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Towards safe and effective femtosecond laser cleaning for the preservation of historic monuments

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Abstract

We explore femtosecond laser cleaning of materials used in the construction of historic monuments, such as stone and steel covered in typical contaminants caused by harsh environments that may be found in urban areas. We address the cleaning of these materials from a conservation perspective, taking as examples the preservation and cleaning of iconic structures such as the steel and the granite of the Sydney Harbour Bridge, Hawkesbury sandstone, a popular building material of a variety of monuments in Sydney (Australia), Makrana marble taken from the Soami Bagh Samadh temple of Agra in India, and also graffiti removal. We demonstrate that femtosecond laser pulses can clean a range of different contaminants such as biofilm, environmental soiling, rust, and spray paints, while preserving the integrity of the underlying substrates. Femtosecond laser cleaning is a fast and effective method and a safer alternative to lasers with longer pulse durations for the preservation of historic monuments.

Keywords Ultrashort pulse (femtosecond) laser · Laser cleaning · Steel · Granite · Marble · Sandstone · Biofilms · Dirt · Contaminant · Environmental soiling · Heritage

1 Introduction

1.1 The development of laser cleaning for heritage conservation

Laser cleaning is now a well-established method in conservation of heritage and has been widely applied since the 1980s in Europe and across the world following the initial works undertaken by Asmus et al. in 1972 [1], where the use of holography for the conservation of marble sculptures was investigated and led to the discovery that a pulsed laser could also be used to remove black encrustations from the deteriorating sculptures without altering the substrate. This new technique seemed very promising for conservation treatments at a time where heritage objects needed cleaning more frequently [2].

Since Asmus' works, many studies on laser cleaning have been conducted and explored the differences induced by changing the laser parameters such as the emitting wavelength, the laser energy, and the pulse duration on different materials and various contaminants including biological colonization (lichens, algae) [3–14], black sulphated gypsum crusts [15–24], dirt and environmental soiling [25], corrosion products [26–34], or graffiti [35–48]. Those are only a few examples of the vast literature available today, many of which can be found in the book series LACONA (Lasers in the Conservation of Artworks), and proceedings of the international conference of the same name. Researchers optimized the working parameters, evaluated the material removal processes through measurements and physical modelling, and generally disseminated the potential of laser cleaning to a wide audience of scientists and conservators [29].

Case studies of important masterpieces stimulated the interest of mass media and gave a consequent international resonance to this new approach. For instance, laser cleaning was applied on the unique and finely carved structures and

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statues of the Acropolis in Athens, Greece, where simultaneous infrared and ultraviolet pulses were applied to remove black encrustations resulting from many years of environmental pollution and increasing industrialization of Athens [49, 50]. It was also applied to the limestone western central portal of Notre Dame in Paris, covered in a thin grey layer [51], and other churches in France including the Chartres cathedral affected by black gypsum crusts [52].

Most of those studies used nanosecond (ns) pulse lasers [26, 29, 53, 54], which rely on thermal processes for the ejection of material and generate thermal-related damage and shockwaves propagating through the substrate [55]. Generally, thermal diffusion to the substrate needs to be avoided. The accumulated heat inside the underlying substrate can lead to the melting of the material, causing heat-related physical and/or chemical changes or damage in surface and bulk material properties, as stresses induced by surface melting and solidification can cause crack formation, exfoliation of flakes from the surface, and annealing/softening of thinner sections of the bulk material [56].

Melting was observed in numerous cases upon irradiation of heritage materials with nanosecond pulse lasers, mainly stone and metals. Moreover, Zinnecker et al. observed that this phase transformation induced cracking in steel, that propagated deep into the substrate from the processed surface, whereas no cracks were found in steel processed with femtosecond pulses [56]. Heat is transported out of the irradiated area for metals and diffuses on a larger area, whereas for organics, heat remains confined in the irradiated area, leading to high temperatures even for moderate fluences [54].

Rapid and intense heating with nanosecond pulses may lead to a pressure gradient that will generate thermoelastic waves propagating through the substrate [54]. These waves are responsible for compression and tensile stress of potentially high amplitude. If the pressure wave exceeds the tensile strength of the substrate, ejection of materials may occur. This photomechanical mechanism can take place without overheating the substrate and is popular in the medical field.

Chemical mechanisms can also be involved upon irradiation with pulse lasers emitting in the ultraviolet domain. Organic materials containing chromophores are particularly sensitive to this type of laser, which dissociate them into reactive fragments that may in turn react to form by-products [54]. With high laser fluence, a high percentage of those fragments can react in sublayers of the material. Additional species can be formed by the thermal or stress-induced breakage of chemical bonds. The accumulation of chemical modifications can result in changes in the physical and chemical properties of the irradiated materials.

These impacts on the fatigue life of components subject to cyclical stresses or under service tension loads are clearly of concern for engineering structures. Fissures, melting, increase of surface roughness, and capillary suction can result over time in the facilitation of further alteration. Thus, a method where the heating is minimised may be of considerable utility for materials of interest in heritage or in highly demanding industries such as aerospace.

Another important side effect was observed when using Nd:YAG lasers emitting in the infrared domain, particularly on stone. Chromatic alteration occurred, either yellowing of marble and limestones [57–63] or loss of colour of granite [37, 64, 65]. Yellowing can have different origins such as the pre-existence of yellowish organic matter soluble in water which can migrate to the surface and lead to a yellow coloration, the formation of residues following the interaction of an infrared laser with the contaminant to remove, a change in the oxidation state of iron compounds contained in the stones as iron strongly absorbs in the infrared domain [66], or a complex mix of scattering and absorption phenomena [63]. Generally, iron compounds strongly absorb in the infrared region, and blackening observed on marble and limestone after irradiation with Nd:YAG lasers emitting at 1064 nm was attributed to changes in their oxidation states as well [67, 68]. The color changes in granite were attributed to the removal of Zn-Fe-rich nanoparticles. Discolorations were also observed during the treatment of metallic objects, as described by Bertasa et al. [26].

Mitigation of these color effects was achieved by increasing the pulse duration and seemed to be promising to avoid yellowing although the results obtained were not entirely satisfactory and sometimes led also to a blackening [63]. Emitting simultaneously ultraviolet and infrared light was also investigated and was successful to reduce the chromatic alterations, as could be seen in 2016 for the cleaning of Pentelic marble with both 1064 nm and 355 nm [49]. It was also noted that pre-wetting the surfaces before applying the lasers usually resulted in higher cleaning efficiency and less intense side-effects [51].

1.2 An alternative approach for laser heritage cleaning

It was recognized for the last 20 + years that femtosecond (fs) laser pulses have the unique ability to remove surface layers without causing thermal damage. Being able to completely remove unwanted layers from steel and stone without melting, cracking, or inducing other damage to the surface will insure the preservation of the materials in the long term [69–71]. There was an obvious opportunity to apply this to high-value heritage items to remove contaminants and coatings without damaging the valuable historic materials.

A "cold ablation" process: the pulse duration is so short that there is not sufficient time for the electrons to transfer energy to the lattice of ions, which remain cold [72].

Therefore, the thermal damage is minimized [73]. This is a non-equilibrium state where the energized electrons eventually reach a threshold of energy allowing them to leave the solid during the pulse time [72]. They escape the solid and create a strong electric field due to the separation of charges with the parent ions. This field pulls the ions out if the electron energy is larger than the atomic binding energy of the ions in the lattice [72]. For this reason, the process can be said to be 'electrostatic' in nature.

The first attempts to use femtosecond laser pulses for conservation were performed, to our knowledge, with paintings and cleaning metal surfaces [55, 74, 75]. Aged varnish was successfully removed using 500 fs laser pulses. It was demonstrated that it was possible to adjust the removal depth by choosing the proper laser fluence and number of pulses. Another successful application was performed on bronze objects with various layers of patina and contaminants; by adjusting the laser parameters, both the outer layers of soot and organic materials and the inner layers of copper corrosion products were selectively removed using the same laser system [55].

Since then, femtosecond laser cleaning studies were made on several other historical materials. Paper contaminated with starch-based stick glue, graphite pencil powder and blue crayon stains, and aged artificially or naturally, was successfully cleaned using 550 fs pulses at 1030 nm [76]. The study showed that minimal side-effects were obtained with this type of laser and that its use is significant for the conservation of historic paper. Calf-skin-based parchments were cleaned from carbonaceous contaminants, without damaging the collagenous structure of the parchment using 120 fs pulses at 795 and 398 nm [77]. Kono et al. investigated the treatment of a gold thread on silk fibres covered in contaminant using 170 fs pulses at 790 nm [78]. The laser effectively removed the unwanted layers without altering the integrity of the gold or the fibre thread, as the technique combined with laser-induced breakdown spectroscopy allowed fine monitoring of the ablation process, and control of the removed layers in the order of tens of nanometers. Further work was undertaken on dirty linen fabrics using 120 fs at 795 nm [79]. The results showed no significant chemical modifications that could have negative consequences for the conservation of the fibres, and morphological damage occurred only for excessive laser fluences or low scanning speeds.

The application of the technique on glasses and stones was also investigated. Colorless French glass used for restoration and covered in permanent ink was treated using 228 fs pulses at 1030 nm [80]. The study showed that safe and effective cleaning was possible without deterioration of the surface of the glass. Biofilm was successfully removed from Galician granite using 120 and 130 fs at 790 and 395 nm, respectively [81]. Moreover, granite minerals were preserved better than with a longer pulse duration, highlighting the potential of the technique for the preservation of heat-sensitive materials. Additional work was undertaken in recent years in this direction for the removal of spray paint from granite surfaces [82].

Bertasa et al. presented an extensive review of the different studies published in the literature and investigated the cleaning of metal artefacts with different laser systems, including a few instances of femtosecond pulse lasers [26]. Femtosecond pulse laser cleaning of corroded archaeological copper alloys was studied by Korenberg et al. using an excimer laser emitting at 248 nm, but the laser fluence used (0.35 J cm^{-2}) was not sufficient to remove the corrosion products [83]. Compared to other conventional cleaning systems, an 800 nm laser with 100 fs pulse duration was found to be the best option to remove corrosion layers from an iron belt pad with gilded silver foil inlay from the ten–thirteenth century, with minimal conversion of goethite into magnetite, and no melting [30]. However, the low repetition rate (10 Hz) made the process highly time-consuming. Taarnskov et al. explored the laser cleaning of tarnished silver on silk textiles using different laser systems (UV to IR, 8 ns to 500 fs) [84]. Their study showed that the femtosecond pulse laser gave the best results in terms of cleaning without inducing discoloration, but induced changes in tensile strength and extension potential of the silk fibres. Corroded outdoor sculptures and copper plates were cleaned using a femtosecond laser emitting 150 fs at 780 nm [85]. This study showed that this type of laser allowed a high selectivity of the cleaning by tuning the fluence, and that all organics, soot, and corrosion layers could be removed successfully without inducing damage or discoloration to the underlying metal substrates.

All these studies proved that the femtosecond pulse laser cleaning method is effective to remove contaminants, unwanted surface layers, and coatings, maintaining the underlying substrate integrity because of its ability to achieve strong selectivity, accurate control, and high precision, with minimal side effects, providing that the irradiation parameters are selected carefully. Many working heritage objects require constant cleaning. Developing a fast and effective method without detrimental effects on the underlying substrate to maintain assets, monuments, sculptures, buildings, and infrastructures whilst retaining their heritage and visual values is of huge importance. With the recent development of high-energy ultrashort pulse lasers, it is now possible to extend the research on femtosecond laser cleaning of heritage items to something applicable on a practical scale, whilst preserving the original properties of the materials.

In this paper, we show several case studies of femtosecond pulse laser cleaning to remove a wide range of surface contaminants from various building materials such as marble, granite, sandstone, and steel. In each case, the cleaning treatment is evaluated using multiple analytical methods. The term 'ultrashort laser pulse' (USP) is used in relation to laser pulses that are shorter than the electron–ion energy equilibration time which, depending on the material properties, typically is in the range between 2 and 5 ps [72].

The first case study focuses on the USP laser cleaning of the Sydney Harbour Bridge's steel arch and stone pylons. The stone is affected by various contaminants such as rust, dirt and other iron-rich deposits, biofilms, and carbonate deposits, while the steel is affected by corrosion under flaking paint. The second case study focuses on the USP laser cleaning of Makrana marble taken from the Soami Bagh Samadh temple in Agra (India), covered in dirt. A third case study explores the use of USP laser cleaning on Hawkesbury sandstone. Finally, a fourth case study focuses on the removal of spray paint from granite.

2 Experimental setup and methods

2.1 Femtosecond pulse laser system

The details of the laser setup and experimental parameters have been described previously in [82]. Briefly, femtosecond laser irradiations were done with a Carbide CB3-40W laser (Light Conversion, Lithuania), producing 275 fs pulses at its fundamental wavelength (1029 nm), with a repetition rate of 100 kHz and a maximum pulse energy of 0.4 mJ. The beam scanned the surface using a 10-facet polygon mirror (Precision Laser Scanning Inc., USA) (y-direction) and a galvanometer scanner (Cambridge Technology Inc., USA) (x-direction). This system can reach beam speeds up to 800 m s^{-1} across a maximum scan area of 280 mm × 280 mm at 52% duty cycle per polygon scan line, high enough to operate in a single shot per spot regime, with the scanner running at 1000 rpm. The beam was focused on the surface of the sample with a quasi-telecentric f-Theta scanning lens of 540 mm working distance (S4LFT1420/449, Sill Optics GmbH, Germany). The experiments were carried out on dry surfaces, in ambient laboratory conditions with a temperature of 23 °C ± 2 °C and an uncontrolled relative humidity typically in the 20–40% range.

Scanning strategy: Femtosecond pulses can remove less than 1 µm with each pulse. It is therefore possible to remove very thin layers of material and achieve a high control of the ablation depth. As a consequence, to remove thick layers of dirt or other contaminants, it is necessary to increase the number of pulses and therefore the repetition rate (in the range of kHz or higher).

The single-pulse ablation regime, where each pulse can be freely triggered, was selected to achieve full spatial separation of the laser spots beyond the characteristic thermal wave propagation length at full laser power output (combination of repetition rate and scanning) allowing to minimise the thermal load on the substrate. The beam step was fixed at 5 µm, giving a shot-to-shot spacing of 894 µm.

Beam shaping optimisation: The intensity distribution and the shape of the beam will significantly affect the geometry and topography of the ablated surface. Beam shapers are diffractive optical elements (DOE) and are made for laser applications that require constant intensity over some area. They transform a Gaussian incident laser beam into a uniform-intensity spot of either round, rectangular, square, line, or other custom well-defined shapes, and were used the first time with a femtosecond laser by Momma et al. [86]. For reshaping the intensity distribution to limit the peak fluence to below the ablation threshold of the underlying substrate and increase the ablation rate, the use of a "flat-top" spatially square-shaped beam is preferable for more homogeneous irradiation of the laser-processed surface. Such a transformed laser beam has then an intensity profile with a flat region at the centre and a 'transfer region' at the beam's edges where the energy decays to zero rapidly. This profile contrasts with the Gaussian beam with high peak intensity in the centre of the beam. The raw Gaussian profile of the laser beam was transformed into a square "flat-top" profile using a square beam homogenizer (ST-220-J-Y-A, Holo Or), with final beam dimensions of 140 µm × 167 µm. This beam profile was selected as it presents a constant intensity through the cross-section of the beam and allows the treatment of rougher samples.

Determination of the damage threshold: Before undertaking any cleaning procedure on a material, it is important to evaluate its damage threshold. The removal of materials occurs once a threshold of laser fluence, called fluence threshold or ablation threshold, is reached. Therefore, the determination of this value is of paramount importance in the preparation of any applications of laser for conservation, such as surface texturization or surface cleaning. To do so, series of grooves have been made in the different materials increasing progressively the laser fluence. The ablation thresholds of each material are presented in Table 1. For steel it was determined at 0.25 J cm^{-2} [56, 87, 88]. For the stones, the ablation threshold of Moruya granite was found to be at 1.1 J cm^{-2}, above which morphological damage started on biotite grains [89], for sandstone at 0.40 J cm^{-2}, above which discoloration started, and for marble at 1.30 J cm^{-2}. Ideally,

Table 1 Damage (ablation) threshold of material upon irradiation at 1029 nm and 275 fs

Material	Ablation threshold (in J cm^{-2})
Steel	0.25 [56, 87, 88]
Granite	1.10 [89]
Sandstone	0.40
Marble	1.30

the cleaning process should be undertaken while keeping the laser fluence below the damage threshold of the underlying substrate, which will avoid the removal of original materials and potential undesirable side effects.

2.2 Characterisation methods

Various characterization methods are available and commonly used to study the effects of the laser treatment on heritage surface such as scanning electron microscopy (SEM) with or without energy dispersive X-ray spectroscopy (EDX), Fourier Transform Infrared spectroscopy (FTIR), X-ray diffraction (XRD), optical microscopy, and Laser-Induced Breakdown Spectroscopy (LIBS), to cite a few [66].

Here, the method developed is as follows. To evaluate the effect of the laser on the material and any potential damage, the surfaces are inspected with optical and scanning electron microscopies, visually assessing if any change occurred, down to very fine scale, which may be useful for the detection of micro-cracks or microscopic damage. Non-destructive vibrational spectroscopy is performed with Raman spectroscopy in the case of stones, to check the integrity of the crystal structures and any damage such as melting, amorphization or induced stresses. This technique is also helpful to identify minerals constituting the rocks. The surface texture, depth of ablation and surface roughness are evaluated with optical profilometry in vertical scanning interferometry mode.

Optical microscopy and SEM are also used to study the effectiveness of the cleaning treatment, and to locate any residues left. Organic residues are detected using FTIR in combination with EDX, and Raman spectroscopy detects pigments residues in the case of graffiti removal. Colorimetry is performed before and after the treatment to assess if the laser induced any colour changes that may not be noticeable to the naked eye and is also an indicator of the treatment's outcome when expressed in the CIELab color space in terms of distance between reference points and cleaned points (ΔE).

3 Case study 1: cleaning the Sydney Harbour Bridge

3.1 An Australian heritage icon

The Sydney Harbour Bridge is one of the most important built heritage icons of Australia. It is a steel arch bridge located in Sydney, New South Wales (Australia), and a major crossing of Sydney Harbour, from Dawes Point in The Rocks area to Milsons Point in the lower Northern Shore area. The Bridge was a turning point in the development of Sydney and its modernisation, a symbol of modernity and progress. The Sydney Harbour Bridge has been in continuous use since 1932 and represents a vital part of the city's transport infrastructure, as a multimodal bridge with an initial daily traffic of 6000 cars that has increased to more than 150,000 today [90]. The Bridge is made of a steel arch flanked by two stone pylons made of reinforced concrete faced with granite. Eight smaller pylons support the approach spans on each side of the shores. Those pylons are also made of concrete faced with granite. The arch is 503 m long with its summit at 134 m above mean sea level and allows 49 m clearance for marine traffic under the deck. The materials are still original but are showing signs of alteration after nearly a hundred years of exposition to the coastal and urban environment of Sydney. The weathering of the materials is therefore within natural expectations.

3.2 Materials

3.2.1 The steel arch: Composition, current condition, and maintenance

The steel of the arch is mainly silicon steel and was imported from England, while the carbon steel used for the approaches, rivets and deck was supplied locally [91]. Carbon steel (or mild steel) contains the minimum amount of carbon possible (approximately 0.05–0.25%) [92], making it malleable and ductile. Carbon is used in steelmaking as a hardening agent where the greater the level of carbon, the harder and stronger the steel is through heat treatment. The more carbon, the less ductile, but the lower the melting point. This type of steel is the most common form of steel due to its low price and huge versatility. Silicon steel has a higher concentration of carbon (0.32–0.42%) [92], making it harder, stronger and tougher than regular mild steel. The use of silicon steel for the Bridge was rather unique.

The steel arch is protected with a primer and several layers of epoxy coating. The degradation of the paint and corrosion of the steel at certain locations is illustrated in Fig. 1 and is accelerated by the harsh coastal environment of the Bridge with high humidity and high amounts of saltwater spray.

Over the years, abrasive blasting has been performed over large areas of the Bridge [93]. This process is complex and challenging, especially with respect to current safety standards for workers, and environmental regulations to deal with dust and large amounts of hazardous waste at heights or in confined spaces.

3.2.2 The stone: composition, current condition, and maintenance strategy

For the cladding of the pylons, granite was sourced from Moruya, a coastal town of New South Wales, 300 km south

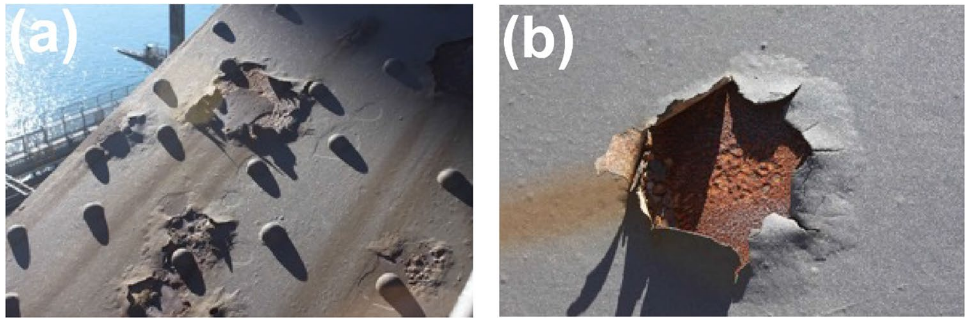

Fig. 1 Photography of an arch of the Sydney Harbour Bridge with **a** paint flaking off the surface of steel and **b** corrosion visible under the paint

of Sydney. Moruya granite is a granodiorite, mainly made of plagioclase, quartz occurring as smaller grains, biotite mica and hornblende found as small aggregates with potassium-feldspar, and traces of opaques, titanite, and apatite, as summarized in [94].

The texture is hypidiomorphic granular with grains of average size 5–6 mm [95]. Xenoliths occur in the stone (rock fragments included in a larger body of rock) and can be of two origins: sedimentary or igneous, the former consisting mainly of plagioclase, biotite and quartz, and the former consisting of feldspars, biotite and hornblende [96].

Various contaminants are visible on the stone of the pylons today, mainly under deck level, and are described more in detail in [97]. Two types of biological colonization can be observed in different locations under the deck: black and green biofilms. The huge towers are also affected by rust stains, forming superficial dripping patterns, and covering the entirety of the vertical surface of the tower below the railway. Other rust stains can be observed around other steel features embedded in the granite all over the Bridge (e.g., nails in Fig. 2b).

The smaller piers supporting the approaches are covered in a mixture of dirt and iron oxides (brown/orange), as well as carbonate deposits (white). Carbonate stains are particularly visible around the joints between the granite slabs.

Contaminated granite samples were collected from the Sydney Harbour Bridge directly. Sampling the pylons of the Bridge was done on small pylons under the deck, which were highly covered in dirt or biofilm, and had some flaking, in such a way that the visual impact is minimal and not deleterious to the heritage values of the Bridge.

3.3 Results

3.3.1 Removing corrosion from steel

Femtosecond pulse laser cleaning was undertaken on different parts of a corroded metallic structure shown in Fig. 3a. Various fluences and number of laser scans were investigated to determine the best set of parameters necessary to obtain a total cleaning of the selected area. Figure 3b presents cleaned bands at 1.0, 2.0 and 3.0 J·cm^{-2} (left to right)

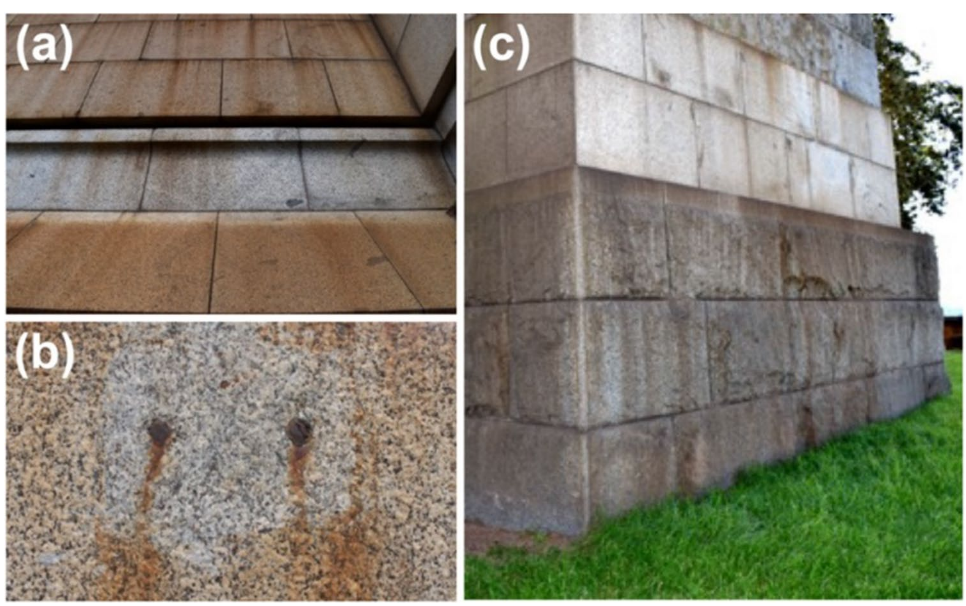

Fig. 2 **a** View of the side of the abutment tower, Western face, directly under the railway—rust stains, **b** close up on rusty stain formed around nails. **c** Environmental soiling and rust on the base of a Sydney Harbour Bridge pylon supporting the approach spans, facing South

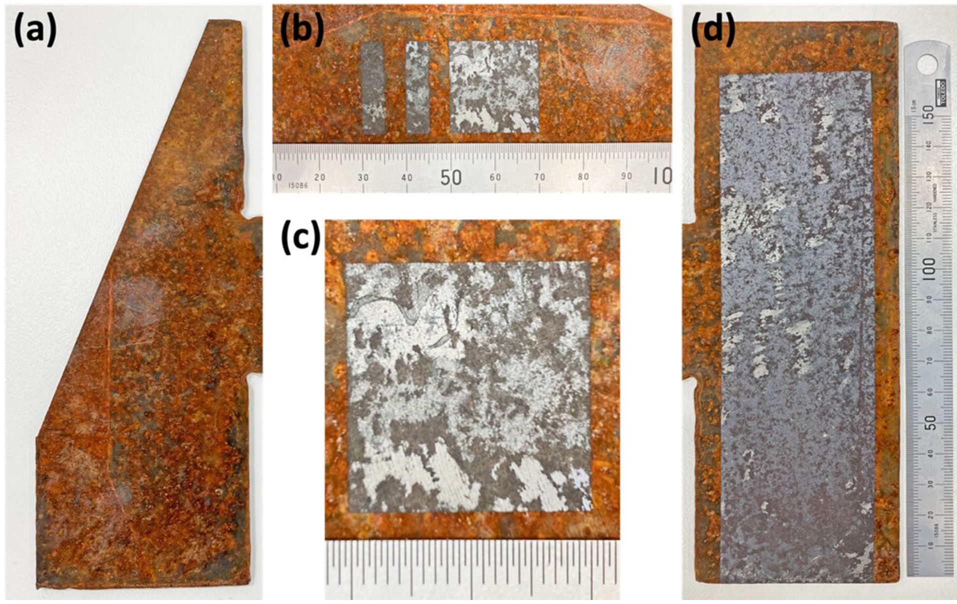

Fig. 3 Femtosecond pulse laser cleaning of corrosion on steel. **a** Steel covered by corrosion. **b** Cleaning of a small area with five laser scans and varying the fluence from 1.0 to 3.0 J·cm^{-2} (left to right) with **c** magnification of the largest square. **d** Cleaning of a large area at 2.0 J·cm^{-2} in a single laser scan

each with 5 laser scans. At 1.0 J·cm^{-2}, more than one laser scan was necessary as some orange dots were still left on the surface. Removing the entire crust on the steel surface was then possible while minimising the damage to the steel by applying a low laser fluence, as presented in Fig. 3c, d.

Characterisation of the steel surface was made after laser cleaning to search for any damage caused by the laser pulses. SEM proved that the steel surface was preserved, and no presence of cracks nor melting was observed at any applied fluence, as previously observed in [56].

3.3.2 Cleaning the granite

Samples cleaned with femtosecond pulses are presented in Fig. 4. A laser fluence of 1.0 J·cm^{-2} and five laser scans were enough to completely remove all the dirt and dust from the stone surface, as presented in Fig. 4b, leaving all the minerals of the stones undamaged and visible again. The total removal of the biofilm was also achieved with five laser scans and a laser fluence of 1.0 J·cm^{-2}, as seen in Fig. 4c, d. No biofilm was left on the surface after laser cleaning, even at cracks and grain boundaries, and the rough surface was treated as well as the flat surface without laser focusing problems. It is worth noting here that biofilm removal in other pulse duration regimes (e.g., nanosecond) is often influenced by the selected wavelength, or the type of micro-organism encountered [7]. Indeed, UV lasers were found to be generally more efficient to remove micro-organisms with nanosecond pulse lasers [53]. Here, the cleaning effectiveness was not hindered by the organic nature of the film.

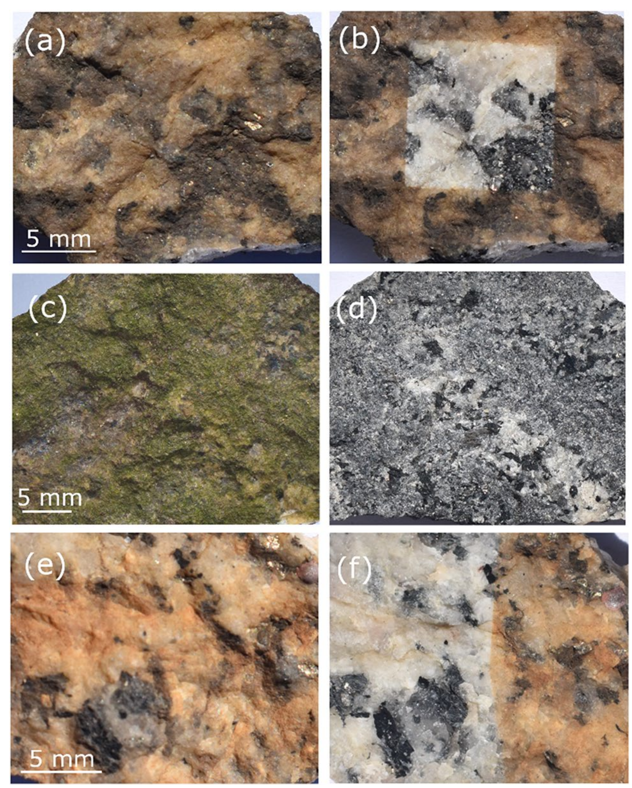

Fig. 4 Femtosecond laser cleaning of granite: **a** granite sample covered by environmental soiling, **b** after femtosecond laser cleaning at 1.0 J·cm^{-2}, **c** Granite covered by green biological colonisation, **d** cleaned area after 5 laser scans at 1.0 J·cm^{-2}; **e** Granite covered by a rust stain layer; **f** cleaned area after five scans at a fluence of 1.0 J·cm^{-2}

Laser cleaning was then applied to remove strongly adhered rust. Figure 4e shows a granite sample covered by rust, and Fig. 4f the same granite sample where five laser scans have been done at 1.0 J·cm^{-2} on half of the surface. One scan was enough to remove the majority of the rust layer, but a thin layer of contaminant was left on the surface, so four more scans were applied and significantly improved the treatment, but some residues are still visible mainly at cracks and grain boundaries in the middle area where there is an importance crevice. More laser scans would easily remove the last residues of rust.

The FTIR confirmed the success of the femtosecond laser cleaning for the dirt and biofilm as the characteristic peaks of organic matter and sulphates were not visible, indicating that no residues were left on the surface. Colorimetry revealed that the color of granite was successfully retrieved as well. Figure 5 shows the energy-dispersive X-ray spectra taken on the dirt layer and on the cleaned surface of the granite.

The spectrum of dirt is characterized by the presence of phosphorus, sulfur, iron (from rust), chlorine (from sea spray), and zinc. It can be seen on the spectrum taken on the clean surface that these elements have significantly decreased or disappeared which indicates a successful cleaning treatment.

To gain a deeper understanding of the effectiveness of femtosecond pulse lasers over time, it would be interesting to study the redeposition of the contaminants in Sydney (rate, extent) on the cleaned samples.

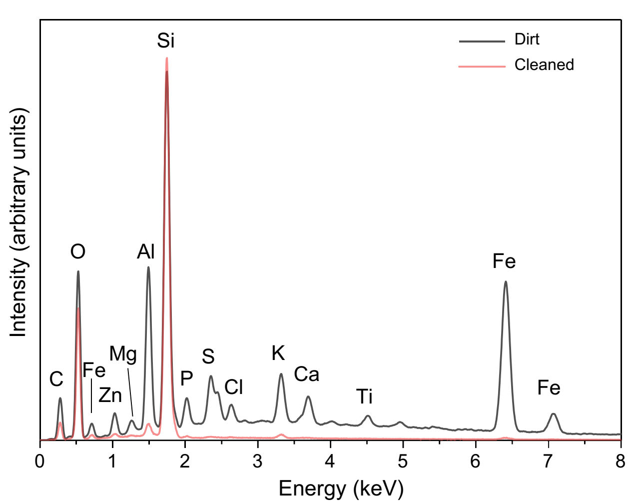

Fig. 5 EDS spectra of the cleaning treatment before and after, on dirt. (Hitachi TM4000II desktop SEM in BSE mode, 15 keV, 15 mm working distance, non-coated sample)

4 Case study 2: cleaning Makrana marble

The second case study focused on the cleaning of the marble used in the construction of the Soami Bagh Samadh temple, located in the outskirts of the city in DayalBagh, Agra (India). This temple is very similar to the Taj Mahal (Agra, India) for its complex and intricate lattice of stonework and was commissioned in 1908. The marble is of various colors; white, pink, green, yellow, and other various colors of distinct shades obtained from Makrana and different parts of India such as Ambaji, Vadodra, Jaislamer, Gwalior and Nowshera (Pakistan). The marble was cut in the most unique way, and the intricate design showcases the exceptional craftsmen skills with mesmerizing carvings (an example is given in Fig. 5a).

The Makrana marble is a white metamorphic stone mainly composed of recrystallized calcium carbonate minerals with granoblastic texture [98]. Small amounts of impurities can be found**, s**uch as silicon dioxide (quartz grains or silicate), iron oxide such as hematite, or limonite, manganese oxide, alumina, or pyrite [99].

Makrana marble is popular for sculpture and building decor and is most famously used in the construction of the Taj Mahal in Agra (India) and the Victoria Memorial in Kolkata (India). It is mined in the town of Makrana in Rajasthan, India, and listed as a Global Heritage Stone Resource by International Union of Geological Sciences.

Figure 6a presents parts of sculptures from Soami Bagh Samadh covered by a thick layer of dirt and dust. USP laser cleaning was done on a dirty area presented on Fig. 6b, c and revealed to be effective at the low fluence of 1.0 J·cm^{-2}, below the damage threshold of the stone.

The laser treatment was successful, with removal of the dirt layer without damaging the underlaying substrate, allowing to retrieve the shiny white color of the stone.

5 Case study 3: the challenge of cleaning Hawkesbury sandstone

Sydney sandstone is the common name for Sydney Basin Hawkesbury Sandstone, a variety of sandstone which is historically known as “yellowblock”, or “yellow gold”, and is named after the Hawkesbury River, north of Sydney, where it is particularly common. Sydney sandstone was deposited in the Triassic Period probably in a freshwater delta and is the caprock that controls the erosion and scarp retreat of the Illawarra escarpment. Well known for its durable quality, it was a popular building material from the late 1790s to the 1890s, particularly for public buildings, as it gave cities a distinctive appearance. The most notable buildings

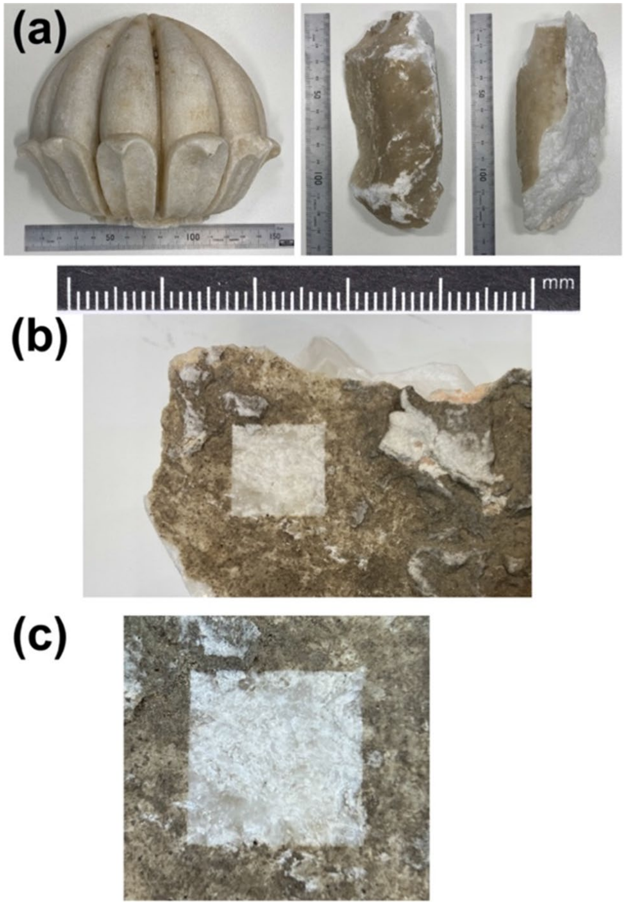

Fig. 6 **a** Photograph of a marble sculptures from Soami Bagh Samadh covered by soiling. **b** Femtosecond pulse laser cleaning of marble covered by environmental soiling at 1.0 J·cm^{-2} and **c** magnification of the cleaned area showing undamaged minerals

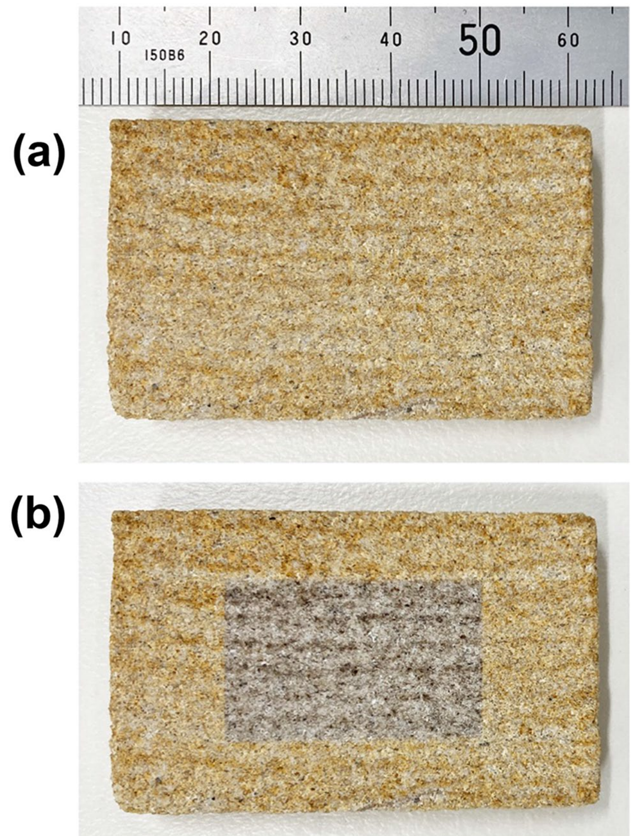

Fig. 7 **a** Femtosecond laser cleaning of Hawkesbury sandstone: **a** sample before laser cleaning, **b** after femtosecond laser cleaning at 0.9 J·cm^{-2} showing the discoloration that has occurred on the central targeted area

in Sydney are the central railway station, the Museum of Contemporary Art, the Art Gallery of New South Wales, the Australian Museum, and Queen Victoria building.

Sandstones, including Sydney sandstone, are fragile stones with often a high porosity and low hardness, which makes conventional cleaning methods often unsuitable as damage occurs quickly, which poses problems for long-term conservation. Therefore, finding a gentler method is highly desirable from a conservation and asset maintenance point of view. An example is the Museum of Contemporary Art of Sydney, covered in biofilm. The stone was previously cleaned with low- and high-pressure water washing which is known to be aggressive for this type of stone. Biocides were therefore trialled and showed very promising results [100]. However, exposure to toxic substances can be harmful to the users and the environment, and also can affect the stone.

Sydney sandstone usually contains a high proportion of clay in the binding matrix, and composition varies depending on the quarries. Tiles of Hawkesbury sandstone were acquired from a commercial supplier in the Sydney region.

Figure 7 shows a billet of sandstone before and after irradiation with the laser at a fluence of 0.9 J·cm^{-2}. It can be observed that the processed area has discolored from the sandstone's famous golden color to a dull grey, even at the low energy used in the experiment. This change of color is highly undesirable and may be due to the interaction of the laser radiation with organic parts of the stone, although further analysis should be performed in order to understand this change in depth and confirm or correct this hypothesis. Petrographic investigation was also recommended but was not undertaken in this preliminary study.

The laser's second and third harmonics (515 nm and 343 nm) were trialled, in an attempt to find a more suitable wavelength to work, but discoloration occurred in both cases, and even at lower fluences. A potential solution may be to proceed at higher wavelengths, such as Short Wavelength Infrared or Mid wavelength Infrared (SWIR, MIR > 1400 nm).

This case study illustrates that, although femtosecond pulse laser was found to be successful in most experiments described so far, some challenges still occur and require careful tailoring of the laser parameters with systematic study of the effects of the laser-matter interaction with the substrates in order to minimize undesirable changes or damage.

6 Case study 4: removal of graffiti from stone

Removal of spray paint, or graffiti, is a very current issue, both for the maintenance of public and private infrastructures and for the conservation of cultural heritages. Cleaning graffiti is an expensive endeavour for city councils and governments around the world, who spend each year astronomical amounts of money trying to remove unwanted spray paints, for sometimes only partial results [82]. Moreover, sandblasting, which is most common, may lead to considerable damage to the underlying materials.

Cleaning with short pulse laser systems (e.g., Nd:YAG at the fundamental 1064 nm wavelength in nanosecond pulse regime) has been investigated extensively [48, 101], and showed to be limited in terms of effectiveness and versatility. Indeed, some colored spray paints do not interact well with the nanosecond pulse duration and infrared wavelength and were therefore much harder to remove, introducing a need to use other wavelengths [29, 42, 46]. Research also demonstrated that the simultaneous use of UV and IR enhanced the removal of black and blue spray paint, with minimized damage [42], but the cleaning of the other paint type (silver) was proven to be more difficult and resulted in aluminium particles left on the surface. Consequently, further research to find a solution yielding effective cleaning results as well as offering better protection of the substrate is important.

Here, a selection of red, green, and blue paints from Montana® Colors paints were used and sprayed over a diamond-sawn sample of Moruya granite to replicate real conditions of graffiti (potential overlay of several paints to create visual effects, but no intentional thick layer). A brush was used to create the brushstroke pattern visible on the surface in Fig. 8a.

Femtosecond pulse laser cleaning was undertaken at a fluence of 1.0 J·cm^{-2} and demonstrated complete cleaning of all the different paints layers after 10 laser scans, as seen in Fig. 8b. Figure 8 shows promising results for the application of USP laser cleaning on graffiti and spray paints. We demonstrated in [82] that more spray paint colors, including silver paint, can be successfully cleaned with this technique.

Characterization of paint removal was undertaken in [82] with optical microscopy, Raman spectroscopy and colorimetry. The observations showed that the removal of paint was

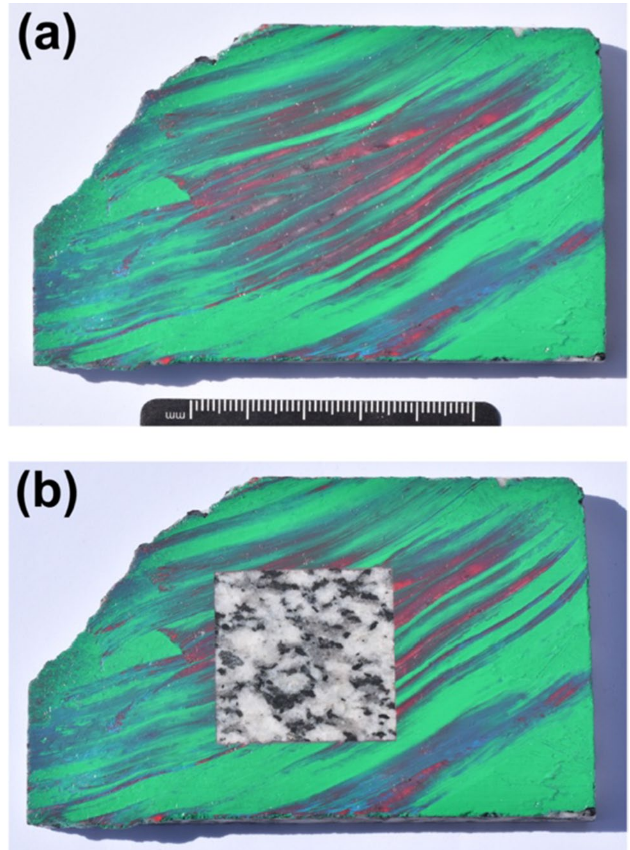

Fig. 8 Femtosecond pulse laser cleaning of granite covered by spray paints: **a** sample covered by green, red, and blue spray paints, **b** after femtosecond laser cleaning at 1.0 J·cm^{-2}

complete for each type of paint (red, green, blue here, as well as yellow and silver in [82]). No residues were found on the surface after the treatment. Raman spectroscopy, illustrated in Fig. 9, showed no signal for paint after cleaning, which indicated the success of the femtosecond pulse laser to remove the paint. Moreover, colorimetry showed that the grey color of the stone was retrieved well in each case.

7 Discussion and conclusion

The femtosecond pulse laser technique offers an alternative for cleaning various contaminants and stains from heritage monuments, sculptures, and buildings without physical contact or the use of chemicals. We demonstrated that those lasers can clean a wide range of contaminants, from biofilm, environmental soiling, and rust, to spray paints, while preserving the integrity of the underlying substrates. Developing the femtosecond laser technique that delivers fast and effective cleaning results and could easily be deployed and implemented on a wide range of materials is significant for

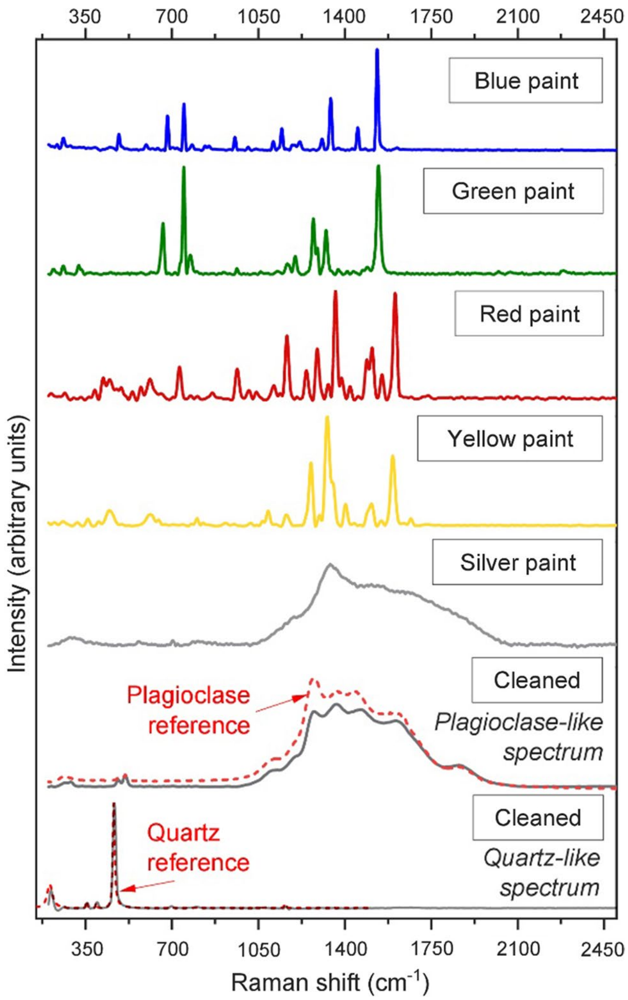

Fig. 9 Raman spectra of painted and cleaned granite surfaces. Paint spectra correspond to modified alkyd resin. Clean spectra show the typical features of plagioclase and quartz, highlighting the total removal of the paints. Reprinted with permission from [82] © Optical Society

various industries such as conservation of cultural heritage. The benefits of removing paints and coatings without damaging the underlying substrates are enormous and directly address critical challenges faced for asset maintenance (public transport, bridges, energy resources and utility equipment whilst in use) and in automotive, space, and defence industries. Moreover, the versatility of the method will significantly simplify maintenance work. Economic benefits arise to apply this technology for reduced maintenance costs of infrastructure, graffiti removal, and also for restoring the visual appeal of iconic structures/objects.

The examples developed here illustrate the potential of femtosecond pulse laser cleaning, and some existing challenges for the conservation of cultural heritage. If most of them were quite successful, they were however laboratory-based experiments. The current setup limits the technique's applicability to samples transported to the laboratory, of small to medium size, and excludes on-site applications. We think that the success and effectiveness of the technique make it relevant to start the integration of the technique to something more portable and practical in order to answer real conservation and asset maintenance needs on-site.

Scaling up and integrating the process to test on different significant heritage structures and sites is the next step, for future implementation as a maintenance technique, which may help disseminate the potential of femtosecond pulse lasers as a safer cleaning process.

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Declarations

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

References

1. J.F. Asmus, G. Guattari, L. Lazzarini, G. Musumeci, R.F. Wuerker, Holography in the conservation of statuary. Stud. Conserv. **18**(2), 49–63 (1973). https://doi.org/10.1179/sic.1973.005
2. M. Cooper, *Laser Cleaning in Conservation: An Introduction, ed. M. Cooper* (Butterworth-Heinemann, Woburn, 1998)

3. A. DeCruz, M.L. Wolbarsht, A. Andreotti, M.P. Colombini, D. Pinna, C.F. Culberson, Investigation of the Er:YAG Laser at 2.94 µm to Remove Lichens Growing on Stone. Stud. Conserv. **54**(4), 268–277 (2009). https://doi.org/10.1179/sic.2009.54.4.268
4. B.T. Gemeda, R. Lahoz, A.T. Caldeira, N. Schiavon, Efficacy of laser cleaning in the removal of biological patina on the volcanic scoria of the rock-hewn churches of Lalibela, Ethiopia. Environ. Earth Sci. **77**(2), 36 (2018). https://doi.org/10.1007/s12665-017-7223-3
5. J.S. Pozo-Antonio, P. Barreiro, G. Paz-Bermúdez, P. González, A.B. Fernandes, Effectiveness and durability of chemical- and laser-based cleanings of lichen mosaics on schists at archaeological sites. Int. Biodeterior. Biodegrad. **163**, 105276 (2021). https://doi.org/10.1016/j.ibiod.2021.105276
6. M. Sanz, M. Oujja, C. Ascaso, A. de los Ríos, S. Pérez-Ortega, V. Souza-Egipsy, J. Wierzchos, M. Speranza, M.V. Cañamares, M. Castillejo, Infrared and ultraviolet laser removal of crustose lichens on dolomite heritage stone. Appl. Surf. Sci. **346**, 248–255 (2015). https://doi.org/10.1016/j.apsusc.2015.04.013
7. M. Sanz, M. Oujja, C. Ascaso, S. Pérez-Ortega, V. Souza-Egipsy, R. Fort, A. de los Rios, J. Wierzchos, M.V. Cañamares, M. Castillejo, Influence of wavelength on the laser removal of lichens colonizing heritage stone. Appl. Surf. Sci. **399**, 758–768 (2017). https://doi.org/10.1016/j.apsusc.2016.12.032
8. P. Barreiro, A. Andreotti, M.P. Colombini, P. González, J.S. Pozo-Antonio, Influence of the laser wavelength on harmful effects on granite due to biofilm removal. Coatings **10**(3), 196–213 (2020). https://doi.org/10.3390/coatings10030196
9. P. Barreiro, P. Gonzalez, J.S. Pozo-Antonio, IR irradiation to remove a sub-aerial biofilm from granitic stones using two different laser systems: an Nd: YAG (1064nm) and an Er:YAG (2940nm). Sci. Total Environ. **688**, 632–641 (2019). https://doi.org/10.1016/j.scitotenv.2019.06.306
10. M. Mascalchi, I. Osticioli, O. Adriana Cuzman, S. Mugnaini, M. Giamello, S. Siano, Laser removal of biofilm from Carrara marble using 532 nm: the first validation study. Measurement **130**, 255–263 (2018). https://doi.org/10.1016/j.measurement.2018.08.012
11. T. Rivas, J.S. Pozo-Antonio, M.E. López de Silanes, A. Ramil, A.J. López, Laser versus scalpel cleaning of crustose lichens on granite. Appl. Surf. Sci. **440**, 467–476 (2018). https://doi.org/10.1016/j.apsusc.2018.01.167
12. A. Andreotti, M.P. Colombini, A. De Cruz, Er:YAG laser cleaning of a marble Roman urn. J. Inst. Conserv. **43**(1), 12–24 (2020). https://doi.org/10.1080/19455224.2019.1706593
13. A.J. López, T. Rivas, J. Lamas, A. Ramil, A. Yáñez, Optimisation of laser removal of biological crusts in granites. Appl. Phys. A **100**(3), 733–739 (2010). https://doi.org/10.1007/s00339-010-5652-x
14. S. Pozo, C. Montojo, T. Rivas, A.J. López-Díaz, M.P. Fiorucci, M.E. López de Silanes, Comparison between methods of biological crust removal on granite. Key Eng. Mater. **548**, 317–325 (2013). https://doi.org/10.4028/www.scientific.net/KEM.548.317
15. A. Zanini, V. Trafeli, L. Bartoli, The laser as a tool for the cleaning of Cultural Heritage. IOP Conf. Ser. Mater. Sci. Eng. **364**(1), 012078 (2018). https://doi.org/10.1088/1757-899X/364/1/012078
16. L. Pereira-Pardo, C. Korenberg, The use of erbium lasers for the conservation of cultural heritage. A review. J. Cultural Herit. **31**, 236–247 (2018). https://doi.org/10.1016/j.culher.2017.10.007
17. S.S. Potgieter-Vermaak, R.H.M. Godoi, R.V. Grieken, J.H. Potgieter, M. Oujja, M. Castillejo, Micro-structural characterization of black crust and laser cleaning of building stones by micro-Raman and SEM techniques. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. **61**(11), 2460–2467 (2005). https://doi.org/10.1016/j.saa.2004.09.010
18. P. Mazzinghi, F. Margheri, A short pulse, free running, Nd:YAG laser for the cleaning of stone cultural heritage. Opt. Lasers Eng. **39**(2), 191–202 (2003). https://doi.org/10.1016/S0143-8166(01)00133-6
19. G. Marakis, P. Pouli, V. Zafiropulos, P. Maravelaki-Kalaitzaki, Comparative study on the application of the 1st and the 3rd harmonic of a Q-switched Nd:YAG laser system to clean black encrustation on marble. J. Cult. Herit. **4**, 83–91 (2003). https://doi.org/10.1016/S1296-2074(02)01208-6
20. S. Siano, F. Fabiani, R. Pini, R. Salimbeni, M. Giamello, G. Sabatini, Determination of damage thresholds to prevent side effects in laser cleaning of pliocene sandstone of Siena. J. Cult. Herit. **1**, S47–S53 (2000). https://doi.org/10.1016/S1296-2074(00)00194-1
21. S. Pozo, P. Barreiro, T. Rivas, P. González, M.P. Fiorucci, Effectiveness and harmful effects of removal sulphated black crust from granite using Nd:YAG nanosecond pulsed laser. Appl. Surf. Sci. **302**, 309–313 (2014). https://doi.org/10.1016/j.apsusc.2013.10.129
22. J.S. Pozo-Antonio, M.P. Fiorucci, A. Ramil, A.J. López, T. Rivas, Evaluation of the effectiveness of laser crust removal on granites by means of hyperspectral imaging techniques. Appl. Surf. Sci. **347**, 832–838 (2015). https://doi.org/10.1016/j.apsusc.2015.04.182
23. J.S. Pozo-Antonio, A. Papanikolaou, A. Philippidis, K. Melessanaki, T. Rivas, P. Pouli, Cleaning of gypsum-rich black crusts on granite using a dual wavelength Q-Switched Nd:YAG laser. Constr. Build. Mater. **226**, 721–733 (2019). https://doi.org/10.1016/j.conbuildmat.2019.07.298
24. B. Silva, N. Aira, A. Martinez-Cortizas, B. Prieto, Chemical composition and origin of black patinas on granite. Sci. Total Environ. **408**(1), 130–137 (2009). https://doi.org/10.1016/j.scitotenv.2009.09.020
25. E. Isella, D. Bonelli, S. Cerea, F. Mancini, V. Ruppen, A. Botteon, A. Sansonetti, *Experiences at the Academy of Fine Arts of Brera in Milan, Italy: the application of laser-technology on three case studies of the historical heritage*, pp 229–240 (2017)
26. M. Bertasa, C. Korenberg, Successes and challenges in laser cleaning metal artefacts: a review. J. Cult. Herit. **53**, 100–117 (2022). https://doi.org/10.1016/j.culher.2021.10.010
27. T. Palomar, M. Oujja, I. Llorente, B. Ramírez Barat, M.V. Cañamares, E. Cano, M. Castillejo, Evaluation of laser cleaning for the restoration of tarnished silver artifacts. Appl. Surf. Sci. **387**, 118–127 (2016). https://doi.org/10.1016/j.apsusc.2016.06.017
28. Y. Koh, I. Sárady, Cleaning of corroded iron artefacts using pulsed TEA CO2- and Nd:YAG-lasers. J. Cult. Herit. **4**, 129–133 (2003). https://doi.org/10.1016/S1296-2074(02)01140-8
29. S. Siano, J. Agresti, I. Cacciari, D. Ciofini, M. Mascalchi, I. Osticioli, A.A. Mencaglia, Laser cleaning in conservation of stone, metal, and painted artifacts: state of the art and new insights on the use of the Nd:YAG lasers. Appl. Phys. A **106**(2), 419–446 (2011). https://doi.org/10.1007/s00339-011-6690-8
30. D.S. Prokuratov, A.S. Davtian, O.S. Vereshchagin, N.S. Kurganov, A.A. Samokhvalov, D.V. Pankin, A.V. Povolotckaia, A.A. Shimko, A.A. Mikhailova, P.A. Somov, V.A. Parfenov, Laser cleaning of archaeologically corroded iron objects with inlays. Opt. Quant. Electron. **52**(2), 113 (2020). https://doi.org/10.1007/s11082-020-2231-z
31. E. Drakaki, A.G. Karydas, B. Klinkenberg, M. Kokkoris, A.A. Serafetinides, E. Stavrou, R. Vlastou, C. Zarkadas, Laser cleaning on Roman coins. Appl. Phys. A **79**(4–6), 1111–1115 (2004). https://doi.org/10.1007/s00339-004-2657-3
32. S. Siano, R. Salimbeni, The gate of paradise: physical optimization of the laser cleaning approach. Stud. Conserv. **46**, 269–281 (2001). https://doi.org/10.2307/1506776

33. C. Korenberg, A. Baldwin, P. Pouli, Investigating and optimising the laser cleaning of corroded iron. Lasers Conserv. Artworks Proc. Int. Conf. LACONA **7**, 291–296 (2008). https://doi.org/10.1201/9780203882085.ch46
34. Y.S. Koh, *Laser Cleaning as a Conservation Technique for Corroded Metal Artifacts* (Luleå tekniska universitet, Luleå, 2006)
35. S. Chapman, Laser technology for graffiti removal. J. Cult. Herit. **1**, S75–S78 (2000). https://doi.org/10.1016/S1296-2074(00)00153-9
36. I.M. Cortea, L. Ratoiu, R. Rădvan, Characterization of spray paints used in street art graffiti by a non-destructive multi-analytical approach. Color. Res. Appl. **46**(1), 183–194 (2020). https://doi.org/10.1002/col.22561
37. M.F. Costa, M.P. Fiorucci, J. Lamas, A.J. López, T. Rivas, A. Ramil, Laser cleaning of graffiti in Rosa Porrino granite. Int. Conf. Appl. Optics Photonics. (2011). https://doi.org/10.1117/12.892158
38. A. Costela, I. García-Moreno, C. Gómez, O. Caballero, R. Sastre, Cleaning graffitis on urban buildings by use of second and third harmonic wavelength of a Nd:YAG laser: a comparative study. Appl. Surf. Sci. **207**(1–4), 86–99 (2003). https://doi.org/10.1016/s0169-4332(02)01241-2
39. M.P. Fiorucci, A.J. López, A. Ramil, S. Pozo, T. Rivas, Optimization of graffiti removal on natural stone by means of high repetition rate UV laser. Appl. Surf. Sci. **278**, 268–272 (2013). https://doi.org/10.1016/j.apsusc.2012.10.092
40. V. Gomes, A. Dionísio, J.S. Pozo-Antonio, T. Rivas, A. Ramil, Mechanical and laser cleaning of spray graffiti paints on a granite subjected to a SO2-rich atmosphere. Constr. Build. Mater. **188**, 621–632 (2018). https://doi.org/10.1016/j.conbuildmat.2018.08.130
41. J. Penide, F. Quintero, A. Riveiro, A. Sánchez-Castillo, R. Comesaña, J. del Val, F. Lusquiños, J. Pou, Removal of graffiti from quarry stone by high power diode laser. Opt. Lasers Eng. **51**(4), 364–370 (2013). https://doi.org/10.1016/j.optlaseng.2012.12.002
42. J. Pozo-Antonio, A. Papanikolaou, K. Melessanaki, T. Rivas, P. Pouli, Laser-assisted removal of graffiti from granite: advantages of the simultaneous use of two wavelengths. Coatings **8**(4), 124–144 (2018). https://doi.org/10.3390/coatings8040124
43. J.S. Pozo-Antonio, T. Rivas, M.P. Fiorucci, A.J. López, A. Ramil, Effectiveness and harmfulness evaluation of graffiti cleaning by mechanical, chemical and laser procedures on granite. Microchem. J. **125**, 1–9 (2016). https://doi.org/10.1016/j.microc.2015.10.040
44. A. Ramil, J.S. Pozo-Antonio, M.P. Fiorucci, A.J. López, T. Rivas, Detection of the optimal laser fluence ranges to clean graffiti on silicates. Constr. Build. Mater. **148**, 122–130 (2017). https://doi.org/10.1016/j.conbuildmat.2017.05.035
45. C. Ricci, F. Gambino, M. Nervo, A. Piccirillo, A. Scarcella, F. Zenucchini, A. Ramil, J.S. Pozo-Antonio, Enhancement of graffiti removal from heritage stone by combining laser ablation and application of a solvent mixture. Constr. Build. Mater. (2020). https://doi.org/10.1016/j.conbuildmat.2020.119934
46. T. Rivas, S. Pozo, M.P. Fiorucci, A.J. López, A. Ramil, Nd:YVO4 laser removal of graffiti from granite. Influence of paint and rock properties on cleaning efficacy. Appl. Surf. Sci. **263**, 563–572 (2012). https://doi.org/10.1016/j.apsusc.2012.09.110
47. S. Samolik, M. Walczak, M. Plotek, A. Sarzynski, I. Pluska, J. Marczak, Investigation into the removal of graffiti on mineral supports: comparison of nano-second Nd:YAG laser cleaning with traditional mechanical and chemical methods. Stud. Conserv. **60**(sup1), S58–S64 (2015). https://doi.org/10.1179/0039363015Z.000000000208
48. P. Sanmartín, F. Cappitelli, R. Mitchell, Current methods of graffiti removal: a review. Constr. Build. Mater. **71**, 363–374 (2014). https://doi.org/10.1016/j.conbuildmat.2014.08.093
49. P. Pouli, E. Papakonstantinou, K. Frantzikinaki, A. Panou, G. Frantzi, C. Vasiliadis, C. Fotakis, The two-wavelength laser cleaning methodology; theoretical background and examples from its application on CH objects and monuments with emphasis to the Athens Acropolis sculptures. Heritage Science **4**(1), 1–11 (2016). https://doi.org/10.1186/s40494-016-0077-2
50. A. Nevin, P. Pouli, S. Georgiou, C. Fotakis, Laser conservation of art. Nat. Mater. **6**(5), 320–322 (2007). https://doi.org/10.1038/nmat1895
51. M. Labouré, P. Bromblet, G. Orial, G. Wiedemann, C. Simon-Boisson, Assessment of laser cleaning rate on limestones and sandstones. J. Cult. Herit. **1**, S21–S27 (2000). https://doi.org/10.1016/s1296-2074(00)00195-3
52. P. Bromblet, M. Labouré, G. Orial, Diversity of the cleaning procedures including laser for the restoration of carved portals in France over the last 10 years. J. Cult. Herit. **4**, 17–26 (2003). https://doi.org/10.1016/S1296-2074(02)01222-0
53. J.S. Pozo-Antonio, T. Rivas, A.J. Lopez, M.P. Fiorucci, A. Ramil, Effectiveness of granite cleaning procedures in cultural heritage: a review. Sci. Total Environ. **571**, 1017–1028 (2016). https://doi.org/10.1016/j.scitotenv.2016.07.090
54. C. Fotakis, D. Anglos, V. Zafiropoulos, S. Georgiou, and V. Tornari, *Series in Optics and Optoelectronics, Lasers in the preservation of cultural heritage, principles and applications*, ed. T. Francis (2007)
55. A.V. Rode, K.G.H. Baldwin, A. Wain, N.R. Madsen, D. Freeman, P. Delaporte, B. Luther-Davies, Ultrafast laser ablation for restoration of heritage objects. Appl. Surf. Sci. **254**(10), 3137–3146 (2008). https://doi.org/10.1016/j.apsusc.2007.10.106
56. V. Zinnecker, S. Madden, C. Stokes-Griffin, P. Compston, A. Rode, L. Rapp, Ultrashort pulse laser ablation of steel in ambient air. Optics Laser Technol. **148**, 107757 (2022). https://doi.org/10.1016/j.optlastec.2021.107757
57. J. Berthonneau, P. Parent, O. Grauby, D. Ferry, C. Laffon, A. Colombini, B. Courtois, P. Bromblet, Yellowing of laser-cleaned artworks: formation of residual hydrocarbon compounds after Nd:YAG laser cleaning of gypsum plates covered by lamp black. J. Cult. Herit. **39**, 57–65 (2019). https://doi.org/10.1016/j.culher.2019.02.014
58. C. de Oliveira, P. Bromblet, A. Colombini, V. Vergès-Belmin, Medium-wave ultraviolet radiation to eliminate laser-induced yellowing generated by the laser removal of lamp black on gypsum. Stud. Conserv. **60**(sup1), S34–S40 (2015). https://doi.org/10.1179/0039363015z.000000000205
59. C. de Oliveira, V. Vergès-Belmin, D. Demaille, P. Bromblet, Lamp black and hematite contribution to laser yellowing: a study on technical gypsum samples. Stud. Conserv. **61**(3), 136–145 (2016). https://doi.org/10.1179/2047058415y.0000000003
60. C.M. Grossi, P. Brimblecombe, R.M. Esbert, F.J. Alonso, Color changes in architectural limestones from pollution and cleaning. Color. Res. Appl. **32**(4), 320–331 (2007). https://doi.org/10.1002/col.20322
61. P. Pouli, M. Oujja, M. Castillejo, Practical issues in laser cleaning of stone and painted artefacts: optimisation procedures and side effects. Appl. Phys. A **106**(2), 447–464 (2011). https://doi.org/10.1007/s00339-011-6696-2
62. V. Vergès-Belmin, C. Dignard, Laser yellowing: myth or reality? J. Cult. Herit. **4**, 238s–244s (2003). https://doi.org/10.1016/S1296-2074(02)01203-7
63. M. Godet, *Jaunissement de la pierre par laser: origines et remèdes*, in *École Doctorale Sciences de la Nature et de l'Homme—ED 227*. 2017, Museum National d'Histoire Naturelle MNHN: Paris.
64. C.M. Grossi, F.J. Alonso, R.M. Esbert, A. Rojo, Effect of laser cleaning on granite color. Color. Res. Appl. **32**(2), 152–159 (2007). https://doi.org/10.1002/col.20299

65. E. Urones-Garrote, A.J. López, A. Ramil, L.C. Otero-Díaz, Microstructural study of the origin of color in Rosa Porriño granite and laser cleaning effects. Appl. Phys. A **104**(1), 95–101 (2011). https://doi.org/10.1007/s00339-011-6344-x
66. C. Rodriguez-Navarro, K. Elert, E. Sebastian, R.M. Esbert, C.M. Grossi, A. Rojo, F.J. Alonso, M. Montoto, J. Ordaz, Laser cleaning of stone materials: an overview of current research. Stud. Conserv. **48**(sup1), 65–82 (2003). https://doi.org/10.1179/sic.2003.48.Supplement-1.65
67. D. Eichert, V. Verges Belmin, O. Kahn, Electronic paramagnetic resonance as a tool for studying the blackening of Carrara marble due to irradiation by a Q-switched YAG laser. J. Cult. Herit. **1**, 37–45 (2000). https://doi.org/10.1016/S1296-2074(00)00151-5
68. R.M. Esbert, C.M. Grossi, A. Rojo, F.J. Alonso, M. Montoto, J. Ordaz, M.C. Pérez de Andrés, C. Escudero, M. Barrera, E. Sebastián, C. Rodriguez-Navarro, K. Elert, Application limits of Q-switched Nd:YAG laser irradiation for stone cleaning based on colour measurements. J. Cult. Herit. **4**, 50–55 (2003). https://doi.org/10.1016/S1296-2074(02)01227-X
69. B.N. Chichkov, C. Momma, S. Nolte, F. von Alvensleben, A. Tünnermann, Femtosecond, picosecond and nanosecond laser ablation of solids. Appl. Phys. A **63**(2), 109–115 (1996). https://doi.org/10.1007/BF01567637
70. C. Momma, S. Nolte, B.N. Chichkov, F.V. Alvensleben, A. Tünnermann, Precise laser ablation with femtosecond pulses, in *Conference on Lasers and Electro-Optics*. (Optica Publishing Group, Baltimore, 1997)
71. B.C. Stuart, M.D. Feit, S. Herman, A.M. Rubenchik, B.W. Shore, M.D. Perry, Optical ablation by high-power short-pulse lasers. J. Opt. Soc. Am. B **13**(2), 459–468 (1996). https://doi.org/10.1364/JOSAB.13.000459
72. E.G. Gamaly, A.V. Rode, B. Luther-Davies, V.T. Tikhonchuk, Ablation of solids by femtosecond lasers: ablation mechanism and ablation thresholds for metals and dielectrics. Phys. Plasmas **9**(3), 949–957 (2002). https://doi.org/10.1063/1.1447555
73. M.D. Shirk, P.A. Molian, A review of ultrashort pulsed laser ablation of materials. J. Laser Appl. (1998). https://doi.org/10.2351/1.521827
74. P. Pouli, G. Bounos, S. Georgiou, C. Fotakis, Femtosecond laser cleaning of painted artefacts; is this the way forward?, in *LACONA Lasers in the Conservation of Artworks VI*. (Springer, Vienna, 2005). https://doi.org/10.1007/978-3-540-72130-7_33
75. S. Gaspard, M. Oujja, M. Castillejo, P. Moreno, C. Méndez, A. García, and C. Domingo, *Femtosecond laser cleaning of paintings: Modifications of tempera paints by Femtosecond laser irradiation*. in *Lasers in the Conservation of Artworks—Proceedings of the International Conference LACONA 7*. 2008.
76. T. Ersoy, T. Tunay, M. Uğuryol, G. Mavili, S. Akturk, Femtosecond laser cleaning of historical paper with sizing. J. Cult. Herit. **15**(3), 258–265 (2014). https://doi.org/10.1016/j.culher.2013.07.002
77. M. Walczak, M. Oujja, L. Crespo-Arcá, A. García, C. Méndez, P. Moreno, C. Domingo, M. Castillejo, Evaluation of femtosecond laser pulse irradiation of ancient parchment. Appl. Surf. Sci. **255**(5), 3179–3183 (2008). https://doi.org/10.1016/j.apsusc.2008.09.011
78. M. Kono, K.G. Baldwin, A. Wain, A.V. Rode, Treating the untreatable in art and heritage materials: ultrafast laser cleaning of "cloth-of-gold." Langmuir **31**(4), 1596–1604 (2015). https://doi.org/10.1021/la504400h
79. C. Escudero, M. Martínez, P. Moreno, A. García, C. Méndez, A. C. Prieto, A. Sanz Arranz, *Study of Laser Cleaning of Ancient Fabric with Femtosecond Pulses*. 2007.
80. E.M. Maingi, V. Treil, M.P.A. Abad, L.A. Angurel, M.A. Rahman, R. Chapoulie, S. Dubernet, N. Schiavon, G.F.D.L. Fuente, Challenges in laser cleaning of cultural heritage stained glass. J. Phys. Conf. Ser. (2022). https://doi.org/10.1088/1742-6596/2204/1/012079
81. T. Rivas, A.J. Lopez, A. Ramil, S. Pozo, M.P. Fiorucci, M.E.L.D. Silanes, A. García, J.R.V.D. Aldana, C. Romero, P. Moreno, Comparative study of ornamental granite cleaning using femtosecond and nanosecond pulsed lasers. Appl. Surf. Sci. **278**, 226–233 (2013). https://doi.org/10.1016/j.apsusc.2012.12.038
82. J. Brand, A. Wain, A.V. Rode, S. Madden, P.L. King, L. Rapp, Femtosecond pulse laser cleaning of spray paint from heritage stone surfaces. Opt. Express (2022). https://doi.org/10.1364/oe.468750
83. C. Korenberg, A. Baldwin, P. Pouli, Investigating the laser cleaning of archaeological copper alloys using different laser systems. Lasers Conserv. Artworks Proc. Int. Conf. LACONA **7**, 285–290 (2008). https://doi.org/10.1201/9780203882085.ch45
84. B. Taarnskov, P. Pouli, J. Bredal-Jørgensen, Laser cleaning studies for the removal of tarnishing from silver and gilt silver threads in silk textiles, in *Lasers in the Conservation of Artworks*. (Taylor & Francis Group, New York, 2010)
85. T. Burmester, M. Meier, H. Haferkamp, S. Barcikowski, J. Bunte, A. Ostendorf, Femtosecond laser cleaning of metallic cultural heritage and antique artworks. Lasers Conserv. Artworks (2005). https://doi.org/10.1007/3-540-27176-7_8
86. C. Momma, S. Nolte, G. Kamlage, F. von Alvensleben, A. Tünnermann, Beam delivery of femtosecond laser radiation by diffractive optical elements. Appl. Phys. A **67**(5), 517–520 (1998). https://doi.org/10.1007/s003390050814
87. E.G. Gamaly, N.R. Madsen, M. Duering, A.V. Rode, V.Z. Kolev, B. Luther-Davies, Ablation of metals with picosecond laser pulses: evidence of long-lived nonequilibrium conditions at the surface. Phys. Rev. B **71**(17), 174405 (2005). https://doi.org/10.1103/PhysRevB.71.174405
88. J. Schille, L. Schneider, U. Loeschner, Process optimization in high-average-power ultrashort pulse laser microfabrication: how laser process parameters influence efficiency, throughput and quality. Appl. Phys. A **120**(3), 847–855 (2015). https://doi.org/10.1007/s00339-015-9352-4
89. J. Brand, A.V. Rode, S. Madden, A. Wain, P.L. King, L. Rapp, Ultrashort pulsed laser ablation of granite for stone conservation. Opt. Laser Technol. (2022). https://doi.org/10.1016/j.optlastec.2022.108057
90. Transport for New South Wales. *Traffic Volume Viewer*. 2020. https://www.rms.nsw.gov.au/about/corporate-publications/statistics/traffic-volumes/index.html. Accessed Apr 2020
91. Department of Main Roads New South Wales, *The story of the Sydney Harbour Bridge* 1982.
92. R. Freeman, *Sydney Harbour Bridge: Design of the Structure and Foundations.* Minutes of the Proceedings of the Institution of Civil Engineers, 1934. **238**(1934).
93. G. M. Logan, *Sydney Harbour Bridge Conservation Management Plan 2007*. 2007.
94. T.J. Griffin, A.J.R. White, B.W. Chappell, The Moruya Batholith and geochemical contrasts between the Moruya and Jindabyne suites. J. Geol. Soc. Aust. **25**(3–4), 235–247 (1976). https://doi.org/10.1080/00167617808729030
95. I. A. Brown, The geology of the south coast of New South Wales. Part I. The Palaeozoic geology of the Moruya district. in *Proceedings of the Linnean Society of New South Wales*, 1928. **53**: p. 151–192
96. T.J. Griffin, The Moruya complex, in *Geology*. (Australian National University, Canberra, 1971)
97. J. Brand, A. Wain, A. V. Rode, S. Madden, P. L. King, M. Mohan, W. Kaluarachchi, J. Ratnayake, and L. Rapp, Femtosecond pulse laser cleaning of biofilm and dirt: preserving the Sydney Harbour Bridge. J. Cult. Herit. **60**, 86–94 (2023). https://doi.org/10.1016/j.culher.2023.01.010.

98. S. Garg, P. Kaur, M. Pandit, F. Fareeduddin, G. Kaur, A. Kamboj, S. Thakur, Makrana marble: a popular heritage stone resource from NW India. Geoheritage (2019). https://doi.org/10.1007/s12371-018-00343-0
99. Controller General of the Indian Bureau of Mines Nagpur. *Bulletin No. 12: Marble in India*. 1983. https://ibm.gov.in/writereaddata/files/09282017160715SKM_C224e17092710130.pdf. Accessed Oct 2022
100. E. Long, D. Young, Trials of biocide cleaning agents on Sydney sandstone. in *Fabric, the Threads of Conservation—Australia ICOMOS Conference*. 2015. Adelaide, SA, Australia.
101. V. Gomes, A. Dionísio, J.S. Pozo-Antonio, Conservation strategies against graffiti vandalism on Cultural Heritage stones: protective coatings and cleaning methods. Prog. Org. Coat. **113**, 90–109 (2017). https://doi.org/10.1016/j.porgcoat.2017.08.010