Brockmann *et al. Heritage Science* (2024) 12:34
https://doi.org/10.1186/s40494-024-01152-1

Heritage Science

RESEARCH

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Effects of laser cleaning on the condition of different silk model samples using varying wavelengths and pulse durations

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Abstract

The cleaning of aged silk fibers poses a common challenge in the conservation of textiles, since traditional cleaning techniques often yield unsatisfactory results or even harm objects. In this regard, cleaning objects with laser radiation is a promising addition to the range of available methods. Due to it being contactless, even brittle and touch-sensitive objects with disfiguring or harmful soiling could potentially be cleaned and therefore made accessible for research and presentation. Examples of treatment have sometimes shown spectacular results. Still there is some skepticism concerning the safety of this treatment for textile materials, which has been strengthened through previous 532 nm wavelength nanosecond laser cleaning studies on silk fibers. Taking these published results into account, the range of examined laser parameters has been extended in this study, from 532 nm nanosecond laser to 1064 nm nanosecond and even 800 nm femtosecond laser, reevaluating the effect of this treatment on the fibers. The physicochemical processes taking place on the silk fibers when cleaning with lasers are complex and still not fully understood. The aim of this project was therefore to bring more clarification about potential effects of those processes on the condition of silk samples treated with a set of different parameters for wavelength, pulse duration, energy density and number of pulses per spot. It also looks at the influence of the presence of soiling on the results. The analysis of potential effects was then carried out using statistical methods and advanced analytics. Scanning electron microscopy, Fourier-transform infrared spectroscopy and colorimetry technology provided the required insights to better assess the effects. Results show that laser cleaning of silk fibers, like most other conventional cleaning techniques, is not completely without risk, but knowing what the possible effects are helps making decisions on whether the benefits of the technique used justify these risks.

Keywords Laser cleaning, Cultural heritage, Conservation, Silk, FTIR, SEM, Color measurements

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Introduction

The application of lasers for the cleaning of cultural heritage has been employed in many fields of conservation since its first trials in the 1970s by John F. Asmus et al. [1]. Pioneering work was done by researchers of various disciplines since then, for example by Cooper et al. applying the technique on stone objects [2], Georgiou et al. on paintings [3] or Kolar et al. on cellulose [4]. But it is not a very common measure for the treatment of textiles today. The reason for that might be that the effects on fibrous materials of various complex compositions are not yet fully investigated, causing concerns about negative long-term effects. But especially aged textile objects are often highly delicate and touch sensitive and can also be colored with water- or solvent-sensitive dyes. A contactless and selective method that does not involve water or solvents, such as laser cleaning, could therefore in some cases pose the only possibility to clean an object at all. There are not many publications on laser cleaning of textile materials. Some reports exist on successful practical application on various natural fibers [5, 6]. Other papers focus on cotton, such as those by Sutcliffe et al. [7] and Chillé et al. [8], comparing different wavelengths of nanosecond lasers for the cleaning of cotton, and Bloisi et al. [9] investigating the influence of 532 nm nanosecond laser treatment on clean cotton. Escudero et al. [10] studied femtosecond laser cleaning of historic linen. Chemically closer to silk, which is the topic of this paper, is a study on cleaning wool by Londero et al. [11], in which they used 532 and 1064 nm radiation from a nanosecond laser to clean model samples before treating an object made from wool. They favored 532 nm radiation due to a smaller degree of color change and higher efficiency. Studies that involve silk are relatively rare. Strlič et al. [12] used a 1064 nm nanosecond laser to clean model samples of varied fibrous materials. They found that all materials showed discoloration after treatment, some more than others, and that the change of color in silk was relatively moderate compared to the other materials. They suggest that the discoloration happens due to reductive chemical change. The use of lasers for treating archaeological finds was studied by Belli et al. [13]. They employed 248 nm nanosecond laser radiation to remove soiling and consolidation substances from wool, silk, cotton and flax model samples and concluded that the technique enabled technical examination of the samples after cleaning, and that animal fibers were more sensitive to undergo structural change through the treatment, observed by SEM imaging. Von Lerber et al. [14, 15] focused purely on silk fibers, treating model samples with 532 nm radiation. They saw yellowing at lower and bleaching at higher fluences used and found that thermal degradation of the fibers led to chain scission and crosslinking at the same time. The influence of treatment of silk fibers dyed with cochineal and safflower with an 800 nm femtosecond laser was investigated by Ahmed et al. [16], and they reported that the samples were damaged through irradiation. Additionally, there are a few papers on laser cleaning of metal threads [17–19], which are often wound around a silk core. They all favored lasers operating in the pico- and femtosecond range for the metal, but Taarnskov et al. identified damage to the silk core to happen through treatment (with a 532 nm picosecond laser).

This study [20] aimed to gain a deeper understanding of the processes taking place on silk fibers when irradiated with laser. Due to its ageing properties this fiber is most often problematic when it comes to cleaning. The study is also taking up on previous research and extending it by employing further options of laser parameters. Uniform, comparable samples of four different stages of silk fabric (new, new soiled, aged, aged soiled) were created and treated with 9 combinations of different laser fluences and pulse numbers per spot. All samples were then analyzed using color measurements, FTIR and SEM imaging. That way it was possible to systematically investigate a wide range of factors and put the results into context.

Experimental

Principles of laser cleaning

The portion of laser energy that is absorbed by the irradiated material—depending on the material's composition and the radiation wavelength and intensity—can lead to thermal, photochemical and fluorescence effects, of which the first two can lead to material removal. Under ideal conditions the radiation ablates only soiling particles but induces no change to the underlying material. This can occur through a contrast in absorption: While the soiling absorbs enough energy for photochemical and/or thermal ablation processes to take place, the surface material does not absorb radiation energy above a threshold to induce change. This allows the technique to be self-limiting, meaning the effect stops once all soiling has been removed [6, 21, 22]. Absorption depends on both the material and the radiation properties, therefore the laser parameters—determined by the laser used and its settings—must be carefully selected and if the absorption contrast is found not to be high enough the technique cannot be used. Also important to note is that laser cleaning works best on surface soiling. Removing staining that has penetrated the material is difficult without damaging the object [23]. Parameters that can be changed for laser treatments, among others, are fluence (energy of the pulse per square centimeter), number of pulses (fired on a single spot in total), repetition rate (pulses emitted per second), pulse duration, and radiation wavelength.

Sample preparation

To create uniform, comparable samples, pre-washed degummed silk pongé was prepared to represent four different fabric conditions: New and unsoiled, new and soiled, aged and unsoiled, aged and soiled. This way investigating the influence of ageing and soiling on the results of the experiments was possible. A simplified artificial soiling was performed by automated spraying of carbon dust (pigment"Flammruß", consisting almost purely of carbon particles with small inorganic impurities and traces of tar, KREMER PIGMENTE GMBH & CO. KG), dispersed in white spirit, onto the fabric. This led to very even results. It was decided not to use a more complex system for artificial soiling to be able to draw more direct conclusions about possible links between soiling chosen and results obtained. Additionally, this form of artificial soiling has been used in previous studies of laser cleaning silk, so replicating this allows direct comparisons [14]. The artificial ageing was performed in a dry thermal ageing chamber at 125 °C for 21 days. This was done based on findings of Vilaplana et al. [24] to create fiber properties closest to those that aged naturally.

Laser treatments

For this study, three pulsed lasers were chosen: An Nd:YAG laser ("DINY pQ", IB-Laser) with 8–10 ns long pulses, 500 Hz pulse repetition rate and 1064 nm wavelength, the same machine but using the second harmonic of 532 nm wavelength, and a Ti:Sapphire Laser (Femtopower Compact PRO, Femtolasers) with 30 fs pulse duration, 1 kHz repetition rate and 800 nm wavelength. This way a comparison, within nanosecond laser treatment, between the two most commonly used wavelengths 1064 and 532 nm, could be achieved. While the effects of 532 nm laser on silk have been investigated by von Lerber [14] before, 1064 nm laser has not had that much attention yet. Furthermore, the evaluation of the suitability or possible benefits of ultrashort pulse lasers, which interact with materials in different ways [25] and could reduce impact on surrounding surfaces, was possible.

Silk shows considerable light absorption below 300 nm wavelength but is mostly transparent in the visible and infrared spectral region, within which the laser wavelengths employed in this study fall [26]. For comparison, graphite ("carbon dust"), which was used as artificial soiling, shows linear absorption coefficients of about 6 μm^{-1} for 532 nm and about 4 μm^{-1} for 1064 nm wavelength, respectively [27]. The soiling is therefore opaque for the laser wavelengths used here and the needed contrast for this technique to be successfully employed is to be expected.

The laser pulses were focused on the sample surfaces to Gaussian beam diameters ($1/e^2$) of 450 µm (ns, 1064 nm), 145 µm (ns, 532 nm), and 120 µm (fs), respectively. For nanosecond laser pulses the treatments were carried out through automated scanning over the static sample surfaces with a Galvanometer scanner. In case of the femtosecond laser, a motorized x–y-translation stage was used to move the samples relative to the fixed laser beam. The scanning and moving speeds were set so that the desired pulses per spot could be achieved, considering the repetition rate of 1 kHz. Pulse energies were measured using energy meters (ns: Pulsar-2, Ophir; fs: 3Sigma, Coherent) with the respective pyroelectric detectors. During irradiation an extraction tube was placed next to the sample against treatment direction to remove the ablated particles before they could redeposit on the surface.

Using the three chosen lasers, sensible "safe" treatment ranges of the variable parameters fluence and number of pulses had to be found for each one, within which sufficient cleaning could be achieved without causing obvious damage. It was decided to determine three settings for each of the two parameters. To do this, test treatments were carried out, slowly increasing both parameters

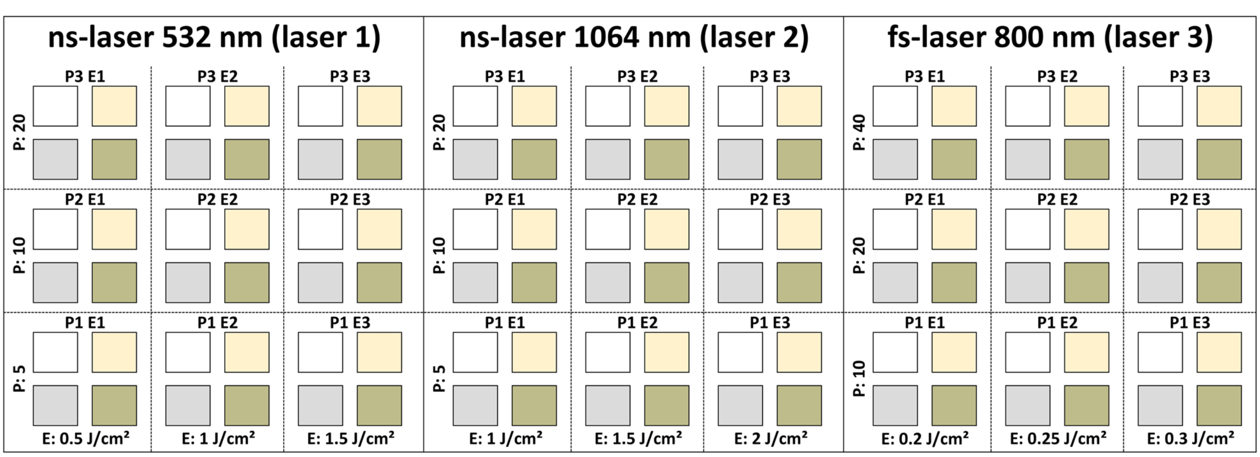

Fig. 1 Chosen settings for the parameters pulse number (short: P) and fluence (short: E) for the three different lasers and four different silk conditions (white: new and unsoiled, grey: new and soiled, yellow: aged and unsoiled, olive: aged and soiled

and investigating the irradiated areas with light microscopy. This way the results would be relevant for practice. The parameters chosen are listed in Fig. 1. When using 1064 nm radiation, higher fluences were required for sufficient cleaning compared to 532 nm.

The femtosecond laser was not able to clean satisfactory without causing damage at all. Light microscopy showed that all samples treated with this laser above a satisfactory cleaning threshold had changed optical appearance in comparison to untreated silk (Fig. 2, showing fiber particles that were present on the samples after treatment). For this reason, the further results for this laser will be discussed only briefly.

For a specific material and a defined laser wavelength, laser damage threshold fluences are lower for shorter laser pulses. The reason for this finding is that the energy cannot dissipate from the excited material volume within the ultrashort (femtosecond) interaction time in contrast to longer (nanosecond) laser pulses. In addition, nonlinear absorption phenomena caused by the much higher laser intensities of the ultrashort laser pulses can lead to increased energy deposition into the material and thus to lower damage thresholds [28].

Combining these 9 settings per each of the 3 lasers with the 4 different fabric conditions, a total number of 108 samples were to be treated and analyzed. Investigating the whole spectrum of combinations systematically enabled obtaining statistically relevant results.

Comparison treatments

Fabric samples from the same batch were also cleaned with two common textile conservation methods: vacuum cleaning with a brush and wet cleaning for approximately two hours in a bath using detergent (0,5 g/l Tinoventin JUN) and a sponge ("Blitz-Fix Saugschwamm", Deffner & Johann GmbH).

Both techniques can quickly reach their limits, as experienced in practice by the authors. Vacuuming with a brush reaches only loose particles and often does not improve the optical appearance of an object. Additionally, some textile objects are too fragile to be touched even by a brush and this technique can already be too abrasive. Even more risk-bearing is wet treatment of textile objects. Exposing fibers to water, detergent and agitation through sponging can pose strains that can lead to irreversible change and damage. For example, fibers can swell, break or even disintegrate and dyes can start running and leeching into surrounding areas. And even though removing harmful substances, such as acids, from textiles through washing is surely beneficial, wet cleaning often does not lead to the optical results desired but leaves heavily ingrained soiling unchanged. Comparing these techniques to laser cleaning in terms of efficiency and possible damage therefore will contribute to a better understanding of benefits and limitations of the latter in the context of textile conservation.

Selection of analysis techniques

Degummed silk is composed of the protein fibroin with the primary structure of polypeptide chains of varied amino acid sequences. The majority of the constituent amino acids are glycine, alanine and serine. Depending on the side groups of those amino acids present, the chain can take different forms spatially. When the side groups are smaller, like in glycine, alanine and serine, intermolecular secondary bonds between chains can be

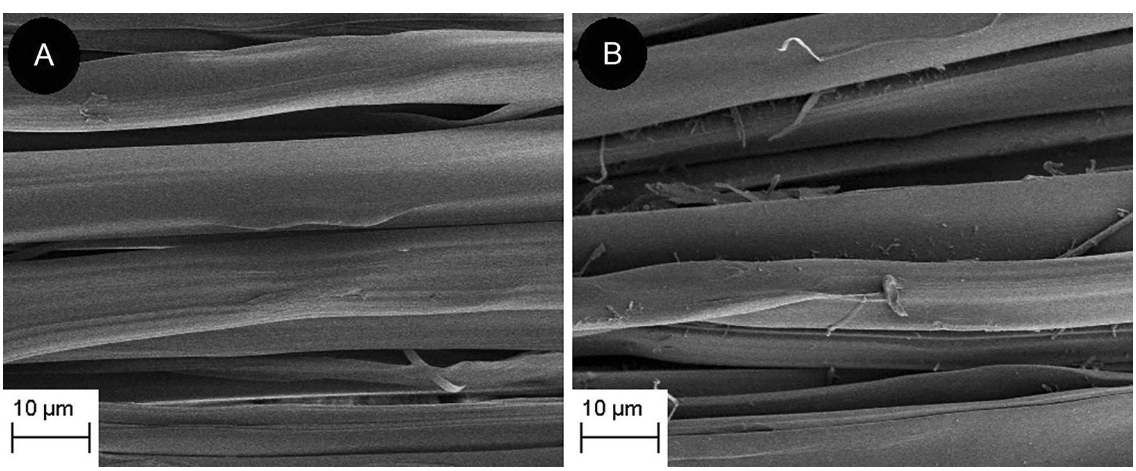

Fig. 2 SEM images of aged and unsoiled silk untreated (**A**) and aged and soiled silk treated with the fs laser at 0.3 J/cm^2 and 40 pulses, particles from disintegrated fibers present (**B**)

built, leading to a ß-sheet structure where the chains are extended and lie antiparallelly to each other. Those regions make up 60–70% of the fiber and are crystalline and ordered, contributing to the strength of the silk. When the side groups are too big to allow intermolecular bonds, intramolecular bonds within a chain lead to an α-helix coil configuration. Those regions are amorphous and unordered, giving the fiber flexibility, but are also sensitive to intrusion of degrading substances, such as water, oxygen and enzymes [29–32]. Thermal oxidation and photochemical degradation can damage silk fibers through building of chromophores, cross linking and chain scissions [33]. Those can be induced by laser irradiation and therefore represent the main dangers to the silk caused by laser cleaning. To investigate potential changes to the fibers introduced by laser treatment, suitable analytical techniques were chosen. Color measurements to look into the regularly observed effect of color change of laser treated surfaces, FTIR to find out about possible changes in the molecular structure of the silk and SEM imaging to examine the fibers' surfaces.

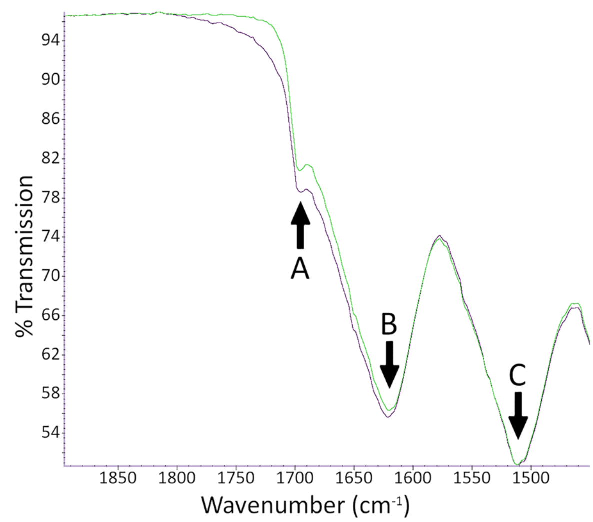

Fig. 3 Comparison of FTIR spectra of new, unsoiled (green) and aged, unsoiled (purple) silk fabrics. The spectra represent averages of 15 measurements each. **A**: Amide I C = O stretching vibration of antiparallel β-sheet structure, **B**: Amide I C = O stretching vibration, **C**: Amide II N–H in-plane bending and C-N stretching vibrations

Color measurements

The device used for color measurements (Portable spherical spectrum photometer Datacolor® CHECK 3, light: D65 10 Deg) measures in the CIELAB spectrum and allows to detect even color changes that are not visible to the human eye. Changes looked at in this study were the lightness value L, the red/green value a, and the yellow/blue value b. The samples were placed on a white ceramic tile and four measurements were taken of each treated area. The averages of those values were then compared to averages/ranges of each 20 measurements of untreated samples of the corresponding fabric.

Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR) in attenuated total reflection (ATR) mode (Thermo Nicolet Nexus FT-IR with Smart Golden Gate Accessory, KRS-5 lenses) was used to examine possible changes to the silk's molecular structure. Spectra were taken from 5 spots of the laser-treated samples and 15 spots of each untreated fabric condition, plus single measurements from the small areas that had been treated with fluences above the expected damage threshold, when the "safe" parameter ranges were determined in the preliminary tests. Those obtained spectra were then analyzed in extinction mode using a method adapted from a publication by Koperska et al. [32] with which they investigated thermal ageing effects on silk. This method mainly looks at the amide-bands, because these allow conclusions about changes of the amide-bonds within the silk-structure, which are most affected by ageing. In this study the analysis of the obtained spectra was done by determining two of the specified estimators (or ratios of specific band-intensities, Fig. 3) they listed.

The first one is the oxidation estimator, which can detect thermal oxidation (changes to the primary structure) and defines as $E_{\text{Amide I/Amide II}}$, the ratio of absorption at 1620 cm^{-1} (Amide I C = O stretching vibration) and 1514 cm^{-1} (Amide II N–H in-plane bending and C-N stretching vibrations).

The second one is the crystallinity estimator, which can detect changes to the tertiary structure and defines as $Ec_{C=O\ 2}$, the ratio of absorption at 1620 cm^{-1} (Amide I C = O stretching vibration of parallel β-sheet structure) and 1699 cm^{-1} (Amide I C = O stretching vibration of antiparallel β-sheet structure). Averages were formed from the 5 results per sample (or 15 for the untreated fabrics).

Scanning electron microscopy

In order to identify possible laser-induced morphological changes to the silk fibers, scanning electron microscopy (SEM) was used. Three 2×2 mm^2 pieces were cut from each sample, including the ones washed in a bath and cleaned with a vacuum, untreated samples and a few that were obviously damaged by parameters purposely chosen far above the determined treatment ranges. The pieces were cut in a diagonal line to avoid pre-damaged fibers reoccurring in all images. Then five randomly selected areas of each piece were examined closely. The instruments used were a Zeiss EVO LS10 and a Zeiss SIGMA VP.

Results and discussion

Color measurements

Looking at the treated samples two main things can immediately be observed: First, cleaning improves when raising fluence and pulse number for all lasers. Second, a color change of the samples towards yellow or brown takes place, but less so when fluence and pulse number are raised. This color change is stronger for 1064 nm radiation and does not occur at all on unsoiled samples.

The L values were mainly used to quantify the cleaning results. It is quite clear that the 532 nm laser is more efficient than the 1064 nm laser when using the same settings for fluence and pulse number as it leads to higher increase of the lightness value in relation to the soiled samples (Fig. 4B, D), but neither of them leads

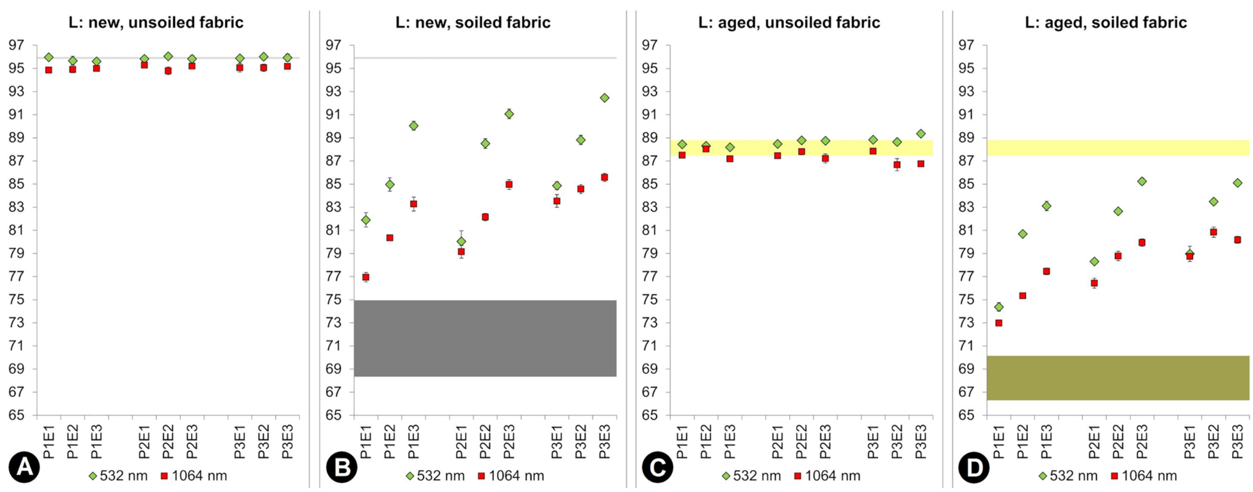

Fig. 4 L-values (rising number = lighter, falling number = darker) after treatment for 532 nm and 1064 nm nanosecond lasers. **A**: new and unsoiled, **B**: new and soiled, **C**: aged and unsoiled, **D**: aged and soiled fabric. The dark grey and dark yellow horizontal bars represent the range of values obtained from untreated soiled fabrics, the light grey and yellow ones those for untreated unsoiled fabrics. X-axis labels see Fig. 1. Note divergences can be covered by dots if very small

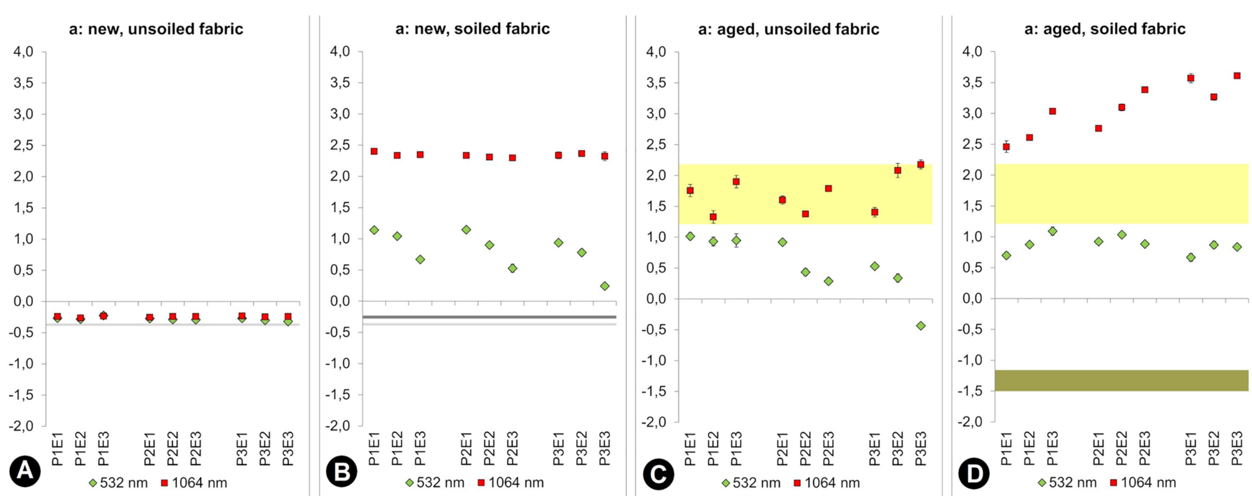

Fig. 5 a-values (rising number = redder, falling number = greener) after treatment for 532 nm and 1064 nm nanosecond lasers. **A**: new and unsoiled, **B**: new and soiled, **C**: aged and unsoiled, **D**: aged and soiled fabric. The dark grey and dark yellow horizontal bars represent the range of values obtained from untreated soiled fabrics, the light grey and yellow ones those for untreated unsoiled fabrics. X-axis labels see Fig. 1. Note divergences can be covered by dots if very small

to brightness levels equal to unsoiled fabric. The cleaning results generally improve when raising either pulse number or fluence. Interesting is the absence of obvious change in brightness when treating unsoiled fabric (Fig. 4A, C). This means that the irradiation on its own had no influence on the overall brightness of the fabric.

The a-values (Fig. 5) show that on unsoiled fabric very little happens for the new samples (Fig. 5A, change below 0.15), but for the aged and therefore yellowed samples the ones treated with 532 nm wavelength show a shift towards green that increases with both pulse number and fluence raised (Fig. 5C, up to 2.06). This finding could be an indication for damage and can also be observed by the eye when looking at the initial trials at higher fluences, and was also found by von Lerber, who saw bleaching of aged silk treated with 532 nm laser [14]. When looking at soiled samples, a-values shift towards red with all three lasers compared to the untreated sample, which can be interpreted as part of the observed color change effect. 1064 nm radiation is causing the stronger shift. Interestingly, the extent of these raised a-values for new fabric decreases for the 532 nm laser when raising parameters (Fig. 5B). That could mean that bleaching took place or that yellowed particles were removed by stronger irradiation.

The b-values allow a further look into the color change effect. Again, there is no significant change in this value when looking at the unsoiled samples (Fig. 6A, C), but the soiled samples shift towards yellow when irradiated (Fig. 6B, D). Here too, higher parameters when using the 532 nm laser tend to lessen the extent of yellowing slightly (Fig. 6B).

Generally, it is important to emphasize that the observed color change, or yellowing, only occurs when soiling is present. This means that it is definitely an effect of interaction of radiation and soiling components.

Fourier-transform infrared spectroscopy

It was noted that when looking at the estimator results of only the untreated samples clear changes from new to aged fibers could be observed already, and the values behaved in the same way as those published by Koperska et al. [32].

For the treated samples, the oxidation estimator $E_{Amide\ I/Amide\ II}$ (Fig. 7A-D) showed that within the chosen ranges of parameters for this study there was no significant change for green and infrared nanosecond lasers. Treating the new silk (Fig. 7A-B) with the green nanosecond laser at 3 J/cm^2 (outside of "safe" ranges) however led to an obvious increase of this estimator. Looking at the aged samples (Fig. 7C-D) showed that there is a smaller rise in this estimator, so potentially the thermal oxidation that had already occurred through the artificial aging procedure could not go much further through laser treatment.

The crystallinity estimator $Ec_{C=O\ 2}$ (Fig. 8A-D) behaves in a similar way, with those samples treated with the green laser showing values above the untreated reference samples when fluences outside the defined "safe" ranges were used. Interestingly, the tendency of change behaves opposite to the effects of thermal ageing only. While the value of the estimator decreased through thermal ageing

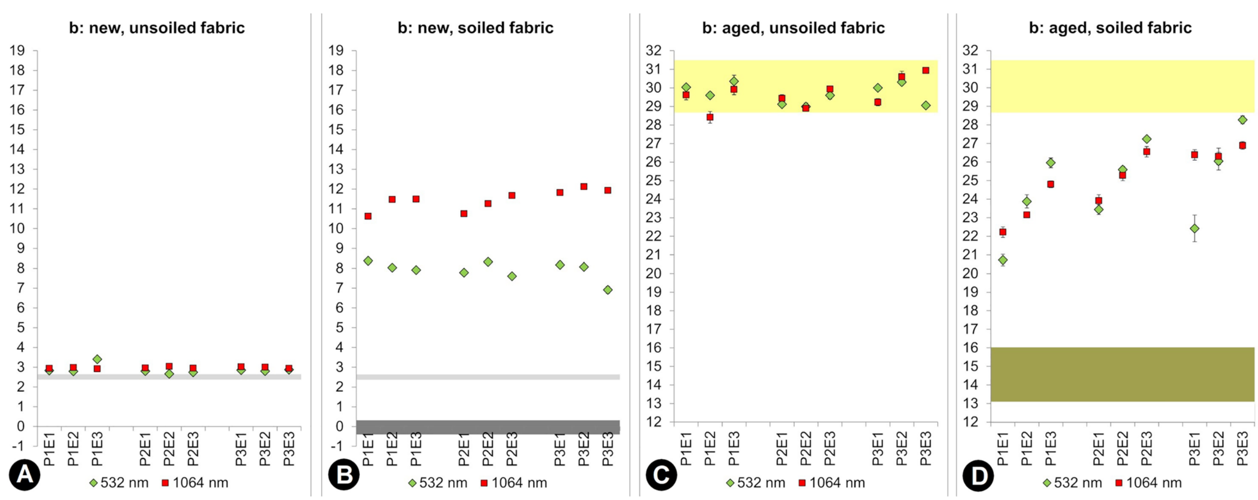

Fig. 6 b-values (rising number = yellower, falling number = bluer) after treatment for 532 nm and 1064 nm nanosecond lasers. **A**: new and unsoiled, **B**: new and soiled, **C**: aged and unsoiled, **D**: aged and soiled fabric. The dark grey and dark yellow horizontal bars represent the range of values obtained from untreated soiled fabrics, the light grey and yellow ones those for untreated unsoiled fabrics. X-axis labels see Fig. 1. Note divergences can be covered by dots if very small

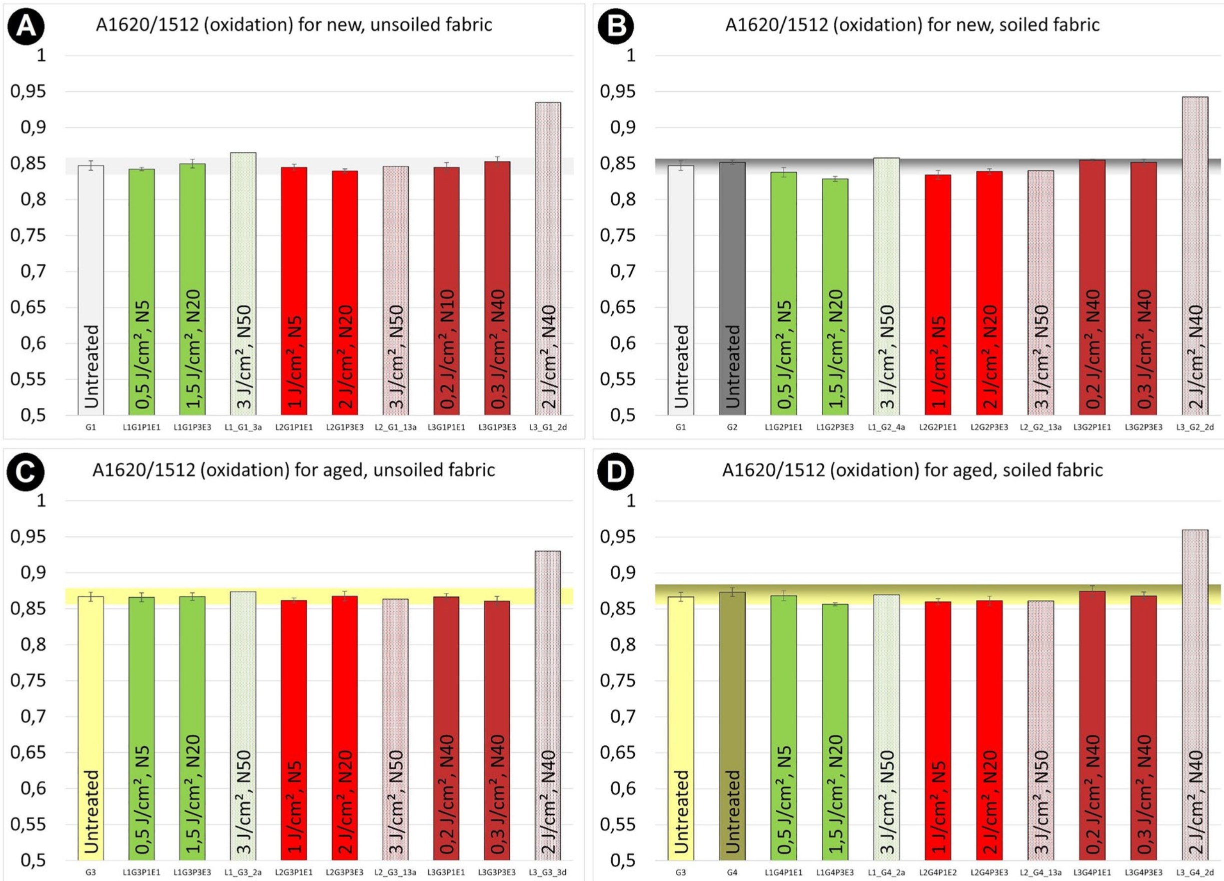

Fig. 7 Oxidation estimator results after treatment with 532 nm (green) and 1064 nm (bright red) nanosecond lasers and 800 nm (dark red) femtosecond laser. **A**: new and unsoiled, **B**: new and soiled, **C**: aged and unsoiled, **D**: aged and soiled fabric. The horizontal bars in the background represent the ranges of values for untreated fabric

(meaning a relative rise in crystallinity), it has a tendency to rise through laser treatment, which means that the crystallinity decreases.

To conclude, within the chosen ranges of parameters, the estimators' values did not exceed the span of untreated reference samples after treatment with the two nanosecond lasers, but 532 nm radiation seems to have a higher potential to cause change when using higher fluences. When looking at the results for the femtosecond laser it is obvious that raising the fluence to a similar degree as the nanosecond lasers, the results are dramatic. Both estimators rise far above the untreated reference range when using 2 J/cm^2, showing that the parameter window for this laser is generally a lot smaller than those for the other two lasers used.

Scanning electron microscopy

As silk is a natural material with many irregularities, it is easy to misinterpret those as laser-induced damage. But the high amount of samples allowed the identification of those four which actually are: Breakages of fibers in perpendicular orientation, fibrils that have peeled off with ends seemingly molten, loose fiber particles and tiny craterlike pits (Fig. 9A-D).

The first two observations (Fig. 9A-B) only occur on those samples treated with the 532 nm laser when using the highest chosen fluence for these experiments (1.5 J/cm^2) and fluences higher than the "safe" treatment ranges. The loose fiber particles (Fig. 9C) were caused only by the femtosecond laser and were found on all samples treated with it. They were interpreted as disintegrated silk fibers.

Only the tiny pits (Fig. 9D) could be found on samples of all laser treatments, but only on those that had been artificially soiled (Fig. 10). Figure 11 shows that those pits cannot be directly caused by the laser beam, as the scale of the pulses is much larger.

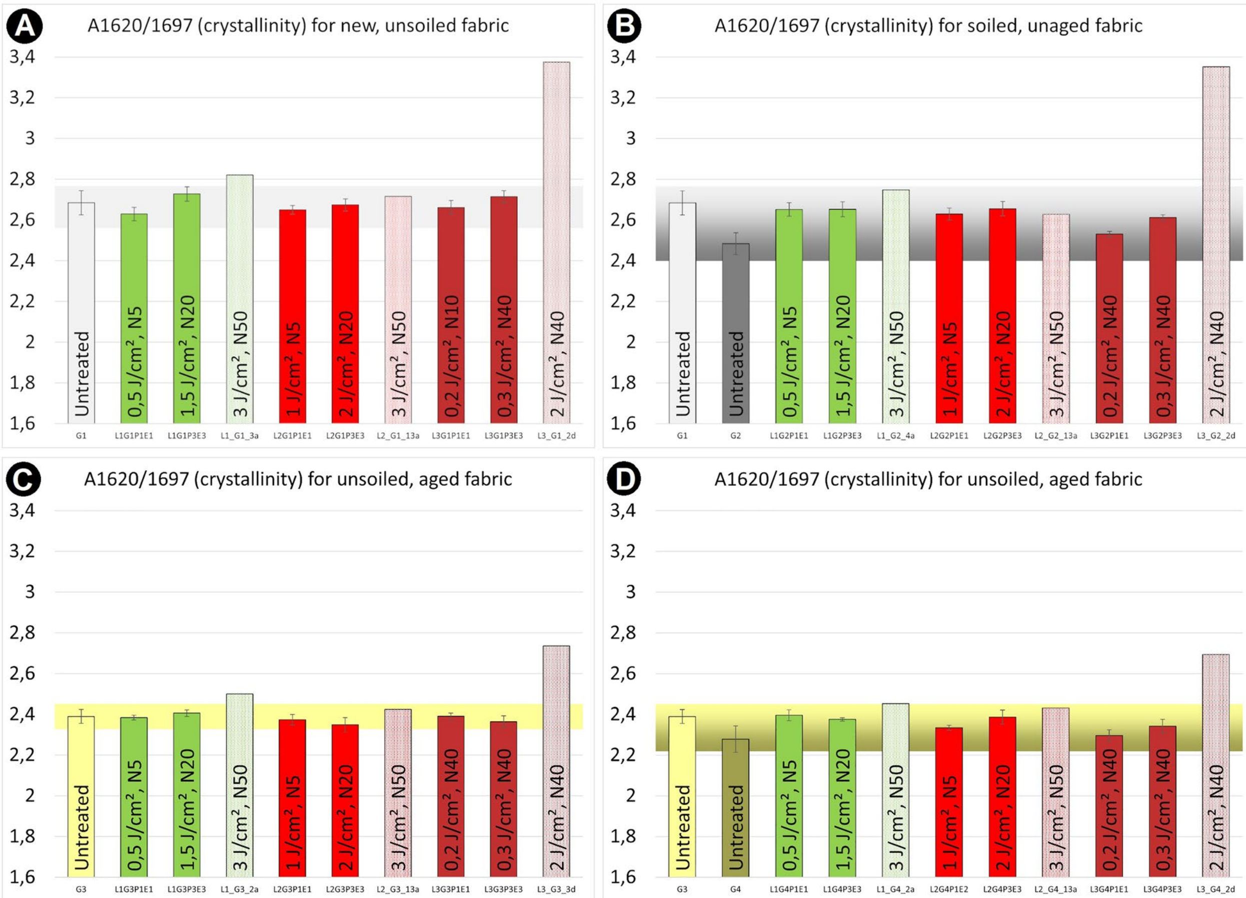

Fig. 8 Crystallinity estimator results after treatment with 532 nm (green) and 1064 nm (bright red) nanosecond lasers and 800 nm (dark red) femtosecond laser. **A**: new and unsoiled, **B**: new and soiled, **C**: aged and unsoiled, **D**: aged and soiled fabric. The horizontal bars in the background represent the ranges of values for untreated fabric

It was decided to investigate this phenomenon further by using a different SEM with higher resolution (Zeiss SIGMA VP). It was found that these tiny pits, often not visible on images taken by the other SEM (Zeiss EVO LS10), were actually on all previously soiled samples examined, also that this effect got stronger if higher fluences were used, and that the scale of the pits correlates with the scale of the carbon dust particles of the artificial soiling (Fig. 12). This suggests that locally restricted effects caused by the particles took place. Mosbacher et al. observed the formation of holes after laser cleaning polystyrene, silica and alumina particles from silicon surfaces. They proved that the holes formed underneath the particles when ablated with laser of different wavelengths and pulse durations and identified optical field enhancement, where the particles act as a form of "lens" to enhance the intensity or fluence in a restricted area, to cause these holes. They suggest that under real conditions, the irregularly shaped soiling particles could lead to varying degrees of enhancement, so that not every particle necessarily creates a hole [34]. The holes present on the silk are likely to be caused by this phenomenon. Von Lerber has also described craterlike holes of 200–1200 nm, and also found those only on previously soiled silk [15].

The examination of those samples cleaned with other techniques showed that vacuuming with the aid of a brush had merely spread the soiling around if not even adding soiling deposited in the brush's bristles, and the sponging in the detergent bath had left some perpendicular streaks or scratches on the fibers in places (Fig. 13).

The samples irradiated with extremely high parameters show what can happen if "safe" treatment ranges are passed. The surface of the fibers has seemingly molten, forming an entirely different surface morphology (Fig. 14). This emphasizes that experience in using this technique and preliminary tests to establish reasonable treatment parameters for every object is imperative.

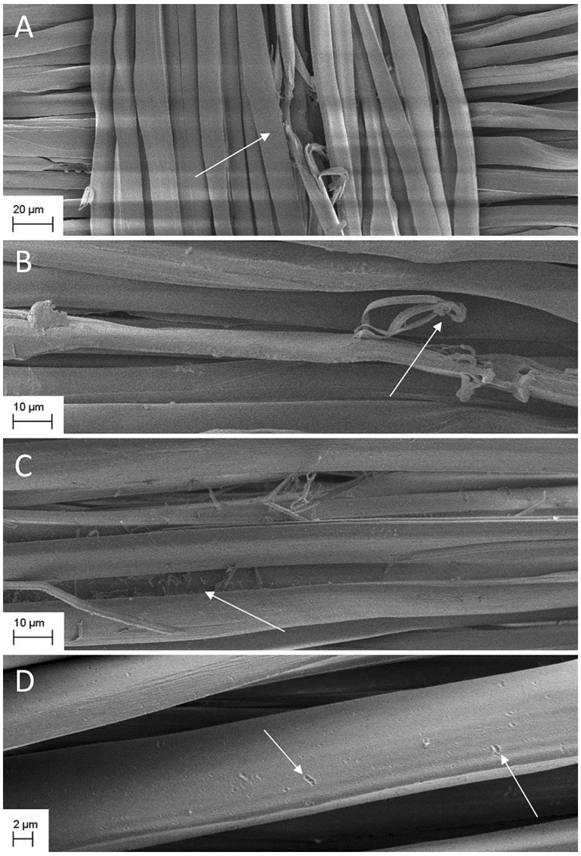

Fig. 9 Identified morphological changes after laser treatment. **A**: Breakages of fibers in perpendicular orientation, **B**: fibrils that have peeled off with ends seemingly molten, **C**: loose fiber particles, **D**: tiny craterlike pits

Further investigation of color changes

The color change of the previously soiled samples during laser treatment is an unwanted effect that should be discussed further. A thought that comes to mind is that the irradiation alters the silk photo- or thermochemically, so that it changes color. But photochemical yellowing is usually induced by UV-radiation [29], also the color change does not occur without soiling being present, so the heating up of soiling particles during laser treatment would most likely be the cause of thermal yellowing, similar to that seen on the thermally aged silk in this study. But thinking about the multitude of materials of varied organic and inorganic composition that all undergo very similar color change through laser cleaning [35, 36] it seems more likely that the color originates from the soiling rather than the substrate material itself. This is backed by the observation that a similarly yellow residue was found underneath treated samples when placed on a white ceramic surface (Fig. 15), possibly consisting of transformed soiling particles that travelled through the fabric.

This theory has been mentioned in other publications too [7]. In a paper by De Oliviera et al. [37] thermal decomposition of carbon particles is suspected to be the cause of the color change. Godet et al. [38] described spherical nanoparticles of the sizes 10–200 nm and a rough nano-layer found on the surface of plaster treated with a 1064 nm Nd:YAG laser, which they suspect to be the cause of the yellow color. They suggest, based on high similarities in composition, that these are transformed, so-called magnetospheres or ferrospheres (coal fly ashes), rich in iron, that were found on the untreated surface covered with a black crust. The carbon pigment used in this study also has some impurities, amongst which are approximately 20 ppm iron. Von Lerber also saw tiny spheres of 400–1100 nm that she thought to have formed from the surface of the silk fibers [15].

With these observations in mind the SEM images with higher resolution were examined again and spheres of a similar size as described were found on the surface of a

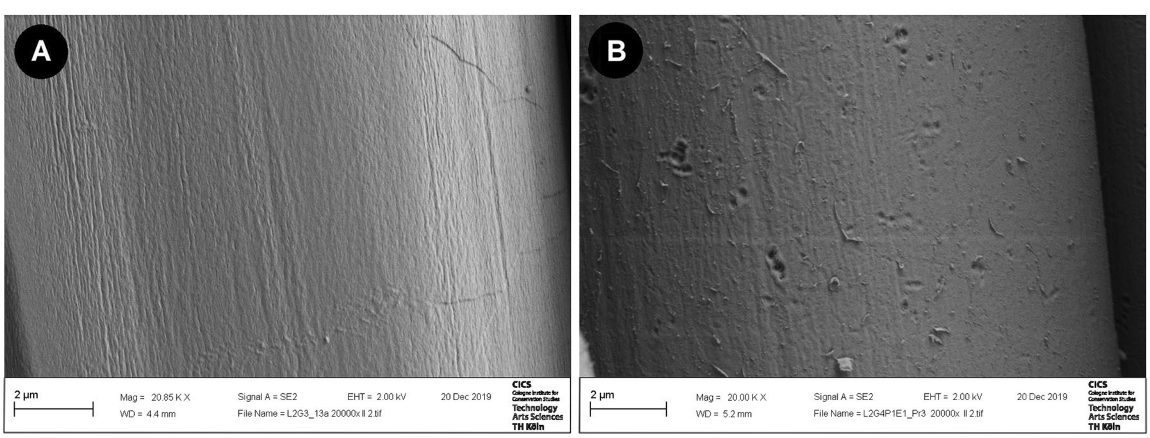

Fig. 10 **A** Unsoiled aged silk, treated with 50 pulses and 3 J/cm^2 with 1064 nm nanosecond laser. No damage visible. **B**: Soiled aged silk, treated with 5 pulses and 1 J/cm^2 with 1064 nm nanosecond laser. Tiny pits visible

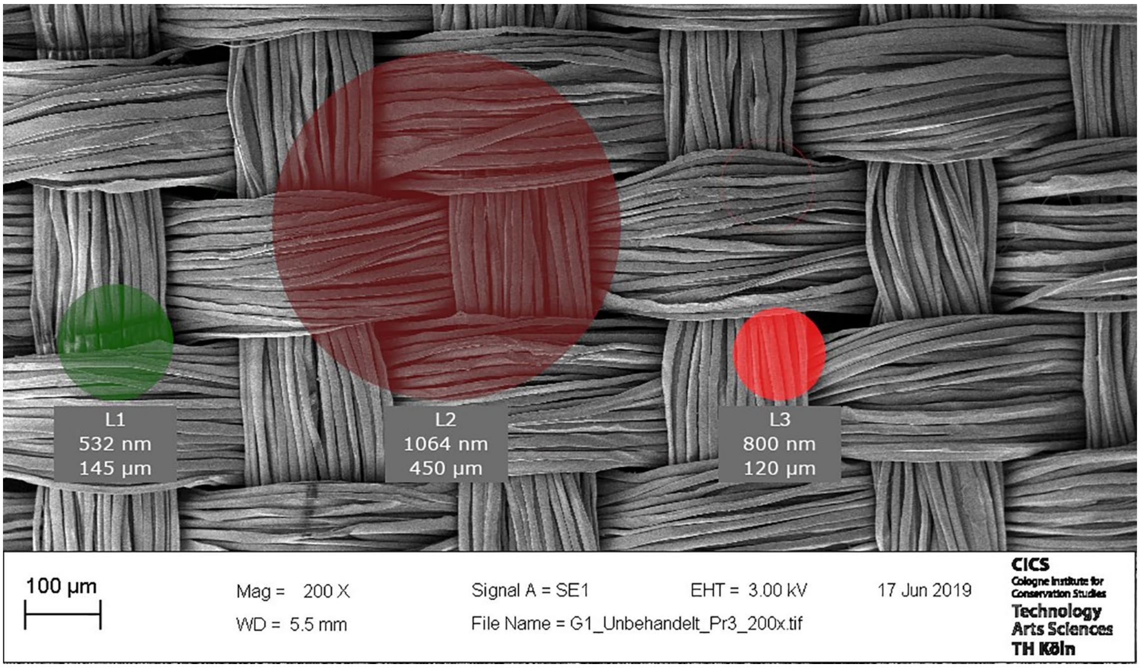

Fig. 11 Depiction of the actual spot diameters of the three different lasers used in this study, against the scale of the silk fibers in the background

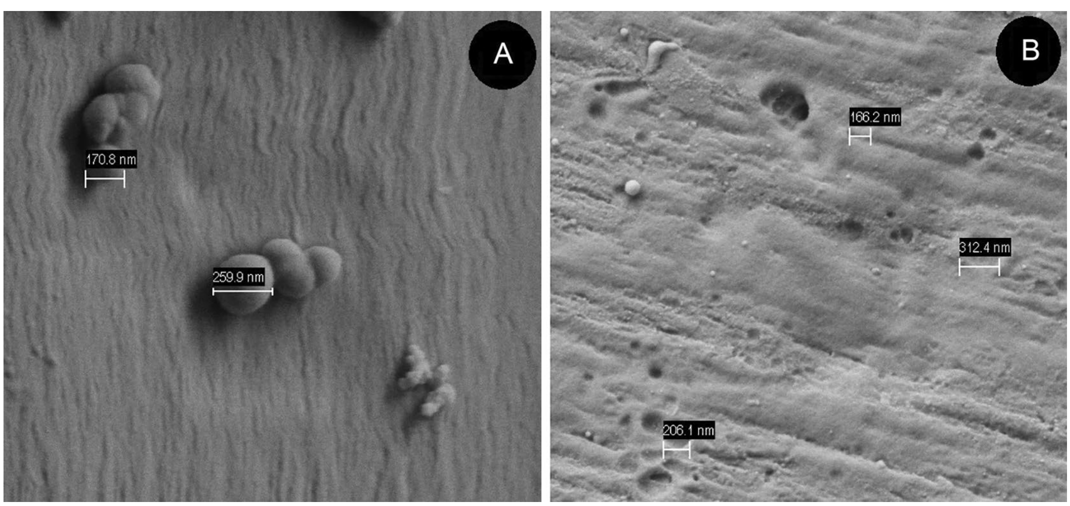

Fig. 12 Carbon dust particles (**A**) and tiny pits (**B**) showing similar size ranges

silk fiber (Fig. 16). That theory could potentially explain the smaller degree of color change when using shorter wavelengths. The induced radiation has a higher photon energy and could therefore be able to ablate the yellow products or lead to different transformations altogether. The decrease of color change when using higher fluences could be caused by a similar potential. Further studying this observation would benefit laser cleaning of cultural heritage immensely, as it would rule out chemical change of the objects' materials as the source of color change.

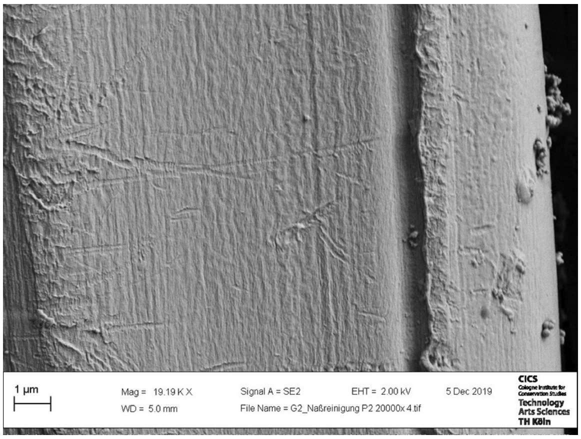

Fig. 13 Silk fiber after cleaning with sponge in detergent bath. Scratches possibly caused by agitation and soiling particles

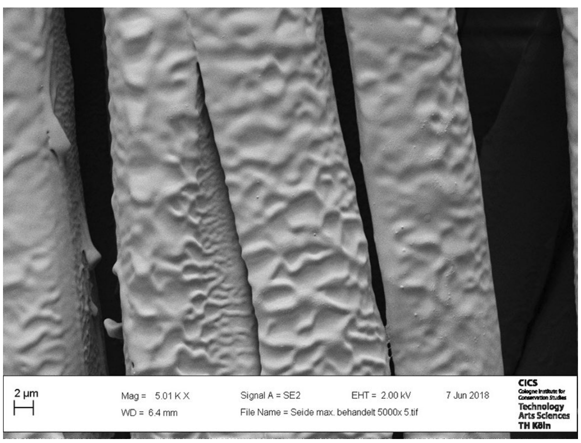

Fig. 14 Silk treated with fluences much higher than the determined "safe" ranges, c. 30 J/cm^2 with a 1064 nm Nd-YAG laser

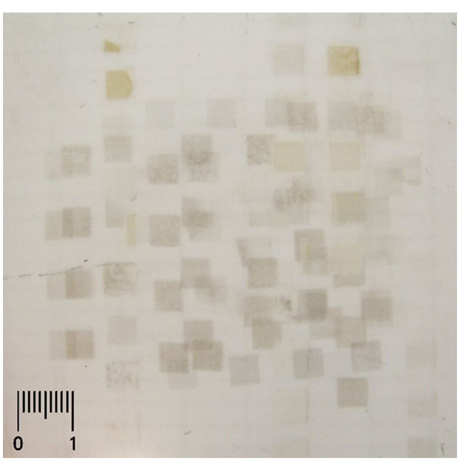

Fig. 15 Deposits of yellowish color visible on a ceramic tile placed under the silk fabrics for test-cleaning

Comparison treatments – cleaning success

The two common cleaning techniques carried out for comparison, dry vacuum cleaning with a brush and washing in a detergent bath with a sponge, were not able to achieve any optically convincing cleaning success as the carbon was heavily engrained into the fabric's structure. Comparing the macro- and microscopic cleaning results, it is obvious that laser cleaning has a much higher potential to clean these samples than usual techniques (Fig. 17). The samples were also investigated with SEM and compared to the laser treated samples (Fig. 18A-D), which confirmed this observation, even though the wet cleaning seems to have removed a lot of the bigger particles. This potential of laser cleaning textiles was also described for other fibers in literature [7].

Conclusion

First of all, it should be emphasized that cleaning the samples with laser radiation led to very convincing results in terms of the amount of soiling that was removed. The direct comparison to vacuum and wet cleaning showed that those techniques did not even come close to the improvement of lightness achieved by the lasers.

It was found that the femtosecond laser used in this study is unsuitable for the cleaning of silk. It could not achieve cleaning without causing damage, which suggests that it is not selective enough. Comparing 532 nm to 1064 nm wavelength nanosecond lasers, this study showed that when using 532 nm the cleaning results appear more convincing and the extent of color change is smaller, but it also bears a higher potential of damaging the silk.

It can be concluded that within determined "safe" parameter ranges of the two nanosecond lasers, 0.5–1.5 J/cm^2 and 5–20 pulses for the 532 nm, and 1–2 J/cm^2 and 5–20 pulses for the 1064 nm laser, no change to the samples except the color change and the tiny pits was detected in this study. The observation of the tiny pits showed that laser cleaning is not without potential damage. But this is the case for many other common treatments, as shown by the SEM images of wet cleaned samples. A real museum object would also not be entirely covered in carbon dust particles as these sample fabrics were, so the extent of the changes would expectedly be much lower.

Laser cleaning can offer a possibility of great cleaning results where everything else fails or is considered too dangerous and therefore cleaning would not be carried out at all. Accepting some changes to materials might be worth considering in specific cases. Those possible changes have to be put into perspective and weighed out against the benefits of cleaning, like raising

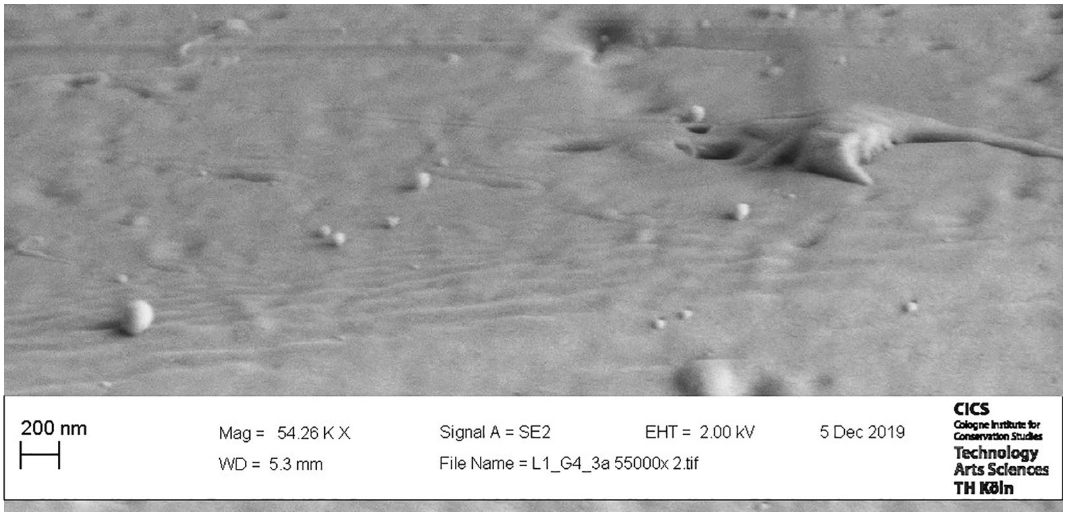

Fig. 16 Previously aged and soiled silk, cleaned with 532 nm wavelength radiation at 2.5 J/cm^2 and 50 pulses

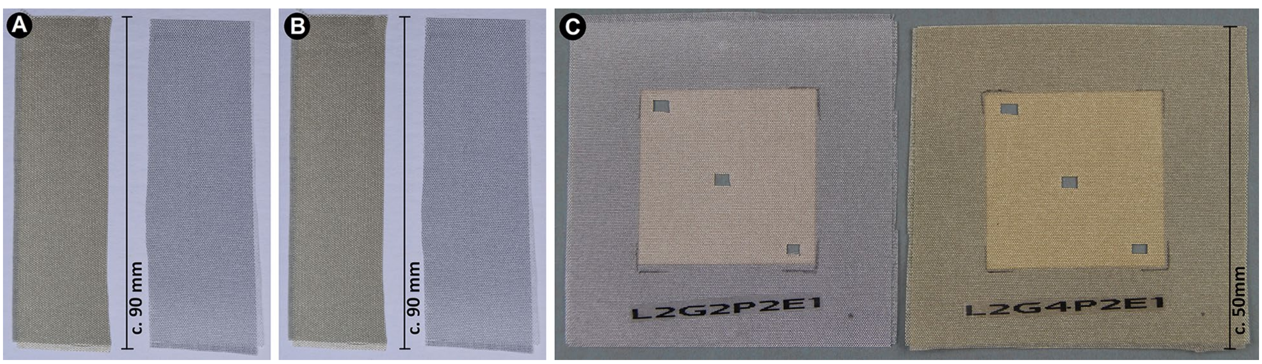

Fig. 17 Comparison between uncleaned samples (**A**), usual cleaning techniques, brush and vacuum first, then washed in a detergent bath with sponging (**B**), and laser cleaning with 1064 nm radiation, 10 Pulses, 1 J/cm^2 (**C**)

appreciation or even making an object beyond recognition accessible for display and research again.

Laser cleaning needs experience and testing. Also, the possibility of different effects with various soiling components or dyes and textile finishes present is a risk that needs to be considered when using the technique. But laser cleaning should be recognized as a further tool available to textile conservation.

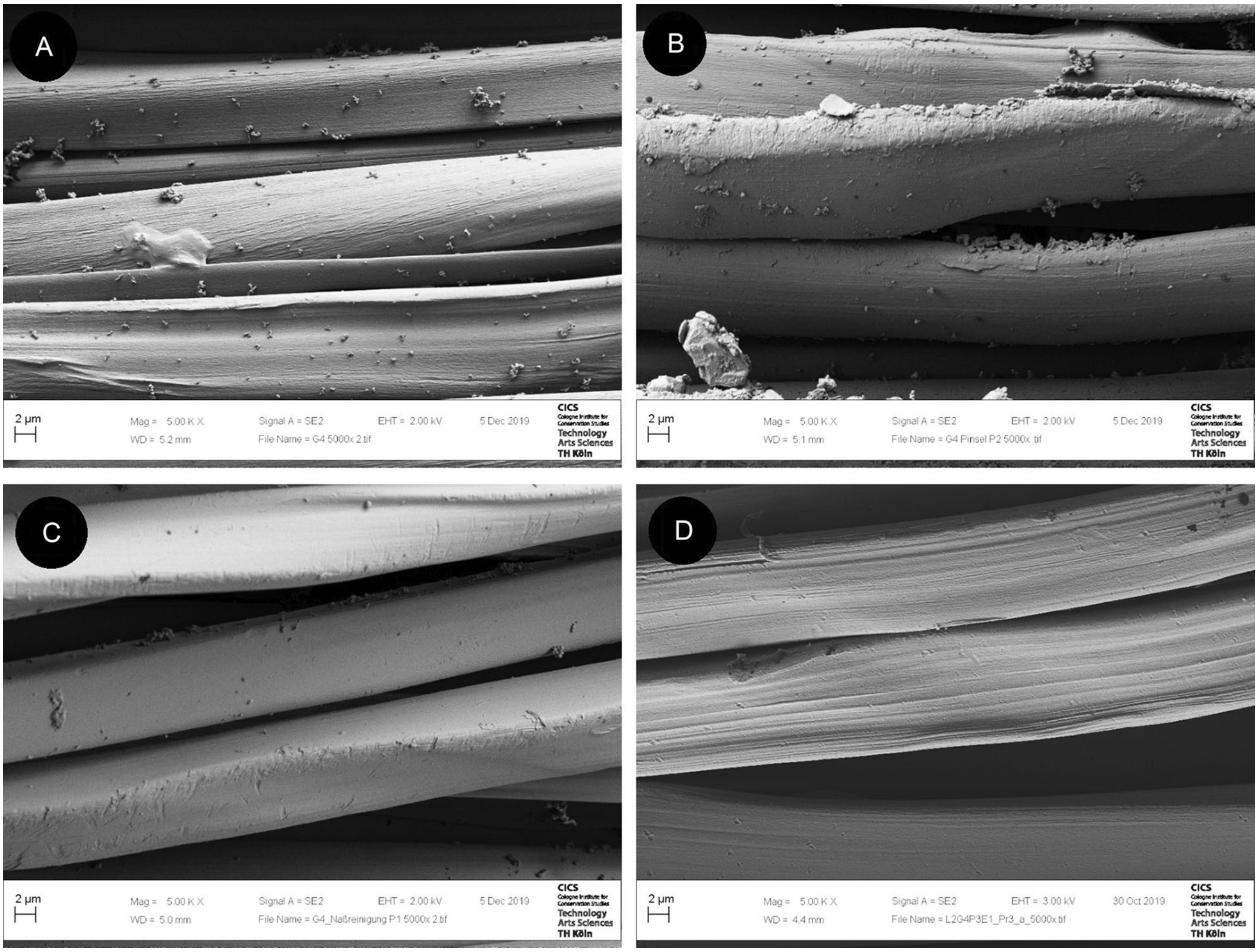

Fig. 18 **A**: Aged and soiled silk, untreated; **B**: Aged and soiled silk, treated with brush and vacuum cleaner; **C**: Aged and soiled silk, wet cleaned in detergent bath with sponge; **D**: aged and soiled silk, laser cleaned

Abbreviations

ATR	Attenuated total reflection
CIELab	Commission Internationale de l'Eclairage (International Commission on Illumination), L*a*b color space
FTIR	Fourier-transform infrared spectroscopy
SEM	Scanning electron microscopy

Acknowledgements
The authors would like to thank Dipl.-Ing. (FH) Simone Pentzien, Dipl.-Ing. (FH) Andrea Conradi for technical assistance with the lasers, Dr. Herbert Legall and Dr. Jörn Bonse for stimulating discussions, Dipl.-Rest. (FH) Ulrike Reichert and Jochen Schaal-Reichert for sharing their experience and knowledge in the field of laser cleaning of textiles, Dr. Stephanie Dietz for supporting the color measurements and the Maria und Otto Heynen Stiftung for the stipend supporting the master thesis this paper is based on.

Author contributions
NB, AS and JK jointly developed the concept of this research. All authors surveyed the literature and contributed to the research methodology. NB carried out the experimental work and analysis in Cologne (CICS) and Berlin (BAM). Academic supervision was provided by AS in Cologne and JK in Berlin. All authors read and approved the final manuscript.

Funding
Open Access funding enabled and organized by Projekt DEAL. This work was financially supported by the Maria und Otto Heynen Stiftung's stipend.

Availability of data and materials
All data generated or analyzed during this study are included in the master thesis this paper is based on, available at CICS—Cologne Institute of Conservation Sciences (in German language).

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare that they have no competing interests.

Received: 6 October 2023 Accepted: 18 January 2024
Published online: 31 January 2024

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