Laser cleaning of stone materials: an overview of current research

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Abstract

This paper presents an overview of current knowledge and recent advances in the application of pulsed laser radiation to the cleaning of works of art, particularly ornamental stone. Special emphasis is put on the critical review of publications from the last six years. The recent history of laser cleaning in art conservation is summarised and a description of laser fundamentals, laser types and practicalities for use in conservation is given. Existing explanatory models of the underlying physics of laser cleaning are briefly described, as are the advances in laser cleaning of different stone types. Common techniques, including on-line monitoring used to detect material damage after laser irradiation, are outlined and examples are given of their application. Finally, current trends and improvements in laser-cleaning efficiency and the reduction of damaging side effects are addressed. It is hoped that this overview will bring greater attention to the issues that are important for future research on the laser cleaning of stone.

Introduction

Laser radiation is commonly used to remove superficial layers and contaminants from different types of surfaces [1-7]. Since the discovery of lasers, much practical and theoretical work has been done on laser/material interaction [8-14]. As a result, a better understanding of laser-induced removal of contaminants has been gained and applied to cleaning [4, 15-23]. Removal of surface layers via laser-induced plasma formation has also received considerable attention [24-27] and in recent decades laser cleaning has gained prominent status as a conservation alternative [28-32].

The deposition of contaminants on ornamental stonework and sculpture that results in soiling and encrustation – the latter being generally dark in colour (e.g. black crusts) – has a significant aesthetic impact and jeopardises the survival of the works themselves [33-35]. This is a widespread problem in polluted environments [36, 37]. In an effort to eliminate these contaminants and their eventual harmful by-products (e.g. sulphates and nitrates), numerous 'conventional' methods have been developed and implemented with varying degrees of success [38, 39]. In the early 1970s, Asmus and collaborators demonstrated that pulsed laser radiation, using a ruby laser, removes contaminants and encrustrations from, for example, Carrara marble sculptures [8, 40-43]. This pioneering research triggered the study and optimisation of laser applications to the cleaning and conservation of stone [44], tiles [45], bricks [46], metals [47], glass [48], paper, textiles and wooden artefacts [6].

Laser cleaning displays significant advantages when compared with conventional mechanical or chemical cleaning methods such as sandblasting, scrubbing, ultrasonic and wet chemical flux or poulticing. In contrast to conventional methods, laser cleaning is a selective, precise and versatile non-contact method. It may limit environmental or health-related side effects when used properly and, in most cases, can be controlled to prevent damage to underlying substrata [6]. However, some practical disadvantages of pulsed laser-assisted cleaning have been reported. Overexposure to laser pulse, for instance, may easily lead to substrate damage when the beam fluence is above a certain threshold, hence the term 'damage threshold'. Clearly, overexposure is to be avoided and an accurate knowledge of laser/material interactions is required to prevent damage.

Knowledge of laser/artwork interaction during cleaning has grown substantially over the last decade. A greater understanding of the processes that underlie laser-induced damage with nanosecond (ns) pulses have rendered Asmus' model of thermal-induced damage inapplicable where short and ultra-short pulses are used. Current models of laser/material interaction now take into account photomechanical processes such as shock-wave generation [12, 49] and particle acceleration due to thermal expansion [4, 17]. A number of photochemical processes [50] are taken into account, which include:

- photon-energy transfer caused by strong vibrational coupling (e.g. resonance)
- bond breaking due to single-photon or multi-photon absorption
- inverse *bremsstrahlung*

Any one of these laser/material interaction mechanisms may be prevalent under varying application conditions and parameters (such as substrate type, wavelength, pulse repetition rate and pulse width).

This paper presents an overview of recent studies on laser cleaning of ornamental stone and stone sculpture. A brief description is given of the basics of laser technology and of the current theories and models of laser/material interactions, with a special emphasis on the laser-assisted cleaning of stone. Although an in-depth analysis of the vast literature on lasers and current theories is beyond the scope of this review, the authors have focused on the understanding of laser/stone interaction, the definition of safe application conditions (e.g. laser fluence and appropriate wavelength) and the monitoring of laser-induced damage. A report of the state of laser cleaning up to 1997 can be found in Cooper [6], who also presents detailed information on laser fundamentals and laser types, as well as providing a glossary of terms. The interested reader may find it useful to check more recent web-based laser glossaries on:

http://www.kentek-laser.com/helpers/glossary.htm

http://aesd.larc.nasa.gov/GL/tutorial/glossary/gloss.htm

http://www.ing.unipi.it/~d7384/com_ottiche/LaserGlossario.html

Since the publication of Cooper's book, *Laser Cleaning in Conservation: An Introduction*, in 1998 there has not been another review of the literature that specifically addresses laser cleaning of ornamental stone. However, there have been four LACONA (Lasers in the Conservation of Artworks) meetings held since 1995, thus generating a large number of papers on the topic. Many publications on related issues have also appeared in specialised journals over the last six years. The existing concerns of the conservation community and the increase in publications on this subject have prompted the present overview, which addresses current knowledge and practical issues that arise from the use of lasers for the cleaning of stone.

Laser fundamentals

Lasers are light amplifiers that produce a highly directional, high-intensity beam that is typically monochromatic [51] and operate using the principle of Light Amplification by Stimulated Emission of Radiation (LASER). The origins of lasers can be traced to the first half of the twentieth century with the studies carried out on masers, devices that operate on the same principle as lasers in the microwave portion of the electromagnetic spectrum [52-55].

Stimulated emission of light has been described in Silfvast [51], Milonni *et al.* [56] and Kelly [57]. If light interacts with excited species (e.g. ions that have absorbed energy), these can be stimulated to emit light with the same frequency, phase, polarisation and direction as an incident beam, which is amplified. Under very intense excitation, laser light is thus produced. The resulting laser light is monochromatic, directional and coherent – properties that have made the laser beam a scientist's dream [58]. In its interaction with matter, laser-light energy is converted into thermal, chemical or mechanical energy. Lasers, therefore, have important effects on solids, liquids and gases, and have a range of applications in many fields, including the conservation of cultural heritage.

The core of a laser is a resonant device for light amplification, which is made by a box or cavity with two reflective sides (mirrors) situated opposite each other. One of the mirrors is usually partially reflecting, allowing light to be coupled out of the cavity. The transmission out of the cavity can be either continuous or pulsed. In some cases a switch (called a Q-switch) is inserted into the cavity to block the light to the mirrors. Depending on the switching frequency, laser pulses of different lengths (τ) can be produced. The pulse length is a crucial parameter since the laser beam power (P in Watts, or energy/unit time) is defined by:

$$P = \frac{E}{\tau}$$

where E is the beam energy (in joules). Ruby lasers with pulse length of a few hundred microseconds (μs, e.g. 10^{-6} s) produce output powers of tens of kilowatts (kW). Shorter pulse lengths provide correspondingly higher peak powers, particularly in modern lasers that incorporate a Q-switching device [51]. For instance, peak power outputs of nanosecond pulses (ns, e.g. 10^{-9} s) as high as 10^{13} W are easily obtained [53].

In routine work, it is convenient to express laser/matter interaction as the pulse energy deposited in a given area (A): this is the so-called laser fluence (F in J/cm^2) and is defined by F = J/A, or joules (J), which is a measure of energy, per unit area (A). Note that no indication of pulse length is given when fluence values are presented. This could create some confusion when comparing fluence values of lasers with different pulse lengths, e.g. when evaluating fluence damage thresholds for laser cleaning in conservation interventions. To avoid this ambiguity, irradiance (I in W/cm^2) or power density (P in W/cm^3) is used.

Components of a laser system

A standard laser consists of a laser medium (active medium or gain medium), a pumping system and an optical (resonant) cavity [56, 59]. The active medium must have a metastable state in which the excited atoms, ions or molecules can be trapped after receiving energy from the pumping system. The pumping system imparts energy to the atoms or molecules of the laser medium, enabling them to be raised to an excited metastable state, creating a population inversion. There are several types of pumping method. The most common is optical pumping, which uses photons provided by a source such as a flashlamp, or another laser, to transfer energy to the active medium. See Figure 1 for a schematic representation of a laser device.

An optical cavity, described in the previous section, is required to provide the amplification desired in the laser and to select the photons that are travelling in the appropriate direction. Photons are produced via stimulated emission and those that travel parallel to the axis of the active medium (which normally has a rod shape) can trigger the emission of other photons, which will be reflected by the mirror on the end of the laser rod or tube. The reflected photons bounce back and forth through the active medium, triggering further emissions along the same path, which are reflected by the mirrors. This way a standing wave is generated that is amplified over time. When the amount of amplification or gain

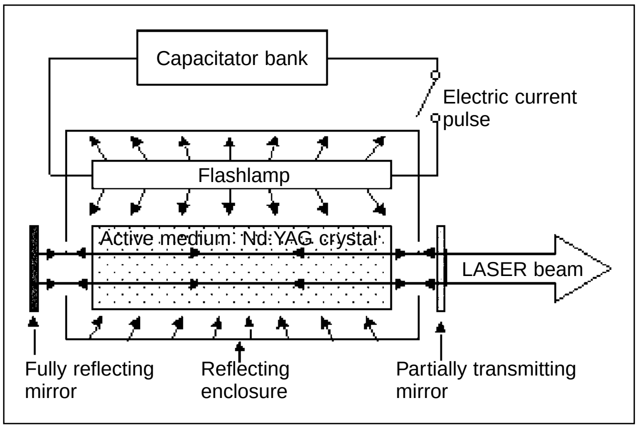

Fig. 1 Simplified diagram showing a Nd:YAG laser pumped by a flashlamp.

through this process exceeds the losses in the cavity, laser oscillation is said to occur. Then, a narrow concentrated beam of coherent light is formed. The laser beam thus generated can be coupled out through the partially reflecting mirror.

Lasers in conservation

The most common types of lasers used in the conservation of stone are solid-state lasers. Solid-state lasers employ a solid matrix as the active medium, which is generally crystalline (although a glass can also be used) and doped with a species, such as Cr^{3+} or Nd^{3+} ions. An example is the ruby laser, which emits in the visible spectrum and was the first laser to be used to clean stone objects [8]. Another is the Nd:YAG laser (see Figure 2). The term YAG is an abbreviation for Yttrium Aluminum Garnet, which is the crystalline matrix hosting the Nd ions. This laser, which is a standard laser device used in current cleaning interventions for stone, emits primarily a near-infrared (NIR) beam (λ = 1064 nm) with continuous power of up to 250 W and with pulsed powers as high as several megawatts (MW). Non-linear crystals can sometimes be used as accessory optical devices to convert the output to other wavelengths, which are fractions or multiples of the fundamental frequency. In the case of an Nd:YAG, this results in visible or ultraviolet wavelengths by generating the second or third harmonics.

The Nd:YAG laser is quite versatile although somewhat expensive. A standard, commercially available Q-switched Nd:YAG laser device – which has to be portable and, ideally, has to include an optical fibre delivery system – may cost around 80,000 and 140,000 Euro. Typically it is ~ 60 × 70 × 110 cm in size and weighs between 150 and 210 kg. Smaller (~25 × 65 × 70 cm) and lighter (~ 40 kg) devices also exist and can cost as little as 20,000 Euro. The use of lasers in conservation is still relatively new and it should be noted that much research and development is currently being carried out. Models and prices will therefore continue to vary.

Fig. 2 Q-switched Nd:YAG laser device, operated on porous limestone (calcarenite) during cleaning at Granada Cathedral (Spain).

Recent developments in laser technology have introduced the use of excimer (or excited dimer) lasers such as ArF, KrF and XeCl to the conservation world. These are gas lasers, which use a rare gas-halide mixture as the active medium. Excimer lasers operate with a pulsed output primarily in the ultraviolet region at 351 nm in XeF, 308 nm in XeCl, 248 nm in KrF and 193 nm in ArF. The high frequency (short wavelength) of the ultraviolet light produced by excimer laser results in pulses of high-energy photons that can break many atomic bonds. This photochemical effect has been exploited in the conservation of painted artworks. Excimer lasers have also been used to ablate materials for analysis with laser-induced breakdown spectroscopy (LIBS) [6]. Despite its current use in related fields, only a few studies have been performed to date on the cleaning of stone with the pulsed excimer laser [48].

Laser/matter interaction and cleaning applications

Laser/matter interaction induces a series of phenomena that have been used advantageously since the discovery of pulsed lasers in the 1960s [55]. The ability of lasers to selectively remove particles and superficial layers from a wide range of materials has led in particular to the use of lasers for cleaning purposes.

The application of laser radiation to the cleaning of stone was first investigated at the beginning of the 1970s by Asmus, Hempel, Lazzarini, Marchesini, Beloyannis and others [6]. Laser cleaning of decayed stone and other materials in sculpture was also tested in museums and laboratories. These experiments were aimed at the removal of black crusts and soiling patinas. For example, Asmus *et al.* [8] conducted experiments on the cleaning of several Carrara marble sculptures in Florence and Venice.

Laboratory and on-site testing was also done throughout the following decade. However, laser radiation was not applied in the actual cleaning of building or monument stones until the late 1980s/early 1990s [62-64]. During the '90s the laser cleaning of stone became a relatively common conservation/restoration practice in both laboratory (statuary) and monument contexts. Projects where lasers have been employed to clean stone have been extensive; a few examples are presented in Table 1. The stone materials cleaned by laser radiation are mainly carbonate rocks – limestones and marbles – and to a lesser extent silicate rocks, such as sandstones. Experience with other types of stones (e.g. granites and other igneous rocks) is still lacking.

Laser radiation has also been used to clean works made of terracotta, plaster, bronze, ivory, glass and wood, and has been used to clean paper, parchment and textiles. In Spain laser cleaning has also been applied to polychrome on wood [65], chromatic patinas on stones from monuments at Castilla and León [66] and ornamental gypsum of the 'Las Francesas' church in Valladolid [67, 68]. Systematic application of the technique in the conservation of paintings is also a relatively recent but significant development [69, 70].

Since Asmus' pioneering work, a few quantitative models have been proposed to predict temperature rise of encrustations and underlying stone following pulsed laser

Table 1 Examples of laser cleaning of stone works of art

artwork	material	author(s)
Lincoln Cathedral	limestone sculptures and fragments (friezes)	Cooper *et al.* [98]
Amiens Cathedral	Façade of the Virgin, decayed limestone, dirt and soluble salts	Weeks [62]
museums pieces	sandstone reliefs	Wiedemann [88]
museums pieces	Graeco-Roman and nineteenth-century marble sculptures	Cooper and Larson [109]
Church of 'Las Francesas', Valladolid	decayed limestone with black crusts	García, *et al.* [67]
Church of 'Notre Dame de La Grande', Poitiers	stone sculptures of façade, dirty and with salts	Groux [64]
Santa Maria dei Fiore, Florence	marble column	Siano *et al.* [106]
Mausoleum of Teodorico, Ravenna	stone: denticulate decoration at base of monolithic dome	Pini *et al.* [111]
Cologne Cathedral	oolithic limestone: angel sculptures	Siedel *et al.* [108]
Notre-Dame, Paris	limestone walls, thirteenth-century west central portal	Labouré *et al.* [105]
Champs-sur-Marne Castle	sandstone paving blocks	Labouré *et al.* [105]
Residence Castle, Dresden	soiled oil paints on sandstone	Siedel *et al.* [134]
Greek monuments	Pentelic marble	Maravelaki-Kalaitzaki *et al.* [143]

irradiation. These models have refined our understanding of laser/artwork interaction and have helped to determine safe application parameters.

Micron and submicron particle cleaning

Early work in the use of laser radiation for cleaning focused on the interaction of lasers with particulates deposited on microelectronic and optical devices. Particles were removed under wet and dry conditions at fluences far below the substrate ablation threshold. Particles, especially those of less than 0.2 μm, are strongly adhered to the substratum due to Van der Walls, capillary (in the presence of condensed water) and electrostatic double-layer forces [4]. Dry laser cleaning acts in two distinct ways, depending on the absorption characteristics of the substrate and the particles. When substrate absorptivity is high, rapid pulse heating can lead to the ejection of micron and submicron particles after sudden expansion of the substrate surface. The temperature rise ΔT following a laser pulse of fluence F and duration τ is approximately

$$\Delta T = \frac{1 - RTF}{\rho C \mu}$$

where R is the reflectivity of the surface, ρ is the density, C the specific heat and μ the thermal diffusion length during laser pulse. The normal expansion, H, of the surface due to temperature rise is

$$H = \sigma \mu \Delta T = \frac{1 - RTF\alpha}{\rho C}$$

where a is the thermal expansion coefficient. Therefore, the acceleration, a, of the supporting surface is

$$a \approx \frac{(1 - R)\alpha F}{\rho C \tau^2}$$

Using the above equation, Tam *et al.* [4] calculated accelerations in the order of 10^{10} cm/s^2 for typical numerical values of the above-mentioned variables. This acceleration is millions of times larger than gravitational acceleration and results in particle ejection from the substrate.

Strong absorption of laser beam energy by particles can also produce significant acceleration and particle ejection [4, 17, 18]. Recent works by Zheng *et al.* [23] and Mosbacher *et al.* [71] stress the importance of optical field enhancement effects during laser-assisted particle removal. These effects can cause substrate damage at fluences below those initially considered safe.

Selective surface-layer ablation

Laser ablation takes place when strongly absorbent superficial layers rapidly heat and vaporise, often forming a plasma plume. This plume is detectable as a spark followed by a snapping sound. Other processes may lead to surface-layer removal such as melting and eventual vaporisation, which is typical with long pulse lengths.

Since the work of Asmus on laser-assisted marble cleaning, it has been assumed that the strong absorbance differences between calcite and surface contaminants in visible and near infrared (NIR) laser radiation brought about the selective removal of the latter, while the substrate remained intact at fluences below its ablation threshold [6, 8]. Selective removal of strongly absorbent contaminants and encrustations was accounted for by the rapid temperature rise and vaporisation following pulsed laser irradiation [6, 8, 28, 72]. Asmus calculated the temperature rise, ΔT, at the substratum surface ($z = 0$) at time, t, (e.g. pulse width) using the following analytical solution for the one-dimensional thermal diffusion in a solid.

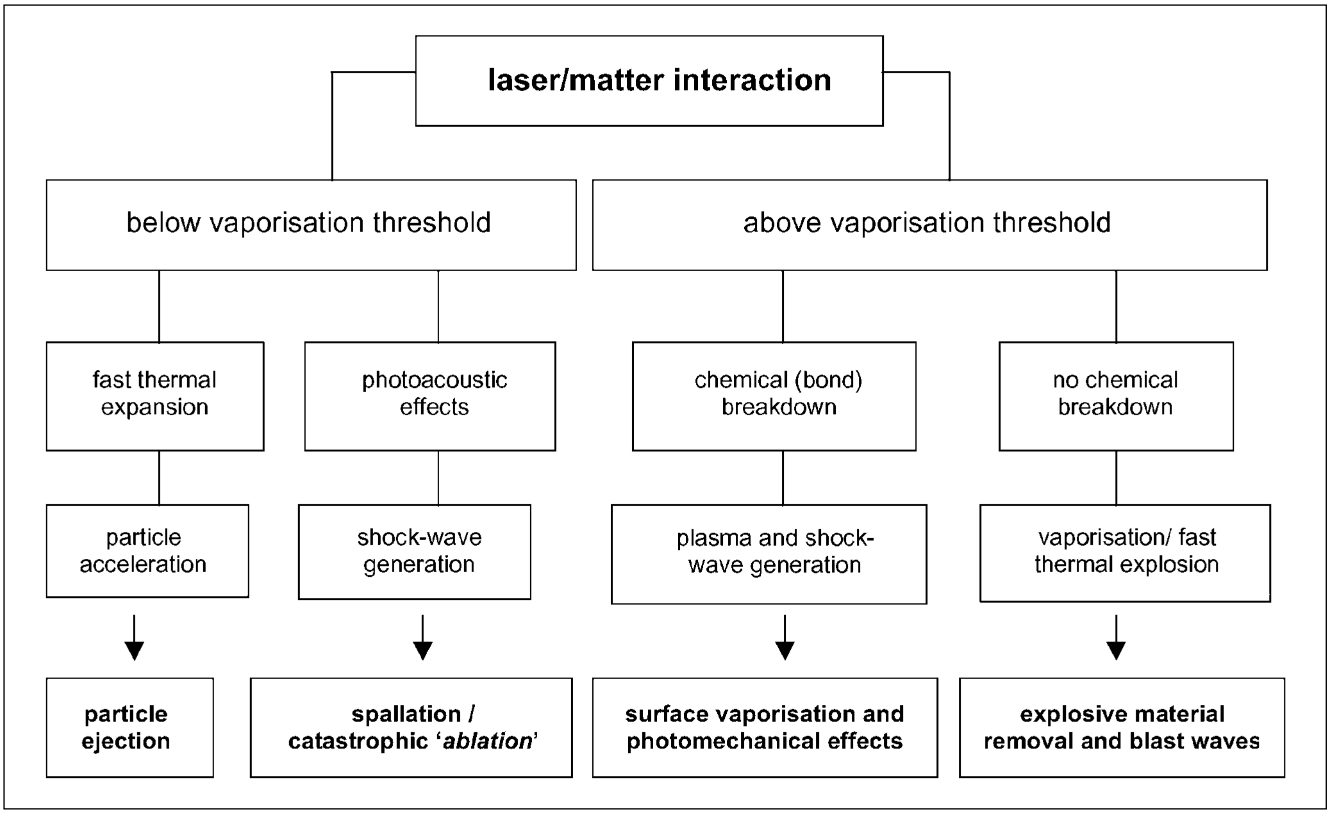

Fig. 3 Summary of current models and mechanisms of laser/matter interaction. (modified from [32])

$$\Delta T(0,t) = \frac{2F_0}{\kappa}\sqrt{\frac{Dt}{\pi}}$$

F_0 is the absorbed laser intensity given by $F_0 = (1\text{-}R)\ I_0$; R is the surface reflectivity; I_0 is the incident laser beam flux; κ is the thermal conductivity; and D is the thermal diffusivity

$$D = \frac{\kappa}{\rho C}$$

Density is ρ and C is the heat capacity at constant pressure. The penultimate equation has been used to predict fluence thresholds for thermal damage of stone substrates [6, 8]. Asmus' ΔT calculations give somewhat similar results to the first equation in this series – that for temperature rise – which is used to evaluate approximate temperature rise in strongly absorbent substrates [4].

Photoacoustic models

The most recent models of laser/matter interaction and energy relaxation consider that short and ultra-short (nanosecond to picosecond) pulses induce very different effects when compared with millisecond (ms) and microsecond (μs) pulses. Nanosecond pulses, which are typically produced with Q-switched Nd:YAG lasers, induce only slight thermal effects on the stone substratum. However, it has been reported that shock waves are generated upon ns laser-pulse irradiation of encrusted marbles [31]. The Asmus and Tam models cannot be applied in these cases, especially when optically transparent dielectrics such as quartz (e.g. a main phase in sandstones) and calcite (e.g. a main phase in marbles) are the target materials. Little thermal effects occur when dielectrics are irradiated with nanosecond Nd:YAG pulsed lasers [20, 73-75]. Photoacoustic effects may also result from diffraction at cleavage steps [75, 76], defect-mediated selective light energy absorption [77-79] and internal reflection leading to increased fluence at the crystal rear-side [20, 75, 76]. Furthermore, absorbent impurities such as iron oxides, commonly present in sandstones or marbles, may induce thermal effects. Such effects cause catastrophic ablation of dielectric materials (e.g. fracturing and the removal of crystal grains) at fluences below the ablation threshold [50, 80, 81]. These phenomena will require further research in order to deepen our understanding of laser/stone interaction.

A recent model of surface cleaning of marble using Nd:YAG lasers with ns pulses was proposed by Siano *et al.* [31]. It viewed thermal effects as irrelevant because of the low absorption coefficient of calcite to near infrared (NIR) radiation. Instead, plasma plume generation upon laser-encrustation interaction resulted in the vaporisation of the latter and in shock-wave propagation. It was concluded that short-pulse laser cleaning using NIR radiation was almost entirely photomechanical. However, some damage was detected. Damage such as marble roughening [82] was produced by the interaction between blast waves and the substratum. Siano *et al.* have since published a model of blast wave stress associated with laser ablation [83].

Other models have been proposed as explanations of laser/matter interaction under highly specific conditions [6, 32]. This is the case for picosecond and shorter femtosecond pulses [27]. The implications of these new developments in laser technology for the cleaning of works of art have yet to be explored. Figure 3 summarizes the current models and mechanisms of laser/matter interaction, reflecting the effects on irradiated targets.

Instrumental and analytical techniques for the study and quantification of the effects of laser radiation

The use of laser radiation for conservation cleaning would, ideally, be a self-limiting process when working with either NIR or visible radiation. This is the case when the ablation threshold for the removal of the superficial crust is significantly lower than the ablation threshold that would cause damage to the base material. The fluence for the actual treatment would be adjusted to fall within the range of the ablation threshold.

Since threshold values vary for each material and also depend on the specific working conditions, tests should be performed prior to each treatment. Klein *et al.* [84] give an example for the treatment of sandstone using a Nd:YAG laser at 1064 nm wavelength (5-7 ns FWHM). The fluence threshold for the removal of the superficial black crust was 0.85 ± 0.04 J/cm^2, while no damage was done to the sandstone until reaching a fluence of 1.25 ± 0.06 J/cm^2. Therefore, safe treatments can be carried out using fluences in the range of 0.85 ± 0.04 J/cm^2 and 1.25 ± 0.06 J/cm^2. Nonetheless, photoacoustic effects triggered by plasma formation or heat transfer from the black crust can cause damage to the substrate at a fluence below the damage threshold of the clean material.

To determine the threshold fluence, which causes damage to the base material, a detailed characterisation of the material is required both before laser application and upon its completion. Laser radiation can affect chemical and/or physical properties. Several analytical techniques should be combined in order to detect changes in colour, surface morphology, texture, crystallinity and chemical or mineralogical composition.

Unfortunately, not all laser-cleaning processes are self-limiting and on-line control may be required during application to avoid damage to the base material. This is the case when the ablation threshold for removing the superficial crust is largely identical to the ablation threshold that causes damage or ablation to the base material. (For example, granites containing biotite strongly absorb NIR radiation.) This effect is more evident when using UV radiation. Thus, continuous monitoring during laser cleaning may be necessary, using, for example, spectroscopic analysis to determine the elemental composition of the plasma emission. Pre-testing is necessary to determine the differences between the elemental composition of the superficial crust and the base material, and to identify certain elements whose appearance or disappearance (increase or decrease) indicate the completion of the cleaning process [48].

García *et al.* [85] noticed that the fluence threshold for the removal of the superficial crust could vary as the cleaning process proceeds. The action of laser radiation on the base material would seem to depend on its capacity to absorb optical energy, which in turn is influenced by its chemical composition. The authors found that the relative concentration of constituents varies in depth, causing changes in the absorption of energy as the cleaning process moved forward. Thus, it is possible that the nature of the laser cleaning process changes from self-limiting to non-self-limiting, or vice versa, in the course of the treatment. Since fluences below the ablation threshold of the base material can cause chemical and structural modifications [84], more experience is needed regarding the long-term effects of laser radiation.

Techniques for monitoring self-limiting laser-ablation processes

Common analytical techniques for the evaluation of laser-induced alterations on the stone surface include scanning electron microscopy (SEM) either alone or coupled with energy dispersive X-ray analysis (SEM-EDX), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and optical microscopy (OM). Researchers have also studied possible changes in the water-vapour diffusion behaviour following laser treatment.

Maravelaki *et al.* [86] evaluated the effects of laser cleaning on Istria stone (limestone) and found that SEM can be used to detect changes after laser treatments at elevated energy densities (Nd:YAG laser, λ = 1064 nm, normal and Q-switched mode, 16 J/cm^2). Vitrification spreading over the surrounding areas, the presence of fissures and the appearance of small grains were observed. SEM also shows a relation between damage caused by radiation and crust morphology. The removal of thick crusts causes more severe damage than the removal of thin ones, even without variations in operating conditions. Maravelaki *et al.* admit, however, that SEM does not allow for complete verification of the radiation effects and that additional techniques are required in order to study surface alteration more thoroughly. They propose Rutherford backscattering (RBS) and X-ray photoelectron spectroscopy (XPS) analyses to verify the products of the vitrified layer.

Vergès-Belmin [87] has proposed using the naked eye to determine colour, homogeneity, cleanliness and the aesthetics of cleaning when comparing cleaned and uncleaned limestone samples. This author employed colorimetry (L*a*b* values) and stereo microscopy to evaluate the precision of naked-eye observations. Petrographic microscopy was used to identify the superficial layers of the thin sections, their mineralogical composition and microstructure, and to examine the sample surface after laser cleaning. SEM analysis made it possible to study structural details of the thin sections as well as the surface morphology of cleaned and uncleaned stone samples. The chemical composition of the superficial layers was determined using SEM-EDX. Additionally, Vergès-Belmin studied the surface roughness of limestone by observing silicon moulds of treated and untreated samples under a binocular microscope and using raking light.

Wiedemann [88] evaluated the effects of laser treatment on sandstone by means of visual inspection, light microscopy and SEM analysis. SEM-EDX analysis was used to determine certain elements (Cl, P, S, Fe, Mg and K) which were not present in the composition of the sandstone and whose quantities gradually decreased during the cleaning process. Capillary water permeability using a Karsten tube and vapour-diffusion resistance following DIN 52615 were also determined before and after cleaning.

Gobernado-Mitre *et al.* [30] used SEM and OM for morphological studies and XRD to identify the mineral phases that form the limestone samples, mainly dolomite and gypsum. FTIR and micro-Raman spectroscopy confirmed the presence of dolomite and gypsum. Using SEM-EDX to detect K and Al, Gobernado-Mitre *et al.* concluded that the stone might have overpainting that contains potash alum. SEM analysis of treated and untreated surface areas in this instance revealed that laser cleaning produces no morphology perturbations. SEM-EDX has shown that the relative concentration of dolomite and quartz does not change upon cleaning. However, gypsum concentration increases in cleaned areas and K and Al concentrations significantly decrease when fluence thresholds are exceeded. Gobernado-Mitre *et al.* also conducted ablation rate studies by recording the penetration depth and number of pulses at different fluences. Penetration depth was then measured using an optical microscope.

Maravelaki *et al.* [89, 90] have used SEM-EDX to determine the elemental composition of the encrustation and the underlying marble. This technique has been applied to monitor the concentrations of Fe, Al and Si during the laser ablation process. The enrichment of these elements is due to atmospheric pollution and their concentrations significantly decrease upon laser cleaning. SEM and FTIR analyses have shown the coexistence of gypsum and calcite on the marble surface, with gypsum concentration decreasing over the course of the treatment. SEM and OM analyses have revealed differences in the crystal morphology of the inner and outer gypsum layer. If the outer darker layer, which contains aluminosilicate minerals, is completely removed, the inner layer, which covers the marble sculpture details, should be preserved. It was determined that the inner layer is reached with significant reductions in Si, Al and Fe. In addition to the above-mentioned techniques, Maravelaki-Kalaitzaki *et al.* [91] have performed XRD analysis to determine the mineralogical composition of the encrustation on Pentelic marble before and after laser treatment. FTIR and XRD analyses have revealed that calcium sulphate dihydrate (gypsum) is partly transformed into hemihydrate and anhydrite following irradiation with an excimer laser. Maravelaki-Kalaitzaki *et al.* used SEM and OM observations of thin-sections to ensure that encrustations are removed to an acceptable level during laser cleaning.

García *et al.* [85] have studied limestone samples from the façade of the 'Las Francesas' church at Valladolid (Spain) both before and after Nd:YAG laser cleaning. This limestone exhibits different forms of alteration phenomena such as black crusts, cracks, micro-fissures along with the presence of lichens and moss. Calcite, gypsum and quartz are the main minerals and were identified using XRD and micro-Raman spectroscopy. The presence of gypsum is due to a degradation process in which calcite reacts with atmospheric SO_2. The depth of the material removed during cleaning was determined by means of OM. The maximum depth, which was 0.2 mm, is similar to the natural roughness of this limestone. SEM microphotographs of the dirty surface/clean surface interface were used to determine both changes in morphology and roughness, and possible vitrification. No changes in texture, crystallinity, relief or porosity were detected. SEM-EDX, laser ablation optical emission spectroscopy (LA-OES) and laser induced breakdown spectroscopy (LIBS) were applied to determine the chemical compositions of cleaned and uncleaned areas. LIBS analyses were performed primarily using a NIR Nd:YAG laser, although an excimer laser was used as a second probe to improve LIBS spectra quality [92]. SEM-EDX analysis showed that S concentrations increased during cleaning, while concentrations in Al and K became lower. This double trend revealed what appears to be a sulphated layer. The cleaned surface was mainly comprised of Ca and Si. Comparing the clean reference stone and dirty samples, LIBS and LA-OES analyses confirmed that the Al, K and C composing the black crust can be attributed to urban pollutants. Colorimetry was used to measure chromatic coordinates ($L^*a^*b^*$) of treated and untreated samples. The L^* and b^* values increase in the treated samples and evidence the yellowish aspect often associated with laser-treated surfaces. In the present case the yellow shade may be due to the sulphated layer, probably an original patina.

The research summarised in this section focuses on the use of analytical techniques to identify laser-induced changes, including damage to objects. Although not considered in the present review, attention should also be drawn to operator health risks of laser cleaning. One example of such research can be found in Feely *et al.* [93] who determined size and elemental composition of particulates using SEM and SEM-EDX.

Techniques for the monitoring of non-self-limiting laser-ablation processes

LIBS has been tested by numerous researchers as a new method for the monitoring of non-self-limiting laser cleaning treatments [48, 90, 91, 93, 94]. In addition, British researchers have applied acoustic monitoring to determine the completion of the laser cleaning process [95]. The acoustic signal can be used to help determine when the ablation has changed just by using the ear.

LIBS is an elemental analytical technique. A minute amount of material is ablated from the surface to be analysed and an intense laser pulse (e.g. Q-switched Nd:YAG or, preferably, KrF excimer laser) is used to produce a plasma plume above the surface. The ablated material is atomised and ionised. As the excited atoms in the plume decay, they bring about an atomic emission spectrum that is characteristic of the elements present in the plume. This technique requires no sample preparation and can be performed *in situ*. It is, however, a destructive technique: craters of a diameter of up to 0.05 mm have been found on sample surfaces following LIBS analysis [94]. When applied during a laser cleaning treatment, this destructiveness is not normally consequential. The same laser can thus be used for laser ablation and as a source of LIBS [90]. Klein *et al.* [48] have described a case in which LIBS was used successfully during laser cleaning of sandstone with an excimer laser. In a first step, two elements (Mg and Fe^{2+}) had been identified that were located mainly in the superficial crust. The concentration of these two elements was monitored during laser application and a significant decrease indicated the completion of the cleaning process.

Maravelaki *et al.* [90] have suggested combining LIBS and an ablation rate study in order to calculate the ablation depth per pulse (mm/pulse) versus fluence (J/cm^2). This combination can yield information regarding composition, depth and morphology of the crust, thus facilitating the choice of appropriate treatment parameters (fluence, number of pulses and overlap between adjacent spots) for specific types of encrustations. The ablation depth was calculated on the basis of profile and area meter measurements. This combined technique is also applicable to self-limiting laser-ablation processes and makes it possible to use above ablation threshold fluences in order to enhance cleaning efficiency. Klein *et al.* [84] found that optical or mechanical profile meters cannot be used to determine ablation depth since stone surface roughness and superficial crust cause significant technical interferences. A digital precision balance was therefore used to measure the ablated weight after irradiation of the surface material. The same authors found good agreement when they compared results obtained using LIBS and traditional analytical techniques (SEM-EDX, FTIR and OM). LIBS has been shown to be suitable for *in situ* monitoring and on-line control, and also enables multi-element analysis. The authors did however note poor detection sensitivity for some elements. It should be noted that LIBS works optimally when using an excimer laser (UV radiation), which is not a standard laser in stone cleaning. The terms *Laser induced plasma spectroscopy* (LIPS) and *laser ablation spectroscopy* refer to basically the same technique, which relies on the spectral analysis of the plasma generated by laser ablation [96].

Cooper *et al.* [95] applied acoustic monitoring to determine the completion of the laser-cleaning process. Rapid ejection of material from the surface of laser-irradiated black crusts creates a shock pulse in the air which is audible as a snapping sound and can be detected by a transducer. They used an oscilloscope to display the output from a simple dynamic coil microphone and found that the amplitude of the acoustic shock pulse decreases and that the shock pulse eventually disappears after removal of the superficial crust. However, in some cases a low amplitude acoustic pulse continues to accompany each laser pulse, indicating that the process is not entirely self-limiting. Cooper *et al.* found that there is a linear relationship between the amplitude of the acoustic shock pulse and the intensity of the spark produced after Nd:YAG laser irradiation. They used a second HeNe laser beam, which is scattered by the ejected particles and brought to a focus on a silicon photodiode. The intensity of the beam can then be monitored using an oscilloscope. Cooper *et al.* [97, 98] have also applied SEM and X-ray induced photoelectron spectroscopy (XPS), to analyse the structure and chemical composition of surface layers during laser cleaning.

Siano *et al.* [31] and Salimbeni *et al.* [32] have used different Nd:YAG lasers (λ = 1064 nm) to clean encrusted marbles (Carrara marble) and other calcareous stones. The lasers work in free-run mode and Q-switching mode with a pulse length that ranges from 200 µs to 6 ns. The propagation over time of shock waves induced by the plasma plume was recorded shadowgraphically using a pump-and-probe diagnostic set-up. Plume spectroscopy was performed to analyse the plasma plume composition. The two techniques have proven to be appropriate for on-line monitoring. The photomechanical effects of the plasma-induced shock waves were responsible for the roughness observed in the marble substratum.

Lee and Watkins [7, 99] have performed in-process monitoring of Nd:YAG cleaning of a variety of materials, including copper, marble and paper. Using acoustic emission and chromatic modulation measurements they conclude that this combination could provide a highly sensitive tool by which conservators can identify when the cleaning process is finished, before damage to the substratum begins.

Klein *et al.* [100, 101] have used LIBS for on-line monitoring of the plasma-plume composition of encrusted marbles cleaned with Q-switched Nd:YAG laser (λ = 1064 nm, 532 nm and 355 nm, τ = 7 ns). They reported marble yellowing when using the Nd:YAG fundamental wavelength. No significant yellowing was observed when the second and third harmonics were employed.

Bregar and Mozina [102] have applied optoacoustic on-line monitoring to the study of contaminant removal from a rough marble plate. They observed a significant reduction in signal amplitude as the process progressed and have concluded that this technique could be useful to estimate the number of pulses needed for complete surface cleaning. Jankowska and Sliweinski [103] also used on-line acoustic monitoring to evaluate Q-switched Nd:YAG laser cleaning of sandstone.

Yavas *et al.* [20] have utilized an on-line plasmon surface probe to measure shock-wave pressure and plasma plume photography to evaluate damage in single calcite crystals irradiated with Q-switched Nd:YAG laser (λ = 1065 nm, τ = 12 ns). It was observed that rear-side ablation of calcite crystals occurs at fluences far below normal fluence for front-side ablation. This observation may shed light on the nature of near infrared-induced damage to scarcely absorbent substrates such as marble.

A summary of techniques currently in use for monitoring laser/stone interaction can be found in Table 2.

Effects of laser radiation on stone

It is extremely important to determine which laser radiation threshold fluences cause damage during cleaning, mainly in non-self-limiting processes. A detailed characterisation of the material is essential both prior to and after laser application. Cooper [6] indicates that some of the energy in an incident laser beam is absorbed by the surface, depending on its absorptivity at a given wavelength, and converted to thermal or chemical energy. The beam power may be high enough for the absorbed energy to bring about a lasting effect on the material, depending on the threshold above which the beam causes a change on the surface.

The damage thresholds for stone largely depend on the main laser parameters (pulse energy, pulse duration and pulse frequency rate) and the irradiation conditions. Laser application is therefore safe only within a given range of values for these parameters. Outside this range a number of phenomena – such as melting, surface texture modifications and colour changes associated with chemical transformations – can affect the stone [104]. Irradiation

Table 2 Examples of techniques used to monitor laser cleaning of stone

technique	application	author and reference
Stereomicroscopy	• determination of changes in surface texture, e.g. study of surface roughness by observing silicon moulds under raking light	Vergès-Belmin [87]
Optical microscopy (OM) using transmitted and/or reflected polarised light	• interpretation of stratigraphy by observing cross-sections, e.g. thickness, composition of corrosion layers and substrate • detection of changes in surface morphology, e.g. vitrification, crater formation, discoloration • determination of mineralogical composition and microstructure by observing thin-sections • measurement of depth of removed material/penetration depth of each laser pulse to determine ablation rate	Vergès-Belmin [87]; Wiedemann [88]; Gobernado-Mitre *et al.* [30]; Maravelaki *et al.* [89, 90]; García *et al.* [85]
Scanning electron microscopy (SEM), secondary electron (SE)/ backscattered electron (BSE) image	• interpretation of stratigraphy by observing cross-sections, e.g. thickness of corrosion layer, substrate • detection of changes in morphology, e.g. vitrification, fissuring, crater formation, roughness • determination of size of particulates emitted during laser ablation	Maravelaki *et al.* [86]; Vergès-Belmin [87]; Wiedemann [88]; Gobernado-Mitre *et al.* [30]; Maravelaki *et al.* [89, 90]; García *et al.* [85]; Feely *et al.* [92]; Rojo [128]; Esbert *et al.* [125]
SEM with energy dispersive X-ray analysis (SEM-EDX)	• determination of changes in elemental composition of surface or cross-sections • determination of composition of particulates emitted during laser ablation	Vergès-Belmin [86]; Wiedemann [88]; Gobernado-Mitre *et al.* [30]; Maravelaki *et al.* [89, 90]; García *et al.* [85]; Feely *et al.* [92]
Laser ablation optical emission spectroscopy (LA-OES)	• determination of changes in elemental composition of surface	García *et al.* [85]
Laser induced breakdown spectroscopy (LIBS)	• determination of changes in elemental composition • on-line monitoring non-self-limiting laser cleaning treatments by observing changes in elemental composition of produced plasma	Anglos *et al.* [94]; Maravelaki *et al.* [90]; García *et al.* [85]; Klein *et al.* [48]; Klein *et al.* [100, 101]
X-ray diffraction (XRD)	• determination of mineralogical composition of encrustation/corrosion layers and substrate	Gobernado-Mitre *et al.* [30]; Maravelaki *et al.* [89, 90]; García *et al.* [85]; Rodríguez-Navarro *et al.* [129, 130]
Fourier transform infrared spectroscopy (FTIR)	• determination of changes in organic and inorganic compounds and mineral phases	Gobernado-Mitre *et al.* [30], Maravelaki *et al.* [89, 90]; Maravelaki-Kalaitzaki *et al.* [143]
Micro-Raman spectroscopy	• determination of changes in organic and inorganic compounds (chemical and structural identification of compounds using reference data)	Gobernado-Mitre *et al.* [30]; García *et al.* [85]
Laser induced fluorescence (LIF)	• on-line monitoring of non-self-limiting laser cleaning treatments by observing changes in elemental composition in inorganic and organic substances	Anglos *et al.* [94]; Gobernado-Mitre *et al.* [92]
Colorimetry (visible light spectroscopy)	• detection of changes in surface color and reflectance	Vergès-Belmin [87]; García *et al.* [85]
High-speed photography	• observation of interaction of laser beam and surface during treatment, e.g. material removal	Cooper [6]
Hygric tests	• determination of changes in capillary water permeability using Karsten tube and vapor diffusion resistance according to DIN 52615	Wiedemann [88]
Acoustic monitoring	• determination of the completion of laser cleaning process by monitoring the acoustic shock pulse	Cooper *et al.* [95]

on wet surfaces usually reduces the probability of thermal and mechanical damage, while increasing cleaning efficiency [6, 95, 104-106]. On the other hand, several authors including Biscontin *et al.* [107] and Siedel *et al.* [108] have pointed out that some physical properties of the material are modified after the application of laser radiation. In short, the effects of laser radiation depend mainly on type of material, laser parameters and conditions of application.

Urban pollution leads to rapid blackening and soiling of exposed stones with black crusts made of gypsum and particulate matter developing on the stone surface. Removal of the dark encrustations by pulsed laser has been thoroughly demonstrated. Much emphasis was put in the past on the prevention of damage to the stone substratum. More recently, however, attention has been drawn to the preservation of natural stone patinas [44, 109-113] and gypsum epigenetic crusts, which preserve the original stone relief [114]. Therefore, laser-induced damage refers not only to damage to the stone surface but also to the removal of patina and epigenetic gypsum. Recent literature emphasises that pulsed laser cleaning of stone is an alternative or a supplement to more traditional cleaning techniques, rather than being perceived as the conservators' 'silver bullet' [115-120].

Effects of laser cleaning on different types of stone

The following sections review the literature on the effects of laser cleaning in a variety of stone types and are therefore divided according to the type of stone being cleaned. The response of each type of stone material to the above-mentioned laser parameters is discussed.

The absorption of laser radiation and its effects depend mostly on the chemical and mineralogical composition of the stone. Specifically, iron is a highly absorbent element, particularly for Nd:YAG radiation at the fundamental 1064 nm wavelength. This is so due to the fact that the laser energy at 1064 nm corresponds to the electronic transitions in d orbitals of the third-row transition metals. Thus, the absorption efficiency of Nd:YAG laser energy depends primarily on the concentration of transition metals [121]. Chromatic modifications are usually attributed to changes in the different oxidation states of iron compounds. Most authors have also found that the use of a thin water layer enhances laser-cleaning efficiency while reducing side effects such as colour changes. On the other hand, damage thresholds also seem to depend on the type of laser and equipment. For instance, a new family of Nd:YAG lasers for conservation has emerged which enhance cleaning efficiency and reduce side effects. These new lasers use fibre optics to provide an homogeneous beam without the so-called 'hot spots' that appear in conventional lasers [122, 123].

Limestone and marble

Cooper *et al.* [97, 98] have measured the distribution of reflected laser radiation (Q-switched Nd:YAG; λ = 1064 nm, pulse length of 20 ns) for different stone surfaces and a reference sample. They calculate the proportion of incident laser radiation absorbed by both clean and polluted stone surfaces, finding that clean limestone (probably buff-coloured) absorb 20 to 30% of the radiation. White marble absorbs less than 10%, whereas polluted surfaces absorb up to 90%. After calculating the surface temperature rise using Asmus' equation [8], they concluded that in a fluence range of between 0.75 and 1.26 J/cm^2 there is a 100% probability of removing material from a black crust without damaging the clean stone.

Eichert *et al.* [124] have observed a blackening effect on veined marble when treated with Q-Switched Nd:YAG laser radiation at fluences as low as 0.45 J/cm^2. A linear relationship has also been observed between fluence and changes in parameters L* and b* (measured using a colour spectrometer). L* decreases and b* slightly rose with higher fluences, thereby confirming a slight darkening and a minute chromatic shift to yellow. Analysis using electronic paramagnetic resonance spectroscopy on calcite powder doped with Fe^{2+} has revealed an increase in Fe^{3+} after irradiation. The authors concluded that the blackening is caused by the oxidation of Fe^{2+} to Fe^{3+}. Since the marble was slightly transparent, they also suggest that increased blackening at higher fluences might be due to a deeper laser/substrate interaction as energy increased.

However, Esbert *et al.* [125, 126] have demonstrated that the presence of some elements or compounds (mainly Fe-rich compounds), which are sensitive to 1064 nm laser radiation, drastically affect the response of stone to laser irradiation. For instance, Macael marble from Almería in Spain was particularly sensitive to laser cleaning (e.g. darkening) because of the presence of micron-sized pyrite (FeS_2) crystals disseminated in the calcite grains.

Aldrovandi *et al.* [127] have detected a grey shade on some samples of white marble irradiated by two types of lasers. The first one was a Q-switched Nd:YAG laser (20 ns pulse), the second, a short free-running Nd:YAG laser with a medium-pulse width of 20 µs. The marble of the greyish samples contained very small fragments of pyrite that displayed appreciable changes after laser cleaning. Short-pulse laser treatment in this instance caused a mechanical effect similar to a micro-explosion of pyrite grains, while long pulses would probably lead to a thermal effect, such as melting and spreading of some particles on the surface. Rojo [128] found a chromatic change towards greyish tones on red and yellow limestones and attributed this change to a probable reduction in iron oxides.

Labouré *et al.* [105] have investigated the effects of laser fluence, spot area, frequency and water spraying on particle emission rate in limestones and sandstones. They tested different Q-switched Nd:YAG laser (λ = 1064 nm) devices, finding that laser-induced changes in colour were nearly identical for all of the devices at the same fluence. However, changes in colour depended on whether or not water was used: it was observed that dry cleaning left the stone greyer than wet cleaning.

Rodriguez-Navarro *et al.* [129, 130] have studied the influence of certain crystallographic parameters on laser cleaning of white marbles. They found that interaction between the Nd:YAG laser beam and the calcite crystals on the marble surface largely depends on crystal size and orientation and on laser energy density. Additional results suggest that in a crystalline aggregate such as marble, damage will not only take place within single crystals (e.g. in crystal defects and weakly-bonded cleavage planes) but will be particularly concentrated on grain boundaries. Fine-grained marbles with a strong crystal orientation will thus be more susceptible to laser-induced damage in very specific directions.

Biscontin *et al.* [107] have studied the effects of Nd:YAG laser radiation in free-running and Q-switched modes at several power levels on limestones and marble. They found that side effects are more evident in the Q-switched mode. Depending on the number of pulses and laser radiation power, the Q-switched mode led to greater surface roughness and to a smaller water/stone contact angle. Normal-mode radiation induced slight colour changes and punctual fusion. The authors point out that clay minerals (present in limestones) display unusual behaviour. After Q-switched laser radiation, even at low energy, clays display significant colour and morphological modifications. Under SEM examination the authors observed that laser radiation decreases clay layer thickness, due perhaps to partial fusion of the clays.

Maravelaki *et al.* [91] have used KrF (λ = 248 nm) and XeCl (λ = 308 nm) excimer lasers to remove encrustations from a marble. The KrF excimer laser was applied to both dendritic crusts and pure marble in order to determine ablation rates and damage thresholds. In contrast with the Q-switched Nd:YAG [90], results have shown that there is no energy range within which ablation becomes self-limiting. At 248 nm the energy density required to ablate marble was lower than that required for encrustation removal. On the other hand, they found that inversion of the absorption trends led to acceptable removal of thick dendritic crusts when using a XeCl excimer laser at an energy fluence of 2 to 4 J/cm^2.

Siedel *et al.* [108] have applied Q-switched Nd:YAG at different energy densities to clean sculptures made of an oolithic limestone. The surface was kept wet while cleaning. They found that increases of energy led to greater surface roughness and capillary suction.

Another effect described by several authors is the yellowing which some carbonate substrates display after Q-switched Nd:YAG laser cleaning. Klein *et al.* [100, 101] have proposed that nanometer-sized Fe spheres on a marble surface are a possible source of this yellowing. Vergès-Belmin and Dignard [131] found that this chromatic effect appears only as a result of soiling removal and not when clean substrates are irradiated. Nonetheless, the yellowing or darkening of clean marble following laser irradiation has been observed and seems to be related to photo-oxidation of micron-sized iron sulphide (pyrite) crystals disseminated in Carrara [127] and in Macael marbles [126]. Marakis *et al.* [132] have reported yellowing of Greek marbles following irradiation with Q-switched Nd:YAG laser at the fundamental wavelength. This undesired effect can be avoided by using the laser third harmonic (λ = 355 nm).

Sandstone

Calcagno *et al.* [133] have observed that black crust removal from sandstone surfaces is best achieved by using a Q-switched Nd:YAG laser, which produces ns pulses. The cleaning is selective enough to preserve the underlying patina.

Siano *et al.* [104] have reported a case of black crust removal from sandstone. Crust absorptivity is very high at the fundamental Nd:YAG laser wavelength. The sandstone tested was lithic arenite cemented by calcite with a yellowish to pale brown shade. In this instance, the colour depended on the quantity of iron oxides dispersed in the rock. The authors point out that iron oxides and ochraceous-altered framework grains (AFG), which derive from the alteration of previous mafic minerals, are the main optical absorbers at 1064 nm. Wet and dry surfaces of samples from a quarry and from a monument were irradiated; quarry specimens displayed darkening of the dry surfaces at a relatively low fluence. Darkening was confirmed by slight variations of the colour coordinates. The authors also observed a constant reduction of spectral amplitude for wavelengths above 500 nm, whereas in the blue region reductions were smaller. The most critical parameter appeared to be laser fluence. In this case threshold fluence was estimated at 4 J/cm^2. Surface darkening was associated with selective ablation of the yellowish calcareous matrix. This ablation exposes non-absorbing phases such as quartz and calcite. Some isolated microscale melting of AFG phases was also detected. Finally, a frequency-dependent invasive phenomenon appears that consists of a ‘red-shift’ in the irradiated area. None of the effects were observed in water-assisted conditions.

Siano *et al.* [104] found similar effects on dry samples from the monument. Under dry conditions, darkening was the most frequent effect and was associated with localised melting of AFG phases, red shift and vitrification. In this instance, darkening resulted from the removal of the calcareous cement, which includes limonite. The natural stone colour finally appeared through the filtering action of semi-transparent quartz and calcite grains. The fact that blue-component reductions were smaller than red ones was related to the reflectance of the exposed grains. Red shift and vitrification were considered thermal. Red shift is associated with the limonite-to-red hematite transformation, which occurs at 350-400°C and is accompanied by a significant loss in iron hydroxide water. The high temperatures generated by irradiation under dry conditions are related to vitrification, which requires at least 1000°C.

Siano *et al.* [104] used Asmus’ thermal modelling to explain this rise in temperature, as did Cooper *et al.* [97, 98], all of whom have indicated that water assistance prevents thermal side-effects up to the ablation threshold of the stone. Water absorbs no radiation at a wavelength of 1064 nm. Cooling is therefore mainly due to thermal exchange. Water has a specific heat that is five times higher than that of sandstone. Heat transfer from absorbing elements to surrounding water thus generates a significant decrease in average substrate temperature. If localised vaporisation around absorption centres occurs, it will be followed by an explosive removal of surface water, thereby efficiently cooling the irradiated volume.

Klein *et al.* [84] have studied the relation between ablation rate and wavelength and laser-induced damage to sandstone and arrive at similar results to those of Maravelaki-Kalaitzaki *et al.* [91] for marble. They have used excimer and Nd:YAG laser radiation for the ablation of a black crust on the sandstone. Test conditions were excimer KrF at 248 nm, Lambda XeCl at 308 nm, Q-switched Nd:YAG at 1064 nm and Q-Switched Nd:YAG at 355 nm. These four wavelengths were employed to remove black encrustations and to ablate the underlying sandstone. Threshold fluences were 0.85, 0.89, 0.7 and 0.56 J/cm^2 for the black crust and 1.25, 0.95, 0.92 and 0.59 J/cm^2 for the sandstone in each of the tested conditions. The fluence threshold for the black crust and the stone were separated by a gap of approximately 0.4 J/cm^2 at 1064 nm. This result suggests that the cleaning of the black crust was efficient without damaging the sandstone. However, a slight colour change of the cleaned sandstone was detected and the authors have indicated that a removal mechanism other than ablation can cause a loss of stone particles. At 248 nm threshold fluences for black crust (0.56 J/cm^2) and stone (0.59 J/cm^2) were lower. The gap between the fluence thresholds was also lower. It was pointed out that neither of the excimer wavelengths (248 and 308 nm) are appropriate for practical cleaning, regardless of the overall cleaning results. This is due to difficulties in the handling of excimer lasers and in their application to large surfaces.

Some minerals such as mica and red iron oxide are highly absorbent at 1.06 µm. Therefore Q-switched Nd:YAG laser cleaning of granite and red sandstone must be carried out carefully to ensure that these minerals are not altered or removed after radiation [6]. For instance, removal of red iron oxide or modification of the oxidation state can bleach red sandstone. Sandstone 'cement' often contains several components which are highly absorbent at 1.06 µm. Cooper [6] mentions the possibility of using different wavelengths as a solution to these problems.

Other authors have used Nd:YAG lasers to clean sandstones, reporting good results (e.g. removal of contaminants without damage to the underlying substratum) [134]. However, these results cannot be readily compared with others since reported laser parameters are incomplete. No information on pulse length, for instance, is given and therefore calculation of laser-power density from reported laser fluences cannot, as yet, be done.

Granite

Rojo [128] and Esbert *et al.* [126] have found some alterations in granite after irradiation with a Q-switched Nd:YAG laser at 1.06 µm. Granite minerals respond differently to this laser energy. Biotite was found to be the most highly affected mineral, displaying melting, vitrification and colour changes to lighter tones. Thermally-induced brittle fractures with cleavage-stepped surfaces were observed in quartz, while feldspars underwent material removal and occasional melting; pinkish microcline (potassium feldspar) became whitish. Goretzki [135] concluded that laser cleaning is unsuitable for porphyry because a change in colour occurs even at low energy densities.

The effects of laser radiation on the above-mentioned stone types have been summarised in Table 3.

Concluding remarks

Stone materials undergo significant weathering when exposed to pollutants and the resulting darkening, soiling and development of black crusts should be eliminated both for aesthetic reasons and for the purposes of conservation. Graffiti, oxidation stains and biological films also cause chromatic and visual changes that should be handled through cleaning. As opposed to conventional mechanical and chemical cleaning methods, the pulsed laser has significant advantages when used to remove particulates and encrustations from decayed stones. The non-contact and selective nature of laser/matter interaction, as well as the sometimes self-limiting character of the laser-cleaning process, has made this a preferred technique for conservators for a number of stone cleaning interventions. Cleaning with micro- and nanosecond near-infrared pulsed lasers using Q-switched Nd:YAG commercial devices has become, in recent tests and *in situ* conservation applications, the most commonly used laser technique for a wide range of stone types. However, limitations resulting from the high absorptivity of certain minerals, such as biotite in granites, suggest that wavelengths other than the fundamental 1064 nm should be tested for specific cleaning interventions. This is especially evident in marbles in which yellowing occurs at 1064 nm, but not at visible or UV radiation. This effect points to the possibility of using Nd:YAG laser at second and third harmonics.

The ultimate mechanism of laser/matter interaction (e.g. absorption) and relaxation will require further research in order to better understand the substrate damage that is associated with laser cleaning of dielectrics (e.g. quartz, calcite, feldspars and dolomite). These are the major phases in most ornamental stones (e.g. marble, sandstones, limestones and granites). Among other emerging topics, future research should explore:

- the role of crystallographic defects, metal inclusions and grain boundaries in selective light-energy absorption
- the role of laser-beam internal reflection in promoting the so-called 'rear-side' ablation and the implications of this effect for laser cleaning of stones
- the possible role of laser-light diffraction at cleavage steps in increased local fluence and substrate damage
- the effects of laser self-focusing upon laser-particle interaction

A model considering these effects and predicting laser/matter interaction has yet to be developed.

On-line monitoring of laser cleaning using various analytical techniques is becoming a common procedure for evaluating the effectiveness of cleaning, while simultaneously helping to prevent damage to underlying substrata. This is highly important since the ideal self-limiting nature of the laser-cleaning process is not as universal as previously assumed.

Another issue that has recently required attention is the possible health risks linked to the use of lasers as cleaning tools for stone artefacts. The interested reader should see the recent review by Vergès-Belmin *et al.* [136].

Table 3 Effects of laser radiation on stones

stone	type of laser	fluence threshold (J/cm²)	observations	author and reference
limestone	*generally:* Q-switched Nd:YAG (λ = 1064 nm, τ = 6-10 ns) *occasionally:* normal mode Nd:YAG (λ = 1064 nm, τ = 100 µs) Excimer laser (KrF, λ = 248 nm, τ = 30 ns)	Q-switched Nd:YAG: around 1.2-1.3 usually safe < 1 cleaning of black crust from 0.1-0.4 sometimes cited thresholds > 5 normal mode Nd:YAG: 7 Excimer: 7	colour variations: to yellowish and grayish, related to changes in the oxidation state of iron compounds (mainly reduction); morphological variations; vitrification and melting; changes in physical properties: capillarity and contact angle	Cooper [6]; Cooper *et al.* [95, 97, 98]; Biscontin *et al.* [107]; Maravelaki *et al.* [86]; García *et al.* [67, 68, 85]; Gobernado-Mitre *et al.* [30, 92]; Siedel *et al.* [108], Labouré *et al.* [105]; Esbert *et al.* [125]
marble	*generally:* Q-switched Nd:YAG (λ = 1064 nm, τ = 7-20 ns) *occasionally:* short free running Nd:YAG (λ = 1064 nm, τ = 20 µs) Excimer lasers (KrF, λ = 248 nm, τ = 30 ns, and XeCl, λ = 308nm, τ = 28 ns)	Q-switched Nd:YAG: < 1.5 non self-limiting 1.5-2 others found self-limiting 2-4 (when presence of black crust) short free running Nd:YAG: 2-4.5 Excimer KrF: 0.9-2.2 Excimer XeCl: 0.5-2.4	colour variations: blackening (even at 0.4 J/cm²) and grayish alteration due to oxidation of Fe^{2+} and mechanical effects on pyrite grains; changes in physical properties: contact angle	Cooper [6]; Cooper *et al.*[97, 98]; Biscontin *et al.* [107]; Maravelaki *et al.* [89, 91], Eichert *et al.* [124]; Aldrovaldi *et al.* [127]; Siano *et al.* [104]; Sabatini *et al.* [44]; Rodriguez-Navarro *et al.* [130, 131]
sandstone	Q-switched Nd:YAG (λ = 1064 nm, τ = 5-7 up to 10 ns) Q-switched Nd:YAG (λ = 355nm, τ = 5-7 ns) Excimer XeCl (λ = 308nm, τ = 28 ns) Excimer KrF (λ = 248nm, τ = 30 ns)	Q-switched Nd:YAG (λ = 1064 nm): around 1.2-1.3 sometimes 3-4 Q-switched Nd:YAG (λ = 355 nm): 0.95 Excimer KrF: 0.59 Excimer XeCl: 0.92	colour variations: bleached surface and changes in the red component; change in the oxidation state of the red iron and water loss by iron hydroxides; darkening by removal of cement with limonite; vitrification; Nd:YAG laser more appropriate than Excimer KrF laser	Calcagno *et al.* [133]; Cooper [6]; Klein *et al* .[48] ; Labouré *et al.* [105]; Siano *et al.* [104]
granite	Q-switched Nd:YAG (λ = 1060 nm, τ = 7 ns)	0.5 up to 1.25	different response depending on the mineral; mica absorbs strongly at 1064 nm; melting and vitrification; in quartz, fissuring and thermal/brittle fracture, with cleavage-stepped fracture; feldspars, material ablation	Cooper [6]; Rojo [128]; Esbert *et al.* [125, 126]
general comments	Damage threshold depends on the type of laser and the equipment. Absorption of laser radiation depends on the chemical composition of the stone and minerals. Iron is a highly absorbing element at 1064 nm. Changes in colour are usually attributed to changes in the different oxidation states of iron compounds. Water improves laser cleaning.			

It should be noted that pulsed laser cleaning of stone has undergone extensive research and *in situ* applications since the first international conference on laser cleaning of artwork was held in 1995 (LACONA I). Thereafter Cooper [6] published an early overview on laser cleaning in conservation. However, publications in specialised journals over the last six years, as well as subsequent LACONA conferences – II in 1997 [in press], III in 1999 [137] and IV in 2001 [138] – have drawn much attention to the topic in both material science and conservation communities. As a result, publications have increased exponentially. This overview clearly shows that much progress has taken place, but it also shows that many questions remain open, such as suitability, limits of application and optimal parameters for safe use in conservation [139]. On-line monitoring techniques used to identify the end of the cleaning process and the beginning of damage to the substrate must be tested and optimised for routine work in laser cleaning interventions. Finally, the recent development of pico- and femtosecond high-power lasers and of new lasers with variable pulse lengths in the μs to the ns range [140-143], as well as the use of optical fibres to deliver the laser beam to the target material [132, 133], will require more detailed research. New development coupled with ongoing research will allow for the future widespread use of lasers in conservation.

Acknowledgements

This work has been financed by grant No. 1FD97-0331-C03-01 from the Spanish government, Comisión Interministerial de Ciencia y Tecnología (CICYT), and by Research Group NMR 0179 of the Junta de Andalucía (Spain).

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Authors

The present paper is the product of a joint project carried out by Carlos Rodríguez-Navarro*, Kerstin Elert and Eduardo Sebastián of the University of Granada and Rosa Maria Esbert, Carlota Maria Grossi, Araceli Rojo, Francisco Javier Alonso, Modesto Montoto and Jorge Ordaz of the University of Oviedo (Spain). The research group, 'Study and Conservation of Construction Materials in the Architectural Heritage', was created in 1988 and is part of the Department of Mineralogy and Petrology at the University of Granada. It includes geologists (CRN and ES) and conservation scientists (KE). The research group from the Geology Faculty of the University of Oviedo has also been pioneering studies of stone decay and preservation in Spain. Its members have a background in applied petrology. The research activities of both groups include laboratory and on-site investigations of natural stones and artificial building materials found in historical buildings. Recently, they were awarded an EU-Spanish government grant to study the application limits of laser cleaning on ornamental stones. As part of this research several articles have already been published.

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