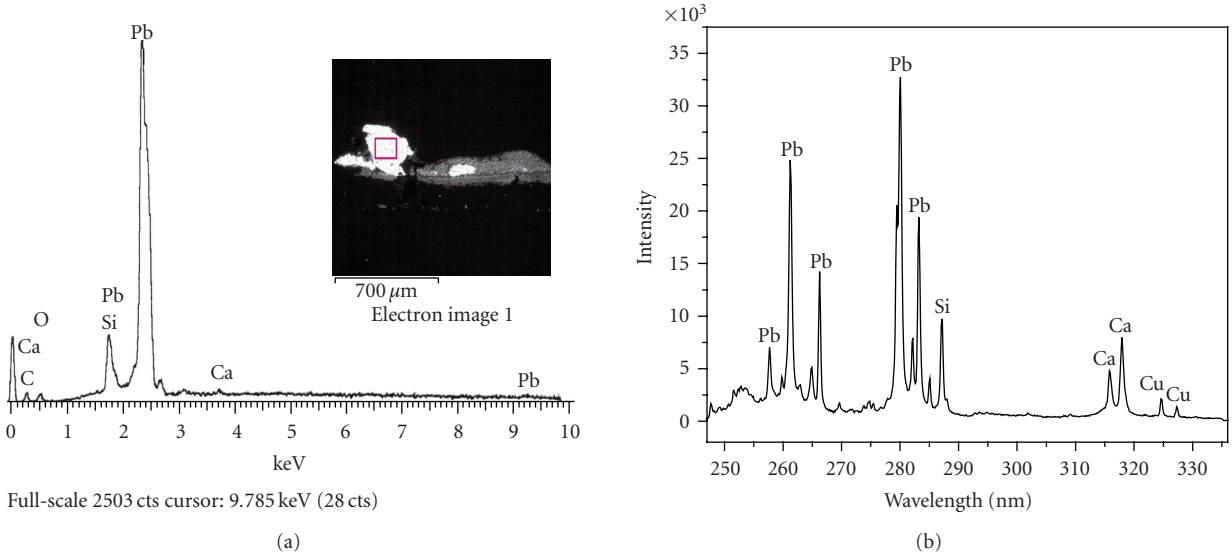


Figure 3: Fragment 2, (a) SEM-EDX of the area indicated in red on the electron image and (b) LIBS analyses on a metallic shiny spot.

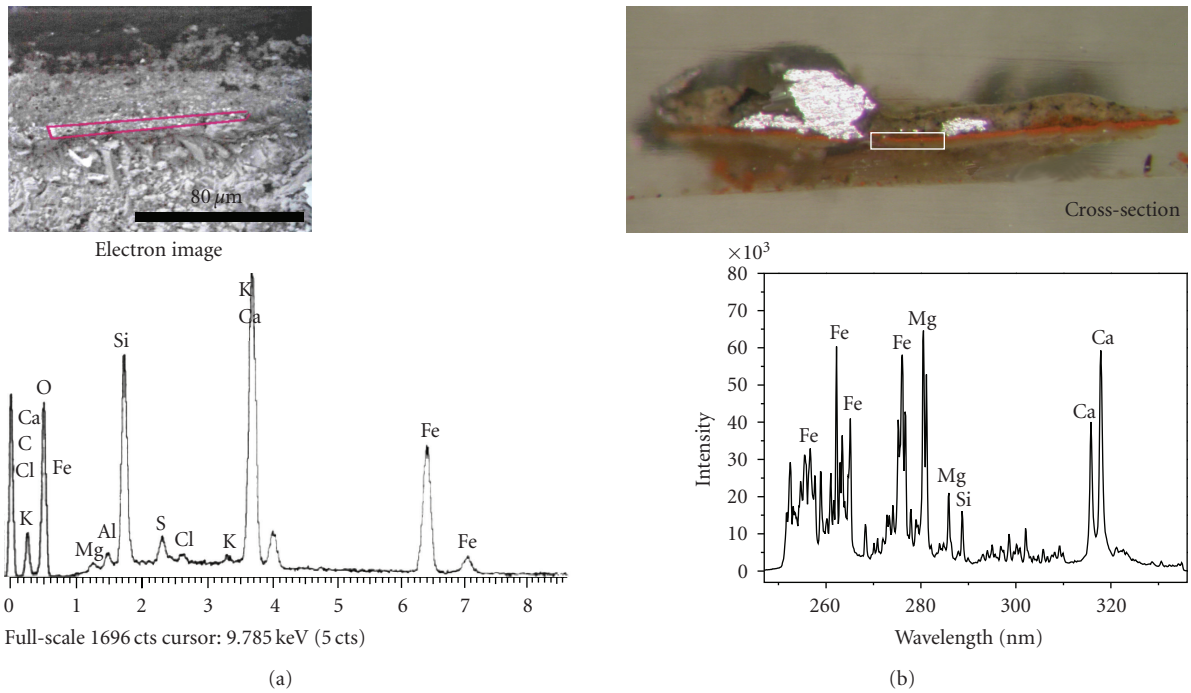


Figure 4: Fragment 2, (a) SEM-EDX of the area outlined in red in the electron image, which corresponds to the area indicated in white on the cross-section and (b) LIBS analyses of the red pigment.

The adhesive is characterized by vibrational bands corresponding to NO_2-O asymmetric stretching bands at 1718 cm^{-1}, 1654 cm^{-1}, and 839 cm^{-1} and a symmetric one at 1282 cm^{-1}. Additional modes are associated with aliphatic C−H stretching bands at 2800–3200 cm^{-1} and O−H stretching at 3200–3400 cm^{-1}. The fingerprint region has distinct stretching bands at 1377 cm^{-1} (C−NO_2), 1161 cm^{-1} (C−OH), and 1066 cm^{-1} (C−OH). Interferences from calcium carbonate are observed in the sample which has a peak at approximately 1428 cm^{-1} which corresponds to the C−O ν_3 stretching vibration.

However, for a more specific characterization of the organic material from the two fragments, PY-GC-MS with silanization "in situ" followed by GC-MS was used. An

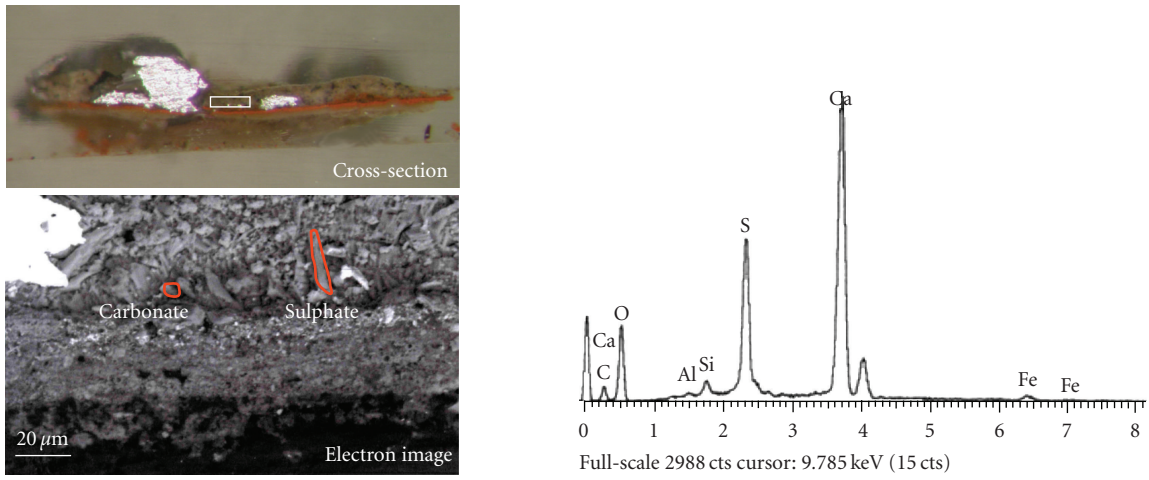


Figure 5: Fragment 2, SEM-EDX of the crystal of calcium sulphate outlined in red in the electron image (corresponding to the area indicated in white on the cross-section) analysis of the superficial crust.

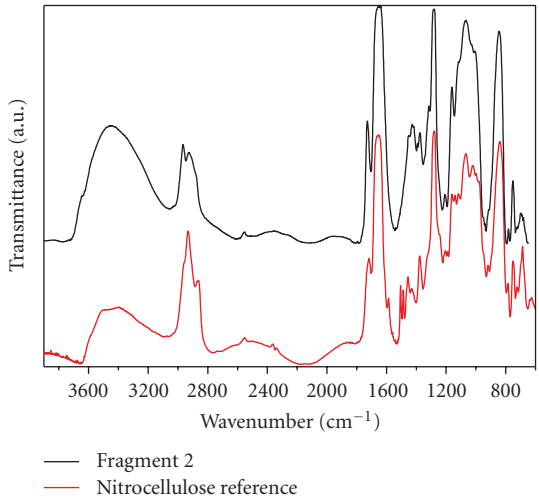


Figure 6: Fragment 2, FT-IR spectra of the white patina.

example of the pyrogram of the superficial white patina from fragment 1 is reported in Figure 7. The extract ions of m/z 217 and 204, characteristic of carbohydrates, indicate the presence of levoglucosane and other sugars, thus confirming the FT-IR identification of the white patina as nitrocellulose. In fact, the most specific pyrolysis product of cellulose is levoglucosane, the anhydro-sugar of glucose. Moreover, the PY-GC-MS investigation of the binding media of the wall painting has indicated the presence of pyrrole, a specific marker of animal glue.

The presence of this proteinaceous material was further confirmed by GC-MS analysis, as shown following statistical treatment using principal component analysis (PCA) [16] of the percentage of amino acids of the proteinaceous fractions collected from fragments 1 and 2 (see Figure 8). Moreover, the study of the lipidic fractions shows the presence of a lipidic material, likely egg due to the presence of traces of cholesterol.

However these products have been found only in trace quantities and they were not widespread in all the fragments analyzed; results therefore suggest that the painting technique was mainly "a fresco" and that the animal glue and egg are probably present as restoration materials.

The different results obtained from the variety of analyses of the superficial layers indicate that they are mainly composed of nitrocellulose and black crusts of heterogeneous materials including metallic lead. The proteinaceous material identified as animal glue and traces of egg likely belong to past restorations, including those from the 19th century; these materials may have penetrated the original matrix, and therefore cannot be removed. The main problem related to the laser cleaning of these wall paintings is not only their compromised condition and the complexity of added materials including deteriorated restoration products and widespread depositions of dirt, but rather the presence of red and yellow ochres and copper pigments, which are well known for their sensitivity to pigment alterations following laser irradiation.

4.2. *Laser cleaning: assessments and evaluations*

Removal of the superficial white patina of nitrocellulose, the thick encrustation, and metallic lead is particularly problematic since all materials are well attached to the upper pigment layers, and are widely distributed on the surface of both fragments. Laser cleaning of the different contaminants using a variety of different pulse fluences and pulse durations was explored in order to identify the most suitable parameters for each type of material and to evaluate the problems associated with different cleaning regimes. Laser parameters employed in the cleaning tests on fragments 1 and 2 are reported in Table 1, together with brief observations of the laser cleaning results after evaluation under the binocular microscope.

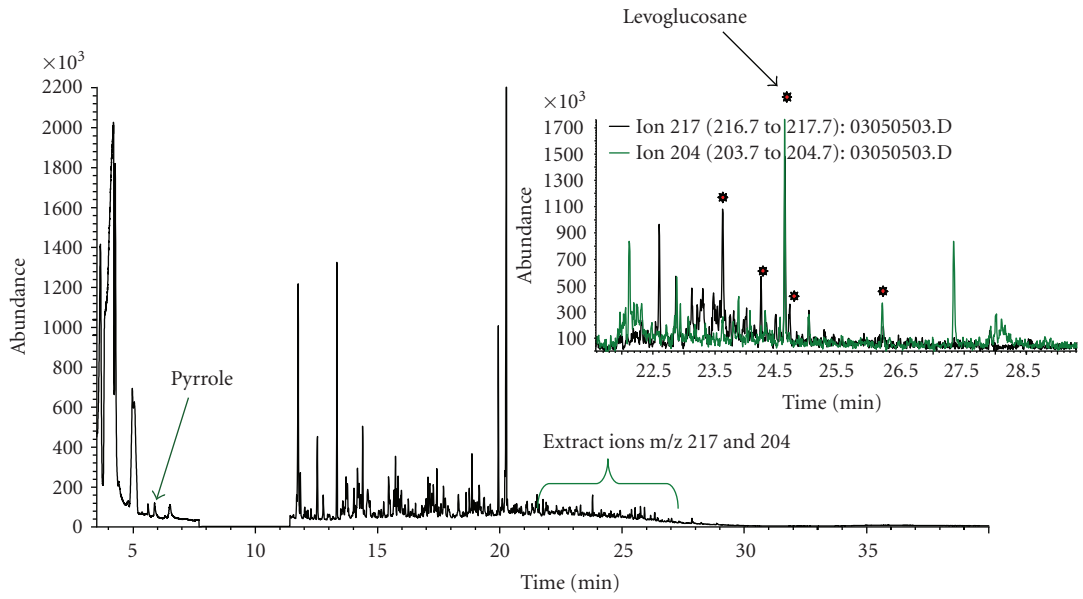


Figure 7: Fragment 1, pyrogram of the superficial crust.

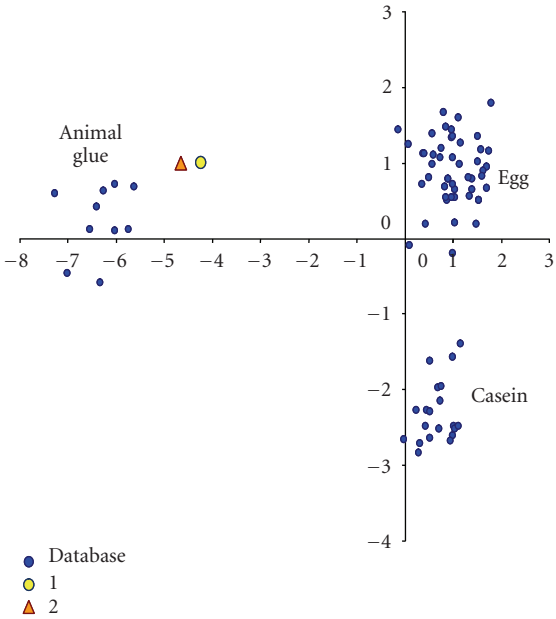


Figure 8: PCA of the amino acids percentage content of the proteinaceous fraction of samples from fragments 1 and 2.

4.2.1. Removal of the white surface patina

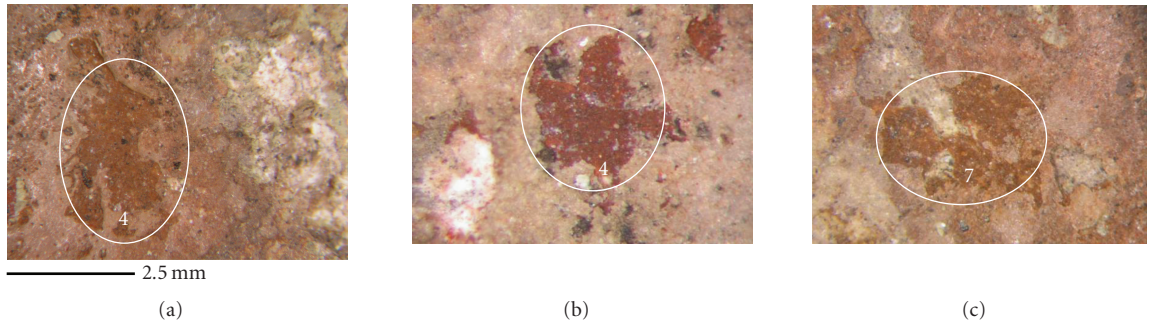
The thin white patina appears to have been successfully removed from fragment 1 with all the laser systems, as visible in macrophotographs seen in Figure 9(a) for the μs laser application of a single pulse at 1.4 J/cm^2, Figure 9(b) for ns laser application of a single pulse at 0.2 J/cm^2, and Figure 9(c) for ps laser application of three pulses at 0.3 J/cm^2.

Similarly good results were observed in fragment 2, as seen in Figure 10; however in this case, in the areas cleaned, the layer of nitrocellulose was slightly different (thicker) but nonetheless similar in behavior to that observed on the surface of fragment 1 (Figure 9).

With the μs laser system, the patina was generally removed using fluences lower than 9 J/cm^2, but unfortunately in a few areas of the fragment, the layer of the patina was thicker, and the application of a single pulse at 11 J/cm^2 caused browning of the red underlying pigment, a particular problem for the cleaning of areas of sensitive pigments. However, an optimal removal test (2.8 J/cm^2, 2 pulses) is reported in Figure 10(a) in which no pigment alterations are observed. With the ns laser, a good removal of the patina was also obtained, without any visible browning of the pigment. A spot test (0.3 J/cm^2, 1 pulse) is reported in Figure 10(b). The photomechanical effects of the picoseconds laser, as compared with lasers of longer pulse duration, permit a controlled removal of the white surface patina. Following ablation, the surface film becomes detached and lifts from the surface of the fragment without removing any pigment particles, and no pigment alterations are observed. One of the spot tests (0.2 J/cm^2, 5 pulses) is reported in Figure 10(c). Additionally, with the ps laser, the superficial patina has been completely removed as confirmed by the PY-GC-MS analysis of a sample from fragment 2 taken of the area following cleaning, in which no traces of the surrounding nitrocellulose were found. The especially sensitive technique hence confirms the complete removal of the surface coating from the sample. Additionally, analysis of removed material indicates that during ablation no molecular changes of the surface coating are detected. In general, cleaning of similar areas using μs pulses requires a higher fluence than that needed for ns and

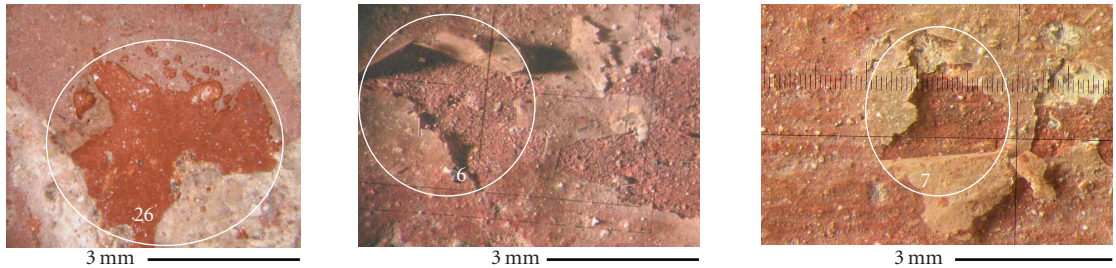
Table 1: Laser parameters adopted in the cleaning tests on fragments 1 and 2 and laser cleaning results (the abbreviations outside of the parentheses indicate the following: A indicates alteration of the pigment, G indicates good removal, I indicates ineffective removal, L indicates loss of pigment, P indicates partial removal. Within parentheses, the area treated with the laser is given and corresponds to C: grey crust, W: white surface film/patina).

Laser	Fragment 1				Fragment 2			
	Laser parameters				Laser parameters			
	Spot number	Fluence (J/cm^2)	Number of pulses	Cleaning results	Spot number	Fluence (J/cm^2)	Number of pulses	Cleaning results
Short free-running Nd:YAG laser (250 μs)	1	8.5	2	L (C)	1	0.7	2	P (C)
	2	7.1	1	L (C)	2(Figure 12(b))	13	1	G (C)
	3	1.4	1	G (C)	3	11	1	G (C)
	4(Figure 9(a))	1.4	1	G (W)	4	9.9	1	G (C)
	5(Figure 13)	2.8	5	G (C)	5	8.5	1	P (C)
	6(Figure 13)	2.8	18	G (C)	6	7.1	1	P (C)
	7(Figure 13)	2.1	50	G (C)	7	5.7	1	I (C)
	—	—	—	—	8	5.7	1	I (C)
	—	—	—	—	9(Figure 12(a))	8.5	4	P (C)
	—	—	—	—	10	8.5	2	P (C)
	—	—	—	—	11	8.5	6	L (C)
	—	—	—	—	12(Figure 11(a))	14	1	G (C)
	—	—	—	—	13(Figure 11(a))	14	1	G (C)
	—	—	—	—	14(Figure 11(a))	14	1	G (C)
	—	—	—	—	15(Figure 11(a))	14	3	G (C)
	—	—	—	—	16	14	1	G (C)
	—	—	—	—	17	14	1	G (C)
	—	—	—	—	18	14	1	G (C)
	—	—	—	—	19(Figure 12(c))	13	1	A (C)
	—	—	—	—	20	11	1	A (W)
	—	—	—	—	21	10	1	G (W)
	—	—	—	—	22	8.5	1	G (W)
	—	—	—	—	23	7.1	1	G (W)
	—	—	—	—	24	5.7	1	G (W)
	—	—	—	—	25	4.3	2	G (W)
	—	—	—	—	26(Figure 10(a))	2.8	2	G (W)
	—	—	—	—	27	1.4	1	G (W)
Q-switched Nd:YAG laser (20 ns)	1	0.2	2	L (W)	1(Figure 11(b))	1.4	3	L (C)
	2	0.2	1	G (W)	2(Figure 11(b))	1.4	2	P (C)
	3	0.2	3	G (W)	3(Figure 11(b))	1.4	30	P (C)
	4(Figure 9(b))	0.2	1	G (W)	4(Figure 11(b))	2.0	20	P (C)
	5	0.3	1	G (W)	5	2.0	5	P (L)
	6	0.3	2	G (W)	6(Figure 10(b))	0.3	1	G (W)
	7	0.3	6	G (C)	7	2	50	P (L)
Q-switched Nd:YAG laser (500 ps)	1	0.2	10	P (W)	1	0.2	23	P (C)
	2	0.3	5	G (W)	2	0.3	10	P (C)
	3	0.2	5	I (W)	3(Figure 11(c))	0.7	27	G (C)
	4	1.1	16	P (C)	4	1.1	18	L (C)
	5	0.2	1	I (C)	5	0.7	1	G (W)
	6	0.3	3	I (C)	6	0.2	3	G (W)
	7(Figure 9(c))	0.3	3	G (W)	7(Figure 10(c))	0.2	5	G (W)
	8	0.7	1	P (C)	—	—	—	—
	9	0.6	1	P (C)	—	—	—	—
	10	1.1	1	P (C)	—	—	—	—
	11	1.6	1	P (C)	—	—	—	—
	12	0.6	6	G (C)	—	—	—	—



(a) (b) (c)

Figure 9: Fragment 1; removal of the white patina with μs (a), ns (b), and ps (c) laser radiations; the numbers within the circles correspond to the laser parameters employed as reported in Table 1.



(a) (b) (c)

Figure 10: Fragment 2; removal of the white patina with μs (a), ns (b), and ps (c) laser radiations; the numbers indicated within the circles correspond to the laser parameters employed as reported in Table 1.

ps, but in the optimum conditions, it is possible to effectively clean without damage to the pigment layer.

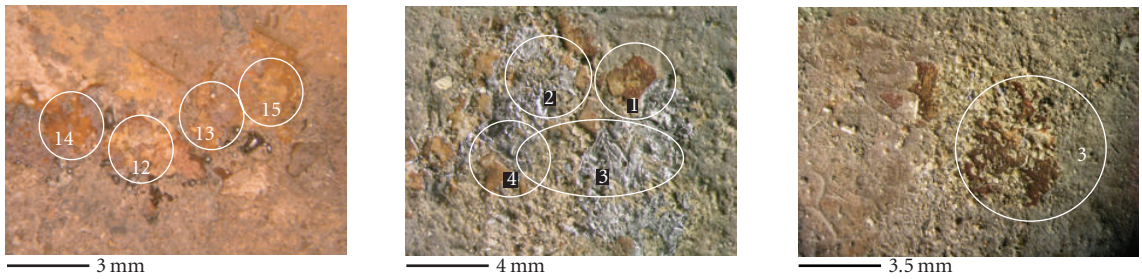
4.2.2. *Removal of the superficial thick crust of deposited metallic lead*

The removal of lead deposits and crusts is compromised as the molten lead from the roof likely caused pigment alterations due to the high temperature interactions with the surface; in addition, the lead droplets were strongly adhered to the surface of the paintings.

With one pulse of the μs laser at fluence 14 J/cm^2 on a wet surface, the lead crust was removed without any observable damage to the underlying pigments. The predominant photothermal effects of the laser radiation with longer pulses induced melting, rather than the mechanical ablation of the lead, thus allowing its gradual removal from the red-paint layer. In Figure 11(a), a laser-cleaned area where a thick drop of lead was originally present is reported (14 J/cm^2, 1–3 pulses, see Table 1 for more detailed laser parameters). In contrast to the μs cleaning, the application of consecutive pulses of the ns laser resulted in the removal of only a superficial part of the lead. In fact, the thicker crust of lead may be detached only under extreme cleaning conditions (e.g., higher number of pulses or higher fluences) but with concomitant removal of the original red pigment layer. In Figure 11(b), it is clearly visible that the grey lead encrustation was effectively rendered shiny or thinned by consecutive laser pulses at 1.4 J/cm^2 or 2 J/cm^2 (spot numbers 2-3-4, 2–30 pulses, see Table 1 for more detailed laser parameters). However, in spot number 1 (1.4 J/cm^2, 3 pulses, see Figure 11(b)), the removal of lead is accompanied by the loss of part of the pigment layer, probably due, in addition to the photomechanical effects, to a local decohesion of the paint layer to the plaster. With the ps laser, instead, removal of lead was quite satisfactory (see Figure 11(c), 0.7 J/cm^2, 27 pulses), however further studies should be performed to confirm the result, as the lead stains at the tested areas were rather thin.

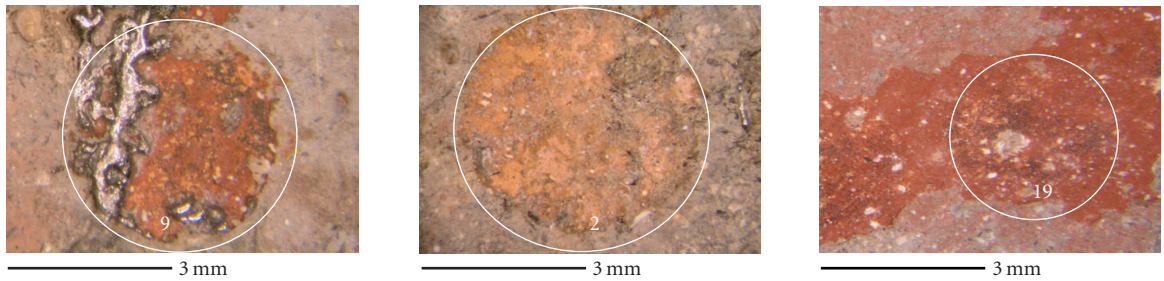
It is stressed that for the removal of hard thick encrustations, the application of consecutive pulses at lower fluences was generally more successful than that of one single pulse at higher fluences. As an example of this issue, three macrophotographs of the μs laser spots are reported in Figure 12. Using the same μs laser, with the application of four consecutive pulses of μs duration at 8.5 J/cm^2 resulted in a rather promising crust removal, while a part of the lead drop still remained after treatment (Figure 12(a)). Therefore it was decided to test one single laser pulse at higher fluence (13 J/cm^2) and the drop of lead was completely removed with no damage to the underlying pigment (Figure 12(b)). On the other hand, when a single pulse of the same fluence (13 J/cm^2) was applied to an area where the stain of lead was thinner, the stain was removed, but the red pigment was clearly altered (Figure 12(c)).

From these comparative studies, it can be concluded that with increasing laser intensities, the removal efficiency is



(a) (b) (c)

Figure 11: Fragment 2, removal of the superficial crust with lead deposits with μs (a), ns (b), and ps (c) laser radiations; the numbers correspond to the laser parameters reported in Table 1.



(a) (b) (c)

Figure 12: Fragment 2, laser cleaning tests (in the μs regime) to remove the superficial crust with lead deposits: four consecutive pulses at 8.5 J/cm^2 were not able to completely remove the metallic lead deposit (a); only one pulse at higher fluence values efficiently removed a relatively thick lead stain (b), while in the case of a thinner lead stain, the result was not successful (c); the numbers correspond to the laser parameters reported in Table 1.

increased for both ns and ps lasers. Significantly higher laser fluences are needed to remove the thicker layers of encrustation in all cleaning regimes (μs, ns, and ps), but side effects include the detachment of the fragile underlying pigment layer with the ns and ps regimes and a higher possibility of inducing pigment color alteration with μs laser pulses.

A further example of laser cleaning of a larger area indicates the type of results obtained with careful treatment. The thick black crusts present in some areas of fragment 1 exhibit very strong adhesion to the pigments; cleaning with lasers was able to only partially remove the crust from the paint layer. The best results were obtained with the laser of longer pulse duration, as shown in Figure 13 for the cleaning of a larger area (spot numbers 5-6-7, fluence in the range of 2-3 J/cm^2; 5–50 consecutive pulses, see Table 1 for more detailed laser parameters).

5. CONCLUSIONS

Particularly important, as exemplified in this study, is the heterogeneity of the surface of the samples studied; with variation in condition, state of conservation, thickness, and type of contaminant and restoration materials, it is impossible to specify optimal conditions for laser cleaning of the entire fragments. In fact, tests illustrate the necessity to optimize laser cleaning for each type of area and the requirement to assess the cleaning results using different and complementary analyses. A good compromise between fluence and the number of pulses always needs to be determined, and the use of lasers for cleaning of wall paintings may be well complimented by other traditional methods for cleaning, as it is not always possible to completely remove surface dirt using laser ablation alone.

Following extensive testing, the optimal conditions for the laser cleaning of specific layers/crusts on the studied fragments of the wall paintings from the monumental cemetery of Pisa were determined. Long-pulse laser radiation, with fluences lower than 7 J/cm^2, provided controlled removal of different patinas. In cases of thicker layers, good results were generally obtained with fluence lower than 14 J/cm^2 and best results were obtained by increasing the number of consecutive laser pulses at a lower fluence, instead of using fewer pulses at a higher fluence, in order to avoid pigment colour alteration. Ablation using the μs laser offers the possibility to remove the drops of lead present on the surface, without damaging the fragile underlying pigment. Wetting of the surface with aqueous solutions before applying the radiation was found to enhance the cleaning. In addition, the novel application of ultrashort pulses of ps duration to the cleaning of wall paintings was considered with very encouraging results,

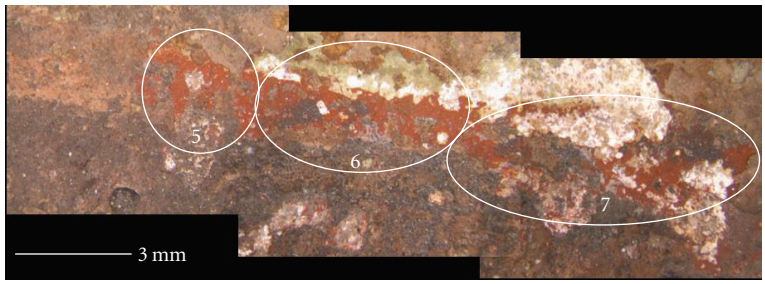


Figure 13: Fragment 1: removal of a larger area of thick black crust with the μs laser; the numbers correspond to the laser parameters reported in Table 1.

providing increased control and minimal observed alteration to the substrate, with fluences lower than 0.7 J/cm^2.

Analysis of laser-cleaned areas was undertaken using molecular spectroscopy. Further, the efficacy of the cleaning was monitored following treatment by examination of samples in cross-section. For the optimized laser parameters adopted, no alteration products were detected. Finally, microscopic observations of the surface and PY/GC/MS analysis of the samples suggested an efficient removal of the different encrustations and of the white patina. In addition, the gas chromatographic analysis has indicated that by using the optimized laser parameters for the different laser systems, no degradation products of the organic materials were detected and that a gradual thinning of the superficial layer is possible by operating under controlled laser parameters. Positive results were associated with each laser employed; however differences in the materials found on the surface of the fragments and different responses to the lasers used yielded significant variations in optimum cleaning conditions. This highlights the importance of further study of mechanisms of laser materials interactions, in order to foster a synergistic approach to the optimization and assessment of laser techniques to the multifacetted problems encountered in the cleaning of wall paintings.

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