Laser removal of mold and foxing stains from paper artifacts: preliminary investigation

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ABSTRACT

In this work we focused on the laser removal of fungi growths and foxing stains from old paper artifacts. Irradiation tests have been carried out using Nd:YAG laser's second harmonic and characterized through morphological analysis by means of optical microscopy and UV-VIS light fluorescence, along with SEM-EDX microscopy. In addition, FTIR spectroscopy and VIS diffuse reflectance spectroscopy have provided, respectively, very useful information on chemical processes of the paper ageing and on the removal effectiveness of the laser treatment. The optimized laser setup with fiber coupling has allowed to achieve significant results in the removal of the foxing and bio-deterioration spots from aged paper. In particular, high selectivity and degree of control were observed in the treatment of metal-induced foxing (Fe and Pb), likely arising from the contact with metal objects. Moreover, similarly good results were pointed out for the removal of fungal colonies without inducing detectable structural damage to the cellulose fibers. The best operating conditions determined have been finally used in order to approach a concrete conservation problem of an original engraving by G. B. Piranesi entitled *Veduta del Ponte e Castello Sant'Angelo* (18th century). Further research will be carried out on both topics in order to evaluate the range of applicability and possible long-term effects of this approach.

Keywords: Foxing, mold, engraving, cellulose, paper, bleaching, Nd:YAG laser

1. INTRODUCTION

1.1 Main causes of foxing stains and mold damage

Books, prints, drawings, watercolours, engravings as well as all collectable objects based on paper can undergo over time to degradation processes, especially if not stored under controlled environmental conditions. Foxing spots, or rusty-red stains, can be considered as a widespread damage of all fiber based-materials. The causes of and detailed descriptions for some types of fox spots have been reviewed in the literature[1-5]. Metal contamination, microorganisms (fungi and bacteria), as well as moisture condensation and capillary localized evaporation processes at wet-dry interface, are suggested as possible causes of foxing. Metal and microorganisms contamination may come either from the papermaking and from airborne dust. It is noteworthy that airborne dust can contain iron measuring up to 15% of the inorganic component. Additional sources of metal ions may be from contact with metal objects or related to the iron gall inks. Research on ink corrosion showed that most iron gall inks contain an excess of iron which is not bound in the complex forming compound of the ink and can migrate on a small distance into the surrounding area. Summarizing, transition metals ions, such as iron (II) and copper (I) can act as catalysts for free radical cellulose oxidation bringing to depolymerization of cellulose chains and increasing discoloration of paper containing cellulose. In addition, carboxyl and carbonyl groups formed from cellulose oxidation can enter an amino carbonyl reaction with nitrogen-containing compounds inherent in paper (gelatin sizing, fungal amino acids) or present in pollution (dust, spores, starch grains). The result of amino carbonyl reaction, also named as the Maillard reaction, is the formation of melanoidin type brown colored compounds which are called age pigments[6-8]. It is worth noting how fungi and related metabolic products are often involved in the formation of melanoidin compounds. Within the context of foxing generated from microorganisms, it was stated that in old paper, fox spots are mainly formed from fungal structures in a limited stage of growth. Tipically, fungal structures found include germinated spores which have died before vegetative growth and a limited amount of hyphae or developed mycelia[9-10]. Fungus-induced foxing results in the formations of spots in various colors. The

browning in foxed areas does not depend exclusively on fungal structure and its pigments, but may come from the Maillard reaction between glucose and amino acids, both of which originate from cellulose degradation products and the fungal body itself. The source of color could be also due to a lipid auto-oxidation process. Lipid comprises up to 50% of the dry weight of spores and a similar amount of mycelia. Through auto-oxidation, lipid forms highly destructive free radicals and peroxide, which results in staining of paper substrate as well as the breakdown of proteins to amino acids. In fox spots, the paper results more acidic, weaker and friable than the uncolored one but not drastically damaged at structural level. Under optimum growing conditions, fungi may grow further by forming vegetative colonies and new viable spores. In a humid environment, paper can absorb water by capillary condensation, preferentially in the hetereogeneus areas of the cellulose chains and a biological attack can takes place compromising structural stability of cellulose fibers. The latter is the main aspect that differentiates foxing from commonly called mold or mildew damage. Biodeteriotion seriously affects the mechanical properties to both the paper and media through enzymatic activity, which breaks down carbohydrates, proteins and fats into simple sugars, amino acids, and fatty acids.

Currently, the most common methods for foxing or mold removal include intensive treatments like washing and bleaching, sometimes in combination with inpainting techniques. Moreover, if the deterioration causes are visible as rusty spots or fungal hyphae, they are mechanically removed as much as possible with fine scalpel blades prior to aqueous treatment. Specifically targeted treatment methods using chelating agents and enzymes have been suggested to treat selectively metallic and biological contaminations. These methods have not widely been applied because the causes of specific foxing spot cannot be clearly determined. Basically, conventional dry and wet cleaning methods are performed on old masterwork only when strictly essential for its recovery. All this justifies in the last decade the great interest in improving laser ablation techniques in order to treat historic paper artifacts. Referring to significant laser cleaning applications on stone, metal and wall paintings, even for paper artifacts must be verified conditions of discrimination[11-12]. If properly optimized laser irradiation of paper can produce selective ablation with high control, minimizing undesired side effects to paper substrate and media graphics.

1.2 Pulsed laser light interaction with cellulose based materials

The influence of pulsed laser radiation with several wavelengths and intensities on old and modern paper has been reported in many studies. Initially, a wide variety of excimer lasers were utilized for cleaning purposes. Thus for example, foxing spots were completely removed from a medieval map, historic paper manuscript and prints using a molecular fluorine laser (F_2*) at 157 nm[13-14]. Excimer pulsed laser at emission wavelengths of 248 nm (KrF*), 266 nm (Nd:YAG 4th harmonic), 308 nm (XeCl*) and 355 nm (Nd:YAG 3rd harmonic), were also proposed for removal of specific 'stains' caused by fungi, metal, inks, self-adhesive tapes, etc[15-17]. Despite their effectiveness, they are indicated as not suitable for the cleaning of cellulose based materials due to of detrimental effects caused by the high energy of the incident light. Absorption of photons with energies greater than $\approx 3,6$ eV ($\lambda < 340$ nm) can lead to direct photolysis, or can induce photo-oxidative degradation of cellulose, which in turn leads to severe immediate decrease of degree of polymerization (DP)[16]. On the contrary, no detectable immediate changes or visible discoloration were observed with laser beam at 532 nm below the ablation threshold. At this wavelength, chemical interaction with cellulose is less pronounced and laser removal appears more promising respect to conventional cleaning methods. The best cleaning result was realized at a laser fluence of 0.8-1 J/cm^2 and pulse duration of 17 ns 18. However, studies on laser treatment of soiled samples suggests discoloration and degradation phenomena caused by the photothermal decomposition of cellulose[19]. Laser irradiation can also results in a substantial bleaching of paper accompanied by additional oxidation[20]. Laser removal of fungi were also achieved at 532 nm after sanitizing cotton and rag paper samples by ethanol[21]. This procedure has provided very satisfactory results in comparison with conventional chemical bleaching by KMnO^4, and was less time-consuming and more selective. Systematic studies on QS Nd:YAG laser irradiation at 1064 nm of pure and soiled cellulose samples have been further reported[22-24]. Results demonstrated that on soiled paper yellowing may occur upon irradiation due to the formation of covalent intermolecular bonds and dehydration reactions. Such detrimental effects are more pronounced if carbon particles has been deposited on the samples and if multiple successive laser treatments are applied.

Considering the present state of the art , in this study we focused on the laser removal of fungi growths and foxing stains from old paper artifacts using Nd:YAG laser's 2nd harmonic in a suitable setup. Cleaning results have been extensively characterized using non invasive methods and possible undesired side effects are discussed.

2. EXPERIMENTAL

Foxing and mold stains of three 19th century rag paper fragments belonging to Department of Drawings and Prints of the Opificio delle Pietre Dure (OPD) in Florence were investigated (Table 1). Q-Switched Nd:YAG laser at 532 nm with variable pulse duration, from 10 ns up to 30 ns at lower output energies, were used. To improve beam quality and efficiency during paper treatment a laser fiber-coupled setup was arranged. The demagnification of collimated laser beam diameter of 6 mm into core fiber of 1,5 mm was achieved with a reverted Keplerian beam expander. Two plano-convex lenses with a focal length of 80 mm and 20 mm, respectively, were positioned with their focal plane nominally coincident. The alignment allowed us to obtain a reducing factor equal to ¼ and a maximum coupling of output energy from the fiber of 25-30 mJ. Energy values more than sufficient for applications on cellulose-based materials.

Samples were irradiated following two systematic procedures: the first one, consists in gradual increasing of fluence (from 50 up to 1500 mJ/cm^2) and repetition frequency (2-5-10 Hz) for short times of exposure (30-60 sec) in order to identify the ablation thresholds of the stains and substrate; the second one, for much longer times (30-60 min.) with shorter values of fluence (<500 mJ/cm^2) and frequency (2-5 Hz).
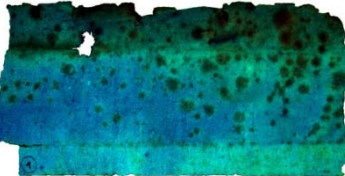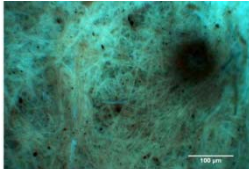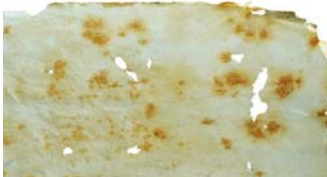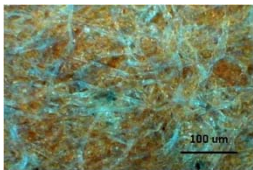
The macro-images were taken on a photographic column stand with a Nikon D80 DSLR camera equipped by a AF-S Nikkor 28/1.8G wide-angle lens. UV fluorescence photography (UVFP) was performed in a suitable setup by a Wood's lamp, used as radiation source and a UV filter with cut-off wavelength of 400 nm mounted on top of the camera lens.

Dark field reflected and trasmitted light along with UV reflected fluorescence microscopies (Exciter filter:380-420 nm, Dichroic mirror: 430 nm, Barrier filter: 450 nm) were exploited to combine prior information from color, morphology and fluorescence of the stains and to evaluate laser treated areas.

Perkin Elmer Spectrum One FTIR equipped with an attenuated total reflectance (ATR) accessory has been used for the analysis of paper composition and degradation. Spectral analyses were acquired with a resolution of 4 cm^{-1} in the range of 4000-400 cm^{-1}. Environmental scanning electron microscopy studies in combination with energy dispersive X-ray analysis (ESEM-EDX) were also performed on a Quanta-200 FEI electron microscope. The accelerator voltage of the system was in the range 22-25 kV, low-vacuum pressure (0.5-1 torr), working distance 10 mm.

Color and diffuse reflectance measurements were carried out using a PR-705 Spectra Scan spectroradiometer provided by Photo Research inc. and a stabilized 10W Tungsten halogen light source with fan cooled positioned at 45 degrees. Data were collected on a measuring area of 3 mm with a spectral resolution of 2 nm in the range 380-780 nm. Calibration was performed by means of 99% Spectralon® diffuse reflectance standard and CIE 1976 L*a*b* color parameters have been calculated considering 10 degrees CIE standards observer values.

Table 1 – Foxing and mold stains of the three 19th century paper fragments

Description	Visible light and UV fluorescence macro-photography		Micro-photography
Sample A woodpulp paper affected by pale brown stains with irregular roundish shape and variable size.			
Sample B rag paper with rusty red stains, irregular shape and variable size.			

Sample C
rag paper heavy compromised from dark-brown stains with a defined spherical shape and size.
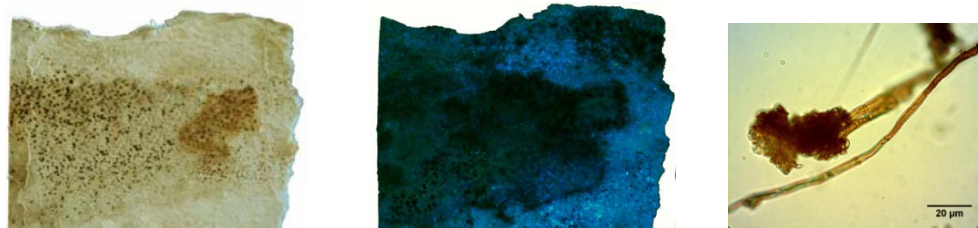
3. RESULTS AND DISCUSSIONS

3.1 Foxing

Fox spots on the sample A had migrated from recto to verso of sheet of paper. As illustrated in Table 1, the UVFP showed a dark blue fluorescence in the middle of the sheet and a more intense bluish-green fluorescence along the folding in the lower and upper edges and around the stains. UV fluorescence microscopy observations (Table 1) put in evidence within the foxed areas a dark center no fluorescent and a prominent fluorescence increase going outwards. No fungal structures or fibers damage were observed through microscopic examination. To fully understand the causes of this type of foxing, the infrared spectroscopy was performed both on the spots and on the neighbouring unstained paper surface. The ATR-FTIR spectrum of the unstained areas is a typical profile of a woodpulp paper (Figure 1).
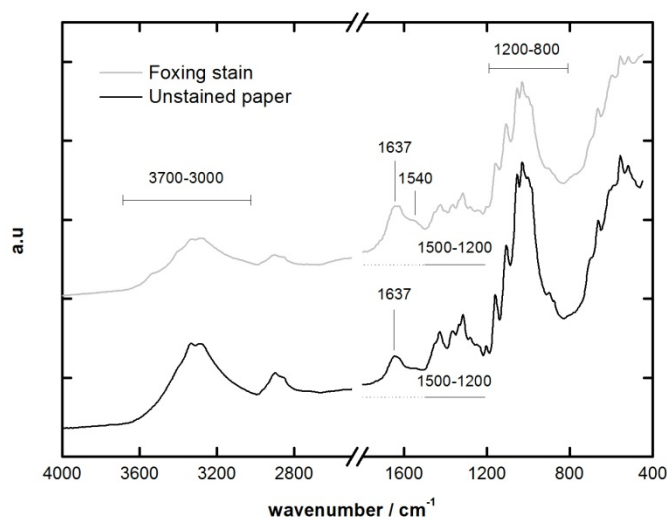

Figure 1. ATR-FTIR spectra of unstained paper characterized by bluish-green fluorescence (bottom) and within a foxing stain (top)

The shape of the fingerprints region between 1200 and 800 cm^{-1} and the absence of typical band of lignin at about 1510 cm^{-1} suggested that the paper has been subjected to chemical processes in order to remove some of the non-cellulosic components such as lignin and colored material. As known this methods were developed and applied by the mid to late 19th century to produce higher quality paper [4]. Both spectra not showed unconjugated carbonyl groups between 1700 and 1740 cm^{-1} but the band shaped tooth in the OH region at about 3335 cm^{-1} is the evidence of a paper strongly degraded by acidity. It is worth noting that the characteristic infrared absorbance of OH groups and absorbed water (3700-3000 cm^{-1} and 1635 cm^{-1}) shows a different degree of paper degradation. In particular, the FTIR spectrum in the stained area is characterized respect to the unstained one by a decreased absorbance between 3700 and 3000 cm^{-1} and on the contrary by an increased absorbance at about 1635 cm^{-1}. In the latter region fall also polypeptide bonds with amide I at about 1635 cm^{-1} and amide II at about 1540 cm^{-1}. These absorption bands are characteristic both of gelatin sized paper and fungal amino acids. As already discussed in the introductory section, the discoloration mechanism involves the reaction

between cellulose and amino groups (Maillard reaction). To differentiate FTIR spectra of paper subjected to biological attack from those simply sized is very useful to examine the region between 1500 and 1200 cm^{-1}. In presence of fungal agents this region should be a broad plateau without overlapping bands typically observable in gelatin-alum or rosin-alum sized papers. In this case, the overall shape of the spectrum suggests only a decreased absorbance in the region 1500-1200 cm^{-1} but not a plateau. In accordance with the microscopic analysis which did not reveal fungal structures, this type of foxing could be only the result of a chemical degradation. Furthermore, the increasing intensity of the peak at 1637 cm^{-1} and its broadening can also be associated to the formation of two shoulder peaks attributable to CO group at 1686 cm^{-1} and COO- group at about 1590 cm^{-1}. These two bands indicate ongoing mixed oxidative and hydrolytic processes. In literature is also reported that in the presence of metallic impurities (Fe^{+++}) CO signal should shift to the 1525–1610 cm^{-1} region due to the formation of coordination complexes[2-3-5].

By means of ESEM-EDX analysis carried out on both sides and on various stains of sheet of paper different elements were detected (Figure 2). Among these the iron, most probably introduced as impurity during papermaking or resulting from airborne dust, may have catalyzed the oxidation processes leading to discoloration and acidification of the paper. The other elements such as Al, Si and Ca come from the added components such as fillers (calcium carbonate, titanium dioxide or kaolin).
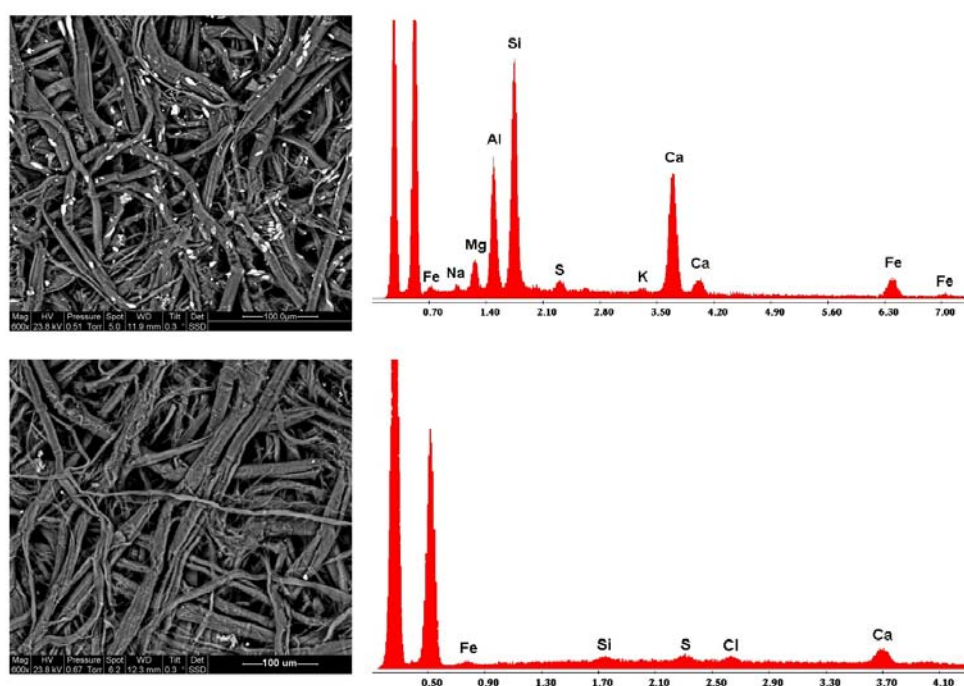

Figure 2. Back scattered electrons (BSE) images and EDX spectra of a stain no fluorescent before (top) and after laser treatment (bottom). Operating conditions were: F=0.6 J/cm^2, 5 Hz, 50 pulses, dry treatment.

After laser treatments performed following the two procedures described above, only a slight color change from a pale brown to yellow-green of the stain was observed. Nevertheless, no detectable structural damage or morphological changes to the cellulose fibers were promoted by laser irradiation under the operating conditions used (Figure 2). From the comparison of the EDX spectra are clearly visible a significant reduction of all added components introduced during the manufacture of paper and the total disappearance of the lines k of Fe. It's now more evident that the iron was not the only cause of the discoloration but rather other reasons, such as oxidation and localized moisture condensation.

On sample B the unaffected paper showed under UV radiation a cool blue fluorescence while on the darker rusty-red stains and surroundings fluorescence appears fully quenched (see table 1). Furthermore, the stain did not completely migrate through the sheet but a slight contamination from verso to recto was visibly appreciable. Through microscopic

observations, the fluorescent fibers of cellulose appeared to be embedded by rusty-red inclusions. BSE images confirmed a widespread presence of such inclusions while EDX analysis allowed to detect iron and lead as metallic contaminants along with additives components such as Mg, Al, Si and Ca. Iron and lead were homogeneously distributed on paper substrate but a significantly higher content was on the stains. In fact, paper substrate in more areas showed wide losses most probably caused by metallic corrosion. Furthermore, within the affected areas in a few spots were also found stacked residues similar to paint layer fragments containing most probably a mixture of red ochre and lead white pigments (Figure 3). These finds led to hypothesize a type of foxing formed by the contact with metal objects or painted surfaces even if, the same elements were distributed in lower concentration anywhere. This hypothesis is still more supported by the fact that stains and surroundings halo hadn't completely migrated through the sheet and the flakes were attached on one side only.
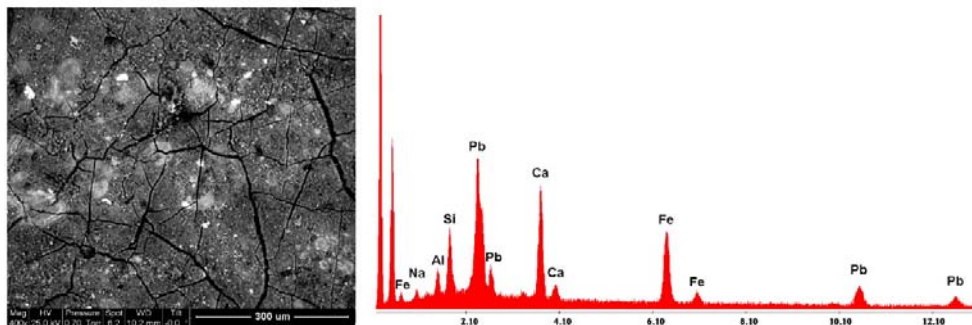

Figure 3. BSE-EDX analysis of a thick and rusty-red fragment centered within of a fox spot.

Cleaning tests initially conducted using a range of fluencies from 0.9 to 1.5 J/cm^2, 2 Hz of repetition frequency with a exposure time up to 2 minutes did not produce promising results. Under these operating conditions, the rusty-red spots were partially ablated but at same times, a light gray veil most likely formed by reduction of Pb remained visible to naked eye. To make sure of this hypothesis, the irradiated surface was exposed to air and after a week a complete reconversion to original color was verified. Surprisingly, cellulose fibers after laser treatment appeared under ESEM observations morphologically undamaged, more spaced apart with lacking of metallic inclusions. All the signals were drastically reduced especially those of iron and lead (Figure 4).
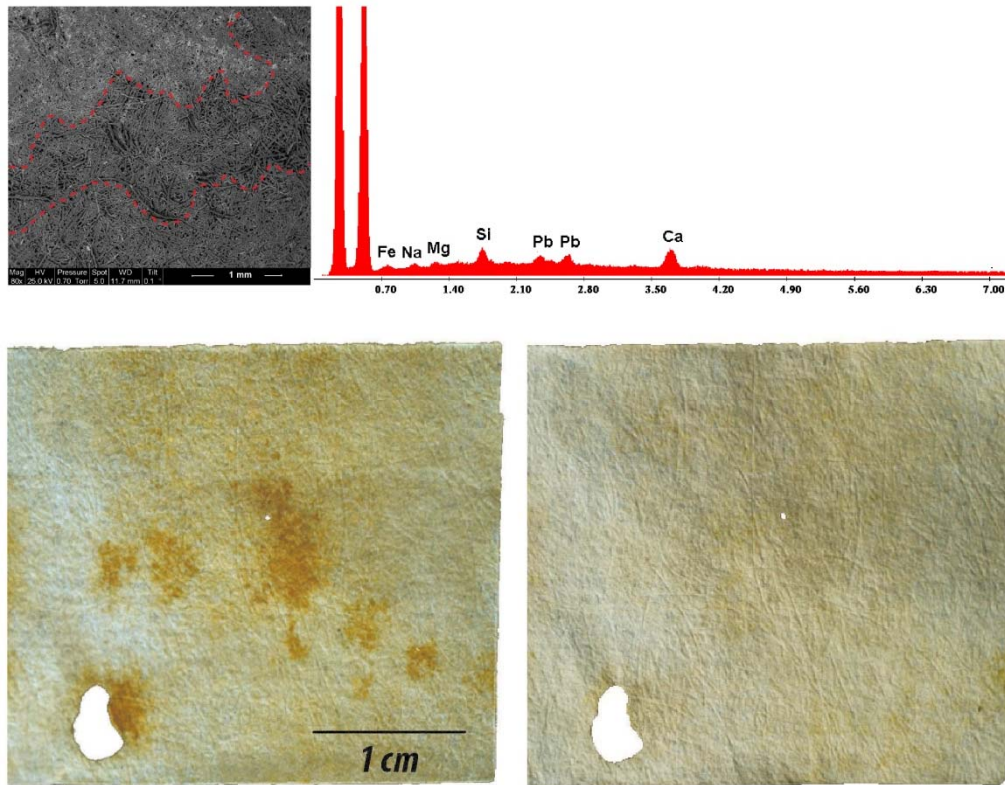
Figure 4. Bottom to top: Macro image of metal induced foxing on sample B before and after laser treatment of an area of 10 cm^2. The operating conditions were: F = 500 mJ/cm^2, 2 Hz, dry irradiation with air flow (30 min.). BSE image of laser treated area (inside dashed lines) and corresponding EDX spectrum.

Although it has been proved that paper ablation thresholds are very high due to of its high mechanical strength, the first procedure of irradiation did not reveal entirely suitable. More promising results were achieved below the ablation thresholds of the stains irradiating by moderate fluencies and for longer exposure times (Figure 4). Optimal operating conditions were achieved at fluence of 500 mJ/cm^2, 2 Hz of repetition frequency and dry irradiation for 30 minutes under constant air flow. By means of this procedure laser removal proceeded in a "soft" manner and stains were slowly bleached away without inducing structural damage or discoloration of cellulose fibers. The laser fiber-coupled setup accompanied by a easier handling and air flow assistance allow to achieve higher control and selectivity during cleaning treatment.

A set of diffuse reflectance spectra selected from a matrix 4x3 of measured points acquired before and after laser removal of widespread foxing stains are reported in

Figure **5**. Basically, in all measured points reflectance is higher in the red zone of the spectrum, decreases in the blue–green region until reaching a minimum at about 400 nm. Moreover, in stained areas the reflectance curve is drastically shifted downward and decays faster than unstained one due to of the presence in the UV zone of absorbing chromophores [25]. In addition, both spectra reported after the cleaning showed an extremely similar sigmoid-like behavior but at same time, the unstained treated paper results slightly bleached. It's difficult to establish if the laser treatment has triggered or not a bleaching effect or if this profile is closer to the original state of this paper artifact. Further observations can be made by considering the variations in the colourimetric co-ordinates a^* and b^*, which give more precise indications on the chromatic 'direction' of the colour variation induced by the laser treatment. The a* and b* co-ordinates evaluated before and after removal of rusty-red foxing stains are compared in

Figure **5**. These data clearly indicate the direction in which the colour change occurred, since the spread of the a* and
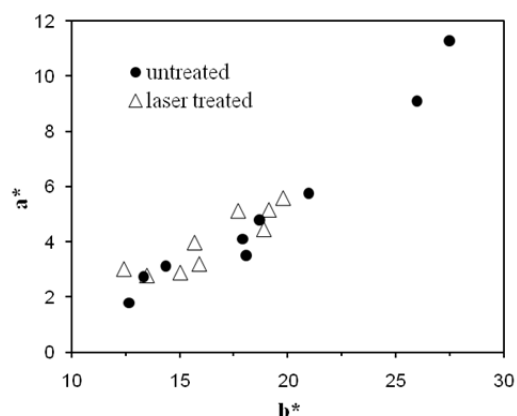
b* co-ordinates was reduced in a range of values markedly narrower after laser treatment. Moreover, the shift for both co-ordinates from higher to lower values proved a recovery of a chromatic uniformity, most likely closer to original tones of the paper artifact. At the same time, the mean value of lightness parameter (L*) calculated from these selected points changes from 74,6 ± 5,1 before the treatment to 80,1 ± 2,4 after the treatment.
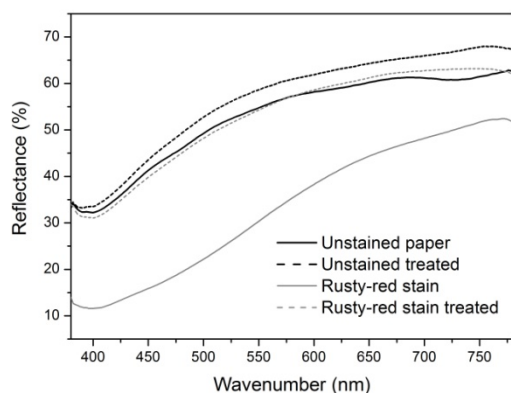

Figure 5. Diffuse reflectance spectra of unstained and stained areas before and after laser removal of metal-induced foxing (left) and corresponding shift in the colourimetric co-ordinates *a** and *b** (right).

3.2 Mold damage

The third of the three samples analyzed showed on both sides a widespread contamination of mold which colonies was clearly visible to the naked eye. The UV florescence showed both not fluorescent developed colonies and fluorescent compounds which are precursor of damage. Morphological details of fungal hyphae were achieved by mounting some isolated colony between two coverslips and then examined in trasmitted light (see Table 1). Within one colony could be easily identified tree-like hyphal aerial structures, also named coniophores and single hyphae well anchored to paper substrate. Spores and germinated conidia with developed hyphae were further detected through ESEM observations (Figure 6).

From the outset, very promising results were achieved in the mold removal using Q-Switched Nd:YAG laser at 532 nm with fiber coupling. The ablation process proceeded in a fast and selective way at the same time and molds were efficiently removed with moderate fluence values of 300mJ/cm^2 in the surface-near regions but more deeply embedded hyphae were still present. Under these irradiation conditions, no structural damage but only irrelevant and sporadic raising to cellulose fibers were induced. An higher fluence of the threshold of 300 mJ/cm^2 allowed to remove the remnants of thick growths of molds from bulk of the sheet but at the same time, the propagation of shock waves led to breakage of the cellulose fibers.

EDX analysis showed a significant decrease of the calcium content most probably introduced as filler during the manufacturing process. Further investigations were also carried out by performing diffuse reflectance measurements in order to evaluate the chromatic response on the entire laser treated area. The spectra recorded before and after the cleaning procedure are reported in Figure 6. The reflectance spectrum acquired on a grossly contaminated area results very shifted downwards due to a high absorption of radiation by the fungal structures. After treatment, the reflectance spectra return again to have very similar profiles but not yet equal than unaffected one, in accordance with the original color features of this paper artifact.
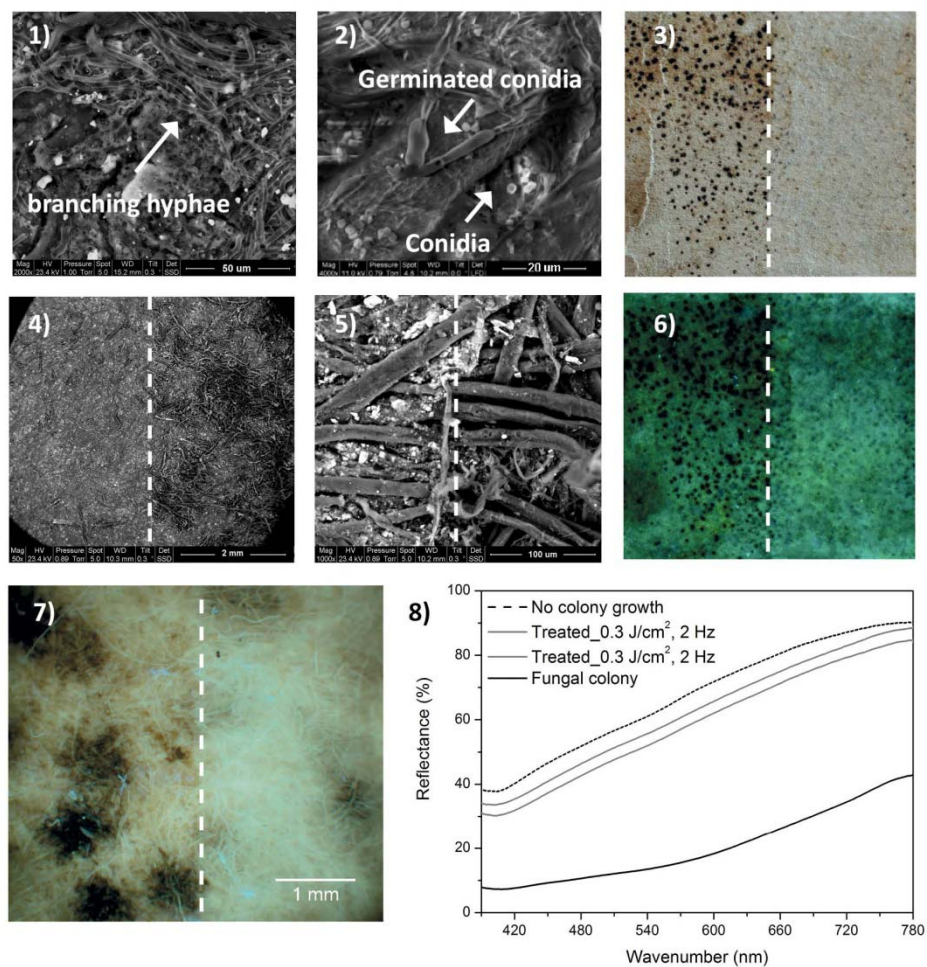
Figure 6. BSE image of a fungal colony with branching hyphae well anchored to paper substrate (1) and morphological details of germinated conidia and of singles conidia (2). Laser cleaning transition performed at a fluence of 300 mJ/cm^2, 2 Hz of repetition frequency without liquid assistant: VIS light macro-photography (3), BSE image (4) and detail of fibers structure after laser treatment (5), UV fluorescence macro-photography (6) and micro-photography (Exciter filter:380-420 nm, Dichroic mirror: 430 nm, Barrier filter: 450 nm) (7). Diffuse reflectance spectra before and after laser mold removal (8).

3.2.1 Case study

The best operating conditions determined have been finally used in order to approach a concrete conservation problem of an eighteenth century engraving by G. B. Piranesi entitled *Veduta del Ponte e Castello Sant'Angelo* (Figure 7).

The state of conservation of this print is greatly compromised due to of an extensive growths of brown-black molds both in the ink zone and along the edges. Under microscopic examinations it was observed that the majority of fungal structures (spores, hyphae etc.) were removed mechanically in a previous and undocumented cleaning treatment scraping off partially also the genuine copperplate ink. The molds were mainly located on the recto of the engraving, while the verso was indirectly affected only by the migration of the same within the thickness of the paper. Laser ablation test were performed on the recto of the artifact on an area of 10x10 mm by means of gradual increases of fluence and frequency. In this way it was possible to obtain different degrees of removal as well as to assess the process advancing. The range of

fluencies tested was between 55 and 250 mJ/cm^2 with frequencies of 1-2-5-10 Hz. It was observed in the zone A that the higher frequencies of 5-10 Hz led to a higher bleaching effect respect to lower frequency. On the contrary in the zone B, better results were achieved in term of efficiency and color rendering at about 200 mJ/cm^2 with a frequency of 2 Hz. Under these conditions the discoloration effect was less pronounced and simultaneously increased the removal effectiveness. The cellulose fibers could be completely cleaned with no apparent residual mold remaining upon examination with light microscopy. At the same time, fibers appeared without structural damage such as lifting or braking.
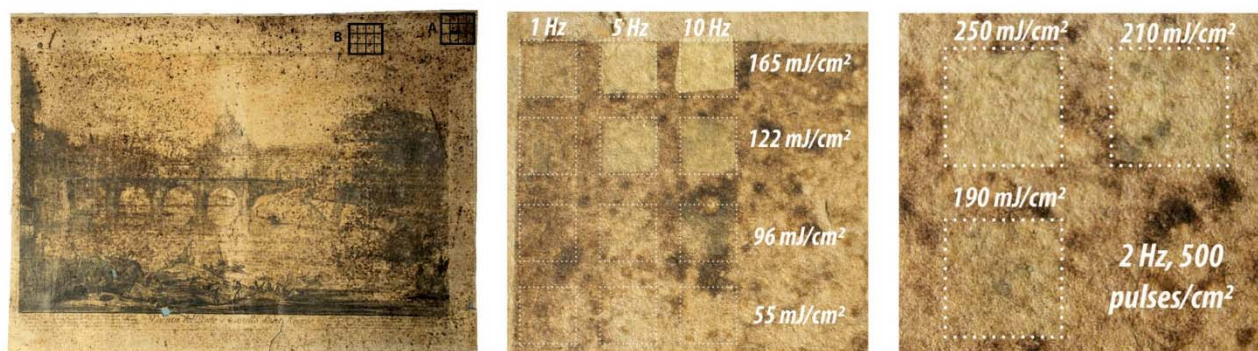

Figure 7. From left to right: engraving by G. B. Piranesi - *Veduta del Ponte e Castello Sant'Angelo* (Courtesy of Opifico delle Pietre Dure, Florence, Italy) and corresponding laser mold removal test performed respectively on zone A e B.

CONCLUSIONS

The use of the second harmonic of the QS Nd:YAG (532 nm) laser with fiber coupling has allowed to achieve significant results in the removal of the foxing stains and mold damage from old paper artifact. High selectivity and degree of control were observed in the treatment of rag paper fragment affected by metal-induced foxing (Fe and Pb), most probably caused by the contact with metal objects. On the contrary, it was stated that on woodpulp paper the laser foxing removal can lead to a yellowing effect. Good results were further pointed out for the removal of fungal colonies without inducing detectable structural damage or discoloration of the cellulose fibers. The present work is a preliminary investigation for further research that will be carried out on both topics in order to evaluate the range of applicability and possible long-term effects of this approach.

ACKNOWLEDGEMENTS

REFERENCES

[1] Choi, S., "Foxing on paper: a literature review", Journal of American Institute of Conservation 46, 137–152 (2007).

[2] Zotti, M., Ferroni, . A. and Calvini, P., "Mycological and FTIR analysis of biotic foxing on paper substrates", International Biodeterioration & Biodegradation, 65, 569-578 (2011).

[3] Calvini, P., and Gorassini, A., "FTIR – Deconvolution Spectra of Paper Documents", Restaurator, 23, 48–66 (2002).

[4] Erhardt, D., and Tumosa, C. S., "Chemical Degradation of Cellulose in Paper over 500 Years", Restaurator 26, 151-758 (2005).

[5]   Manso, M., Pessanha S., Figueira F., Valadas S., Guilherme A., Afonso M., Rocha A. C., Oliveira M. J., Ribeiro I. and Carvalho M. L., "Characterisation of foxing stains in eighteenth to nineteenth century drawings using non-destructive techniques", Anal. Bioanal. Chem., 395, 2029–2036 (2009).

[6]   Rebrikova, N. L., and Manturovskaya, N. V., "Foxing: A new approach to an old problem", Restaurator 21, 85-100 (2000).

[7]   Calvini, P., and Gorassini, A., "The Degrading Action of Iron and Copper on Paper A FTIR-Deconvolution Analysis", Restaurator 23 (4), 205–221 (2002).

[8]   Poggi, G., Baglioni, P. and Giorgi, R., "Alkaline Earth Hydroxide Nanoparticles for the Inhibition of Metal Gall Ink Corrosion", Restaurator 32, 247-273 (2011).

[9]   Florian, M.- L. E., "The Role of the Conidia of Fungi in Fox Spots", Studies in Conservation 41 (2), 65-75 (1996).

[10] Arai, H., "Foxing caused by Fungi: twenty-five years of study", International Biodeterioration & Biodegradation 46 , 181-188 (2000).

[11] Siano S., and Salimbeni R., "Advances in Laser Cleaning of Artwork and Objects of Historical Interest: The Optimized Pulse Duration Approach", Acc. Chem. Res, 43(6), (2010).

[12] Siano, S. Agresti J., Cacciari I., Ciofini D., Mascalchi M., Osticioli I., and Mencaglia A., "Laser cleaning of stone and metal artefacts, wall, and easel paintings: state of art and new insights", Applied Physics A 106 (2), 419-446 (2012).

[13] Sarantopoulou, E., Samardzija, Z., Kobe, S., Kollia, Z. and Cefalas, A. C., "Removing foxing stains from old paper at 157 nm", Applied Surface Science 208-209, 311-316 (2003).

[14] Kollia, Z., Sarantopoulou, E., Cefalas, A. C., Kobe, S. and Samardzija, Z., "Nanometric size control and treatment of historic paper manuscript and prints with laser light at 157 nm", Appl. Phys. A 79, 379–382 (2004).

[15] Kolar, J., Strlic, M., Muller-Hess D., Gruber, A., Troschke, K., Pentzien, S., and Kautek, W., "Near-UV and visible pulsed laser interaction with paper", Journal of Cultural Heritage 1, 221–224 (2000).

[16] Kolar, J., Strlic, M., Pentzien, S. and Kautek, W., "Near-UV, visible and IR pulsed laser light interaction with cellulose", Appl. Phys. A 71, 87–90 (2000).

[17] Friberg, T. R., Zafiropulos, V., Kalaitzaki, M., Kowalskim R., Petrakis J., and Fotakis, C., "Excimer Laser Cleaning of Mold-contaminated Paper: Sterilization and Air Quality Considerations", Lasers in Medical Science 12, 55-59 (1997).

[18] Balakhnina, I. A., Brandt, N. N., Chikishev, A. Y. and Rebrikova, N. L., "Effect of Laser Radiation on 19th Century Paper", Restaurator 33, 30–44 (2013).

[19] Kolar, J., Strlic, M., Müller-Hess, D., Gruber, A., Troschke, K., Pentzien, S. and Kautek, W., "Laser cleaning of paper using Nd:YAG laser running at 532 nm", Journal of Cultural Heritage 4, 185–187 (2003).

[20] Brandt, N. N., Chikishev, A. Y., Itoh, K. and Rebrikova, N. L., "ATR-FTIR and FT Raman Spectroscopy and Laser Cleaning of Old Paper Samples with Foxings", Laser Physics 19 (3), 483–492 (2009).

[21] Pilch, E., Pentzien, S., Madebach, H. and Kautek, W., "Anti-Fungal Laser Treatment of Paper: A Model Study with a Laser Wavelength of 532nm", Lasers in the Conservation of Artworks Springer Proceedings in Physics 100, 19-27 (2005).

[22] Rudolph, P., Ligterink F., Pedersoli Jr. J., Bommel, M. V., Bos, J., Aziz, H., Havermans, J., Scholten, H., Schipper, D. and Kautek, W.,"Characterization of laser-treated paper", Appl. Phys. A 79, 181–186 (2004).

[23] Strlic, M., Kolar, J., Selih, V. S. and Marincek, M., "Surface modification during Nd:YAG (1064 nm) pulsed laser cleaning of organic fibrous materials", Apllied Surface Science 207, 236-245 (2003).

[24] Kolar, J., Strlic, M. and Marincek, M., "IR pulsed laser light interaction with soiled cellulose and paper", Appl. Phys. A 75, 673–676 (2002).

[25] Missori, M., Righini, M. and Dupont, A. L., "Gelatine sizing and discoloration: A comparative study of optical spectra obtained from ancient and artificially aged modern papers", Optics Communications 263 (289–294) (2006).

[26] Boruvka, N., "The Development of Foxing Stains on Samples of Book Paper afterAccelerated Ageing", Journal of the Canadian Association for Conservation, 33 (2008).