Role of marble microstructure in near-infrared laser-induced damage during laser cleaning

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When marble is cleaned by nanosecond neodymium yttrium–aluminum–garnet lasers (1064 nm), strongly absorbing surface contaminants are removed at fluences substantially below the damage threshold for the much less absorptive marble substrate. Recent studies have shown, however, that unacceptable roughening of the marble surface also may occur at low fluences due to removal of individual grains. In order to elucidate this effect, we have compared the low-fluence response of marbles with two different grain sizes and single-crystal calcite, in the fluence range 0.12–1.25 J cm⁻². Damage was greater in fine-grained than coarse-grained marble, and did not occur in the single-crystal calcite at these fluences. The temperature rise following defect-mediated absorption triggers thermal plasma emission and generates shock waves; the concomitant surface damage depends on the size and crystallographic orientation of the crystals. Laser irradiation anneals the defects and increases “crystallite size.” The implications for the laser-assisted cleaning of marble artworks are outlined. © 2004 American Institute of Physics. [DOI: 10.1063/1.1649811]

I. INTRODUCTION

The deposition of contaminants on marble artifacts causes soiling and dark encrustations (the so-called “black crusts”) which endanger the survival of many valuable pieces of architectural and sculptural heritage. This has become a major problem in polluted urban centers. In addition to their significant aesthetic impact, dark surface layers contribute to the damage of these artifacts by fixing gaseous pollutants (i.e., SO₂ and NOₓ) in the form of detrimental sulfates and nitrates. The carbonate minerals composing marble are particularly sensitive to pollutant-mediated secondary phase precipitation (e.g., gypsum) and the development of black crusts. This has led in recent times to an exponential acceleration in the decay of marble artworks. Many cleaning methods have been developed and used with varying degrees of success to remove surface pollutants and dark encrustations from marble, thus preventing further damage. Conventional cleaning methods are based on mechanical or chemical techniques, such as high-pressure gas or solid particle jets (e.g., sandblasting), scrubbing, ultrasonics, and wet chemical flux or poulticing. Recently, pulsed laser radiation has been adopted as a promising cleaning procedure for many ornamental materials including marble sculptures and artworks.

Laser-assisted marble cleaning uses the differential absorbance of dark encrustations and the underlying marble substrate for near-infrared (NIR) laser radiation. The dark deposits are more absorbent than the light colored marble and are therefore selectively removed. At 1064 nm, the fundamental wavelength of a neodymium yttrium–aluminum–garnet (Nd-YAG) laser, which is the standard laser in today’s stone cleaning, a typical black crust absorbs ~90% of the incident radiation, whereas a typical clean white marble absorbs only ~6%–10%. Once the crust has been removed, it is assumed that laser radiation does not damage the poorly absorbent calcium carbonate substrate. Thus, the laser cleaning process is often described as “self-limiting,” and offers substantial advantages for artwork conservation over other conventional techniques. It is a selective, precise, versatile, noncontact method, has no significant impact on the environment, and can in most cases be precisely controlled to prevent damage to the underlying substrate. However, overexposure to the laser pulse may easily lead to substrate damage if the laser fluence exceeds what is know as the “damage threshold.” In fact, damage to the marble substrate has occurred even while using low, supposedly safe, fluence values (i.e., fluence ~2–4 J cm⁻²). Neither melting nor substrate vaporization has been observed in these cases. However, so-called “catastrophic ablation” occurred; i.e., the fracturing and loss of parts or whole calcite grains. This is unacceptable in art conservation, mainly because substrate damage results in roughening (i.e., surface area increase) which accelerates material decay.

A thorough understanding of the relationship between material properties and laser–material interaction is needed to prevent damage to artwork. Marble, one of the most relevant materials in artwork conservation, is a rock made of carbonate crystals (most commonly calcite) that has undergone metamorphism. Metamorphism of calcitic marble includes deformation and transformation processes upon pressure and temperature rise. Metamorphism brings about a large number of crystal defects (e.g., point and line defects), preferred orientation, and recrystallization of calcite crystals. It is known that optical absorption of transpar-
ent wide band-gap materials (e.g., calcite) is strongly connected with crystal defects. However, the role of such defects on laser cleaning of ornamental marble has never been explored. Nor have the effects of other microstructural characteristics, such as grain size and crystal orientation, on laser induced damage been examined. Given that calcite is a highly anisotropic crystal, the laser–crystal interaction should depend on the orientation of the (hkl) planes facing the laser beam. On the other hand, since grain size is a major microstructural feature controlling material strength, it can be influential in laser induced damage.

Our goal was to determine the influence of marble microstructural features, such as crystal size, crystal defects, and crystallographic orientation on laser-induced damage to marble artifacts. To this end, marble slabs with different microstructural properties and optical quality “Iceland spar” crystals cut along different crystallographic directions were irradiated with nanosecond, 1064 nm Q-switched Nd:YAG laser pulses. Optical microscopy (OM), scanning electron microscopy (SEM), and x-ray diffraction (XRD) were used to evaluate the surface damage of laser irradiated samples and to infer how catastrophic ablation may occur in calcite.

II. MATERIALS AND EXPERIMENTS

Two common white marbles were selected. One is from Macael (Spain), a coarse grained (1.5 mm average grain size) marble with a strong crystallographic preferred orientation of calcite crystals due to extensive low-grade metamorphic deformation. The other is from Carrara (Italy), an fine grained (0.15 mm average grain size), and shows no crystallographic preferred orientation of calcite grains due to extensive annealing and recrystallization. Macael and Carrara marble plates (3.5 × 2.5 × 0.3 cm) were cut with a low-speed diamond saw and their larger surfaces were polished to eliminate any roughness or heterogeneities caused by the cutting procedure. Any residual polishing powder (γ-Al₂O₃) was carefully eliminated by thorough washing with ethyl alcohol.

Calcite plates (3 × 2 × 0.2 cm) with different crystallographic orientations were cut from single crystals of optical-quality Iceland spar. Crystals were oriented along one crystallographic direction, i.e., (001), (401), (100), or (110), using a Laue back-reflection diffractometer (Multiwire Lab. Inc.). The hkl Miller notation is used throughout for the sake of simplicity, although the hkl Miller–Bravais notation would be more accurate for calcite: i.e., hexagonal unit-cell, space group R₃c. Once the crystal orientation was selected, the crystal surface perpendicular to the selected crystallographic direction [i.e., (001), (104), (100), and (110) planes] was faced off using a polishing disk. The crystals were then attached to a holder by the polished face and parallel plates were cut out using a low-speed diamond saw.

Marble slabs and Iceland spar calcite plates, both clean (i.e., thoroughly washed in ethyl alcohol) and covered with an artificial dark layer simulating a black crust, were irradiated using a commercial Q-switched Nd:YAG laser (Laser Sistemas Integrados, model LSI R-100). The artificial black crust was ~100 µm thick with a composition (wt. %) of 16% CaSO₄·2H₂O, 19% carbon black, 26% Ca(OH)₂, and 39% CaCO₃, mixed with water and left to set for 72 h.

The laser beam has the fundamental wavelength (λ = 1064 nm), a pulse width of 7 ns [full width at half maximum (FWHM)] and a pulse repetition rate of 20 Hz. The maximum pulse energy output was 356±7 mJ (measured using a pyroelectric energy meter). Pulses were applied near normal to the sample surface, in air and under dry conditions. Burn-paper measurements of the laser spot allowed evaluation of the beam impact area. Only the darker central area of the impact (5 mm diameter) was used for laser fluence calculations (computed by dividing the energy by the irradiated area). The darker central spot closely represented the FWHM of the Gaussian shaped pulse. The fluence was set between 0.12 and 1.25 J cm⁻² by changing the pump voltage of the laser device. Irradiation of burn paper showed that the laser spot geometry remained constant at all working fluences. The marble and Iceland spar plates were placed on a X–Y stage to allow the laser beam to scan the surface. The average number of pulses irradiating on the same spot (i.e., the beam superposition) ranged from 5 to 10 for clean and dark-layer covered samples, respectively.

XRD analyses of marble pieces and calcite monocrystals before and after laser irradiation were performed using a Philips PW-1710 diffractometer with an automatic slit, Cu Kα radiation (λ = 1.5405 Å), 20°–70° 2θ explored area, with steps of 0.028° 2θ and 0.01° 2θ s⁻¹ goniometer speed. The sample area contributing to XRD was determined by irradiating a standard Philips x-ray fluorescent slab at 20° and 70° (2θ). It ranged from 2.10 cm² (70° 2θ) to 2.24 cm² (20° 2θ). Thus, the average number of calcite grains contributing to XRD was ~100 and ~9700 for Macael and Carrara marble, respectively. These values ensured that calcite crystal orientations determined by XRD were statistically representative.

The sharpness of Bragg peaks, i.e., the peak FWHM, is an indication of “crystallite size” (i.e., coherent x-ray scattering domains in a “mosaic-like” single crystal) and strain-related lattice distortions. The strain contribution reflects the abundance or density of slip and screw dislocations, which promote the formation of point defects. In practice, peak broadening gives an estimate of point and line defect density. “Crystallite size,” Dₜₜ, (including lattice distortions) was thus calculated using the Scherrer equation:

$$D_{\text{hkl}} = \frac{K\lambda}{\beta \cos \theta},$$

where K is the crystallite-shape factor, with a value approximately equal to unity (most commonly 0.9), λ is the x-ray wavelength, β is the x-ray diffraction broadening (i.e., Bragg peak FWHM, in radians), and θ is the Bragg angle.

Polarizing light microscopy (Zeiss–Jena, model Jenapol-V) and SEM (Zeiss DMS 950) collecting secondary, and backscattered electron images were used to study topographic/textural changes due to laser irradiation (i.e., damage).

NIR (800–2000 nm) diffuse reflectance spectra (DRS) of both Iceland spar and white marble plates were obtained.
using a Cary 5E spectrophotometer. Reflectivity at 1064 nm was used for calculating substratum temperature increase following laser irradiation.

III. RESULTS

A. Visible observations

Visible flashes of light (accompanied by a snapping sound) were detected following each laser shot on marble and Iceland spar surfaces, their intensity decreasing after a number of shots (5–10). The flashes were most intense in samples covered with the dark layer. However, upon the complete removal of this layer less intense flashes were still produced and were similar to those observed in the uncovered samples. Flash intensity was positively related to the laser fluence: i.e., the higher the fluence the higher the snapping sound and flash intensity (qualitative estimations).

B. Microscopic observations

Optical microscopy and SEM observations of laser irradiated Macael and Carrara marbles showed cracking, fragmentation and loss of surface calcite crystals (Figs. 1 and 2). This effect took place regardless of the presence or absence of the artificial dark layer. Damage in the form of deep “craters” was particularly evident in the Macael marble due to its larger crystal size [Fig. 1(a)]. In the Carrara marble the number of grains lost was higher, but due to their smaller size, no deep “craters” were observed [Fig. 1(b)]. However, the overall surface roughening (i.e., surface area increase) was more significant than in Macael samples.

Figure 2 shows SEM photomicrographs of Macael marble irradiated at different fluences (sections perpendicular to the irradiated surface). Exfoliation along the {104} cleavage planes was observed and first occurred in samples irradiated at a low fluence of 0.5 J cm\(^{-2}\). However, no damage was detected in either the front or the rear surfaces of irradiated Iceland spar calcite plates, regardless of their orientation [i.e., (hkl) plane facing the laser beam] or of the presence or absence of a dark layer. These results showed that the behavior of single crystals upon laser irradiation was quite different from the behavior of an aggregate (e.g., marble).

C. XRD analysis

Macael marble slabs displayed a strong preferred orientation of calcite crystals along specific ⟨hkl⟩ directions as inferred from the Bragg peak intensity differences between the marble and a randomly oriented calcite powder reference [Fig. 3(a)]. Calcite crystals were preferentially oriented along the [001] direction (i.e., c axis). Figure 3(a) shows that the 110 Bragg peak is the strongest. Hence, most crystals had their {110} planes parallel to the marble surface with [001] as their zone axis. This was consistent with the extremely weak 006 Bragg peak, which implied that the {001} planes of most crystals were almost normal to the marble surface. Carrara marble showed no preferred orientation of the calcite crystals. In fact, its XRD pattern was quite similar to that of a random oriented calcite powder [Fig. 3(b)].

Irrespective of the presence of a dark layer on the samples, XRD analyses of the irradiated marbles evidenced a slight intensity change in some hkl Bragg peaks (Fig. 3). The change was most significant in the 104 Bragg peak, particularly in the Carrara marble, and did not significantly depend on the laser fluence. Macael marble underwent a ~5% reduction of its 104 Bragg peak scaled intensity \(I_{104\text{scaled}}\), calculated by

\[
I_{104\text{scaled}} = 100 \frac{I_{104}}{I_{\text{full}}}
\]

(2)

FIG. 1. OM photomicrographs (plane polarized light) of Macael (a) and Carrara (b) marbles before and after laser irradiation at 1.25 J cm\(^{-2}\) (sections perpendicular to the irradiated surface). Laser irradiation resulted in fragmentation and loss of surface calcite crystals in both types of marble. Note that the overall roughening was more evident in Carrara samples in which a greater number of grains was lost. Arrows in (a) indicate calcite twin planes.
where $I_{104}$ and $I_{\text{full}}$ are the integrated intensities of the 104 peak and of the full diffraction pattern, respectively. A ~10% reduction in $I_{104\text{scaled}}$ was detected in the Carrara marble. The observed Bragg peak intensity reductions were connected to the catastrophic ablation of surface calcite crystals oriented with their \{104\} cleavage planes parallel to the sample surface, as shown by SEM observations. Once one of these crystals was lost, it no longer contributed to XRD of this particular set of \{hkl\} planes and therefore the relative intensity of the corresponding Bragg peak was reduced. This effect was more significant in the fine grained Carrara marble, which has a larger number of crystals with their \{104\} cleavage planes parallel to the sample surface, as shown by the XRD pattern [Fig. 3(b)]. Once catastrophic ablation of calcite occurred, the underlying material would lie outside the Ewald sphere and could not therefore contribute to XRD.

Laser irradiation of Iceland spar crystals induced no major Bragg peak intensity changes, irrespectively, of the \{hkl\} plane irradiated. However, a systematic sharpening of the 104 Bragg peak was detected (Fig. 4). Table I shows the $D_{104}$ values for Iceland spar crystals as well as for Macael and Carrara marbles (before and after laser irradiation). Following laser irradiation, a $D_{104}$ increase was observed in the Iceland spar crystal as well as in the Macael marble. No significant changes were observed in the case of the Carrara marble, which had the highest "crystallite size" and lowest defect density. The peak sharpening, implying an increase of Scherrer’s "crystallite size," was attributed to point and line defects disappearance following laser irradiation.

D. NIR diffuse reflectance spectrophotometry

Figure 5 shows NIR diffuse reflectance spectra of both the Iceland spar crystal [plate cut along the \{104\} cleavage plane] and the marbles. The reflectance spectrum of the two marbles is quite similar, although the coarser marble (Macael) shows a slightly lower reflectivity than the fine-grained one (Carrara). This has been associated with increased scattering as grain size decreases.\(^{44}\) Marble reflectance spectra show that limited absorption (~14%) occurs at 1064 nm. These data are consistent with previously published results.\(^{12,18}\) Our DRS also shows that the absorption of NIR radiation is higher by a factor of 2 in the marbles if compared with the Iceland spar single crystals. This differ-

![FIG. 3. XRD patterns of: (a) Macael marble and (b) Carrara marble before and after laser irradiation at 0.5 J cm\(^{-2}\). In both cases, there was a slight but significant reduction in the 104 Bragg peak intensity associated to the lost of surface grains with \{104\} planes parallel to the surface. The inset shows the XRD pattern of a random oriented calcite powder, which resembles the XRD pattern of the Carrara marble (i.e., marble without preferred crystallographic orientation).](image)

![FIG. 4. XRD patterns of Iceland spar calcite crystal cut along \{104\} plane. Note the reduction of FWHM following laser irradiation at 1.25 J cm\(^{-2}\). The peak sharpening was associated to a reduction of crystal defects resulting in an increase of "crystallite size," $D_{104}$.](image)

<table>
<thead>
<tr>
<th>$D_{104}$ ($\text{Å}$)</th>
<th>Before irradiation</th>
<th>After irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iceland spar</td>
<td>384 ± 7</td>
<td>427 ± 8</td>
</tr>
<tr>
<td>Macael marble</td>
<td>399 ± 87</td>
<td>481 ± 15</td>
</tr>
<tr>
<td>Carrara marble</td>
<td>543 ± 26</td>
<td>533 ± 42</td>
</tr>
</tbody>
</table>

![TABLE I. Average "crystallite size" ($D_{104}$) of Iceland spar and marble calcite crystals before and after laser irradiation at a fluence of 1.25 J cm\(^{-2}\). $D_{104}$ was determined using the Scherrer equation [Eq. (1)].](image)
ent behavior can be ascribed to light scattering at grain boundaries or other inhomogeneities present in the marble but absent in the calcite single crystals.

IV. DISCUSSION

A. Laser-induced damage

The selective removal of strongly absorbent contaminants and encrustations is commonly attributed to vaporization caused by a rapid temperature rise following pulsed laser irradiation. Approximate temperature increase $\Delta T$, at the substratum surface at time $\tau$ (i.e., laser pulse width), can be estimated using the following analytical solution for the one-dimensional thermal diffusion in a solid:

$$\Delta T = \frac{(1-R)F}{\rho C \mu},$$

(3)

where $R$ is the surface reflectivity, $F$ is the fluence of a pulse with duration $\tau$, $\rho$ is the density, and $C$ is the heat capacity at constant pressure; and $\mu$ is the thermal diffusion length during the laser pulse (i.e., the $1/e$ folding distance in the exponentially decreasing solution to the one-dimensional heat-diffusion equation), which is calculated by

$$\mu = 2 \sqrt{D \tau} = 2 \sqrt{\frac{\kappa}{\rho C}} \tau,$$

(4)

$\kappa$ being the thermal conductivity and $D$ is the thermal diffusivity of the solid substratum.

Surface contaminants experience a significant temperature increase following NIR pulsed laser irradiation due to the low reflectivity (~0.10) of a typical black crust. Such a high absorbance results from the significant quantity of poorly crystalline (or amorphous) carbon black typically present in black crusts. Following irradiation with a 1064 nm laser pulse ($\tau = 7$ ns; $F = 1.2$ J cm$^{-2}$) the black crust undergoes a temperature rise of $\sim 1.5 \times 10^4$ K [according to Eq. (3)]; $\kappa = 15.9$ W m$^{-1}$ K$^{-1}$, $\rho = 1800$ kg m$^{-3}$, and $C = 711.9$ J kg$^{-1}$ K$^{-1}$; data for amorphous carbon. This very high (perhaps unphysical) surface temperature is enough to vaporize the black crust (the sublimation temperature of amorphous carbon is 3925 K at 1 atm).

Calcite has a high reflectivity at 1064 nm (see Fig. 5) and should remain intact at a fluence below its ablation threshold, i.e., the fluence used here for cleaning the dark layer. Approximate $\Delta T$ of Iceland spar crystals ($R = 0.94$) irradiated with a 1064 nm laser pulse ($\tau = 7$ ns) with fluence of $1.2$ J cm$^{-2}$ is 1208 K ($\kappa = 5.526$ W m$^{-1}$ K$^{-1}$, $\rho = 2710$ kg m$^{-3}$, and $C = 849.3$ J kg$^{-1}$ K; data for calcite). Approximate $\Delta T$ of the marble ($R = 0.86$) irradiated with a 1064 nm laser pulse ($\tau = 7$ ns) with fluence of 0.5 J cm$^{-2}$ is 1174 K. These $\Delta T$ are slightly above the calcite decomposition $T$ (i.e., CaCO$_3$→CaO+CO$_2$ occurs at 1163 K, 1 atm), but well below CaO melting point (2887 K). No damage or decomposition byproducts were observed following irradiation of the Iceland spar crystals at the maximum fluence used in our tests (1.2 J cm$^{-2}$). However, damage (fracturing along cleavage planes; see Fig. 2) was observed following irradiation of the clean marbles at a low fluence of 0.5 J cm$^{-2}$. Nonetheless, no melting or decomposition byproducts were observed following irradiation of the marble, irrespective of the fluence used. Calcite decomposition, as well as melting, have been observed after irradiation of Iceland spar crystals with ns, 7 $\mu$m, and 3.3 $\mu$m infrared (IR) pulsed laser. The latter results are consistent with the strong absorption of calcite at mid-infrared wavelengths. Park and Haglund considered that thermal effects were responsible for damage following calcite irradiation at mid-infrared, but they observed that the dominant damage mechanism for NIR irradiation (Nd:YAG laser, $\lambda = 1064$ nm; $\tau = 12$ ns) was fundamentally thermomechanical. In agreement with Park and Haglund and Yavas et al., our $\Delta T$ calculations do not support a purely thermal damage mechanism for the marble.

It could be argued that electric field enhancement effects following interaction of the laser light with the particles in the dark layer can result in calcite catastrophic ablation. However, field effects are not consistent with the absence of damage following laser cleaning of the Iceland spar crystals covered with the dark layer. In the case of the dirty marble, some damage might be ascribed to the formation and expansion of a hot plasma following vaporization of the dark layer. Siano and Pinj proposed that damage to marble induced by irradiation with short-pulse NIR laser is largely a photomechanical effect. Laser induced vaporization and ejection of the contaminant layer generates a plasma plume and shock waves. The latter then propagate and damage the underlying surface. However, this photomechanical model cannot fully explain why clean marble is also damaged. Neither does it explain why for an almost equal $\Delta T$ the Iceland spar single crystal remained intact ($\Delta T$ of 1208 K for $F = 1.2$ J cm$^{-2}$) while catastrophic ablation occurred to the marble ($\Delta T$ of 1174 K for $F = 0.5$ J cm$^{-2}$).

B. Role of defects

No previous model on laser-induced damage to marble took into account the fact that there is a selective NIR energy absorption due to the presence of defects in calcite crystals.
Defect-mediated laser energy absorption following irradiation of dielectrics such as MgO, NaNO₃, Al₂O₃, and CaCO₃ at fluences below their ablation threshold has been demonstrated and induces the release of photoelectrons, ions, and neutrals associated to point defects.⁵⁹ Many of these particles have energies corresponding to the visible spectra and their emission is observed as a flash of light. Laser energy absorption appears to occur by means of multiple single-photon charge-transfer interaction with surface defects such as F centers or vacancies.⁵⁸ Adsorbed ions or neutrals, which compensate the charge-defect induced by a vacancy, are released following defect-mediated laser energy absorption, which leads to thermal emission of these particles as visible luminescing plasma plumes.²⁹

Our results showed that laser irradiation reduced calcite defect density, presumably due to point and line defects annealing,⁵⁹ as inferred from the sharpening of the Bragg peak profile and the increase of D₁₀⁴ values. The local ΔT following laser irradiation (see previous section) can be accounted for by this annealing effect. Annealing is consistent with the absence of melting features. Surface defect disappearance was also consistent with visual observation of the reduction in light flashes and snapping sound intensity until their complete disappearance after a given number (~5) of laser pulses. Bandis et al.⁵⁸ have reported depletion of ion and neutral emission due to defect site disappearance upon successive laser pulse irradiation of dielectrics (e.g., single crystal NaNO₃ with Nd-YAG low-energy photons (hν = 1.16 eV; λ = 1064 nm) at fluences below the substrate ablation threshold. In our experiments the reduction in the plasma emission intensity and the increase in D₁₀⁴ values following irradiation with successive laser pulses clearly demonstrated that laser energy was absorbed by calcite crystals via defects as reported by Park and Haglund⁵³ and Yavas et al.⁶⁰ Increased laser fluence is expected to generate more surface defects in calcite crystals. However, calcite is highly sensitive to mechanically induced defect formation but not particularly sensitive to photoinduced defect generation.⁴²,⁶⁰,⁶¹ The relatively low D₁₀⁴ values of Macael marble (Table I) were due to its greater density of defects and twins [see Fig. 1(a)]. The latter occurred during the significant deformation of the marble during low-T metamorphism.⁶³ The relatively high D₁₀⁴ values of Carrara marble are connected to the limited deformation and the high-T recrystallization it underwent during metamorphism.⁶⁴ This is consistent with its low twin density [see Fig. 1(b)]. On the other hand, mechanical manipulation (i.e., cleavage, cutting, abrading, or polishing) of a number of crystals, including calcite, tends to create many surface and near-surface point and line defects.²⁹,⁴¹,⁵⁶,⁶¹ This is consistent with the low D₁₀⁴ values of our Iceland spar crystals.

Apparently defects played a crucial role in laser light absorption and, ultimately, in marble damage. Defect-mediated laser energy absorption led to thermal emission of ions from the calcite surface forming a plasma plume, as evidenced by the observed flashes of light. Along with the flashes of light, a snapping sound was detected which corresponded to a shock wave.⁵³ The thermal shock wave associated to the substratum ΔT and plasma plume expansion seems to be the active damage mechanism resulting in the observed “catastrophic ablation” of calcitic marble. The recoil pressure generated by the shock wave created sufficient tensile stress in the calcite crystals so as to induce their fracturing and exfoliation along the weak cleavage planes (see Sec. IV C), as observed by OM and SEM.

C. Effect of crystal size

Responses to laser irradiation differed for single Iceland spar crystals and calcite crystal aggregates in the marble. Besides the slightly lower reflectivity of the marbles at 1064 nm, which led to equal ΔT at a lower fluence than in the Iceland spar case, calcite aggregates in the marble were much more sensitive to laser irradiation than single crystals in terms of mechanical strength. This is in agreement with classical theories explaining the mechanical rupture of solids. Specifically, the ultimate tensile strength of a single crystal is a few orders of magnitude higher than that of an aggregate.⁴⁰ It has been reported that mechanically strained laboratory calcite specimens have extremely high dislocation densities of ~10¹⁰ cm⁻²,⁶⁵ (close to the theoretical maximum of 10¹¹ cm⁻² a solid can have),²⁶ a value higher than that of mechanically strained calcitic marbles.²⁶,⁶⁶ Furthermore, tensile strength is directly proportional to aggregate grain size (other parameters such as porosity, textural orientation, and phase composition being equal). For instance, the rupture modulus of coarse-grained Macael marble is ~25% higher than that of fine-grained Carrara marble.²⁶,⁶⁷,⁶⁸ Therefore, the mechanical stresses generated by the shock waves associated to laser irradiation led to explosive calcite shattering at a slightly lower fluence in the fine-grained Carrara marble than in the coarse-grained Macael marble. The positive effect of the larger crystal size of Macael marble was counterbalanced by its higher crystal defect density, which explains why damage also occurred at the relatively low working fluences. However, the working fluences were not high enough to overcome the tensile strength of the Iceland spar single crystals, even though they possessed a high defect density.

Due to the fine-grained nature of Carrara marble, one must add the large number of grain-boundary defects to the calcite crystal internal or near-surface defects. Boundary defects include many ending dislocation half planes with numerous vacancies and broken bonds.²⁶ Absorption of NIR laser pulse energy at grain boundaries therefore seems more significant in fine-grained than in coarse-grained marbles and thus promotes damage. On the other hand, small cracks or pores may exist at grain boundaries (see SEM photomicrographs in Fig. 2). Bloembergen⁶⁹ points out that the local electric field can be increased by a factor of 2–5 at pores or crack tips with dimensions close to the laser wavelength in low index transparent dielectrics such as Al₂O₃ or NaCl. Thus the damage threshold of such dielectrics can be substantially reduced. Cracks or pores associated to grain boundaries are more abundant in the fine grained Carrara marble as evidenced by the OM and SEM observations.
Thus, local field enhancement effects may have also contributed to marble damage following NIR laser irradiation.

D. Effect of crystal orientation

Calcite \{104\} cleavage planes are the weakest bonded.\(^{38}\) This is responsible for the typical calcite rhombohedral exfoliation, which forms a 45.5° angle with the c axis. Our SEM observations clearly demonstrated that crystals oriented with their \{104\} cleavage planes parallel to the marble surface were preferentially damaged. Fracturing and exfoliation of single calcite crystals along cleavage planes following Q-switched Nd:YAG laser irradiation has been reported.\(^{22,53,60}\) Threshold fluence for catastrophic ablation of cleaved Iceland spar plates (i.e., oriented with \{104\} planes normal to the laser beam) irradiated with a 1064 nm Nd:YAG laser using 12 ns FWHM pulses is reported to be 4.5 J cm\(^{-2}\)\(^{60}\). This fluence is equivalent to 2.45 J cm\(^{-2}\) for 7 ns FWHM pulses. Hence, the fluences we used (up to 1.25 J cm\(^{-2}\)) should not be high enough to cause any damage to the Iceland spar plates. They did, however, approach the threshold fluence for rear-side ablation.\(^{54}\) However, we observed no rear-side damage following laser irradiation of Iceland spar single crystals. Nonetheless, the fluences used were sufficient to cause catastrophic ablation of the marbles due to their microstructural characteristics.

V. CONCLUSIONS

Irradiation with a NIR pulsed laser, at fluences below the ablation threshold for calcite crystals, induced mechanical damage in ornamental marbles: specifically, a preferential fracturing and exfoliation of crystals with their \{104\} planes parallel to the marble surface and an increase in surface roughness. Calcite exfoliation was caused by thermo-mechanical stress generated once laser energy was absorbed (via defects) and thermalized. The recoil pressure associated with the shock waves induced significant tensile stress on the marble surface calcite crystals, resulting in calcite catastrophic ablation.

Because Carrara marble has a smaller grain size and a higher grain boundary surface per unit volume than Macael marble, it has a lower tensile strength than the Macael marble. However, the high defect density of Macael marble calcite crystals counteracted the positive effect of its coarser grain size, also resulting in calcite fragmentation following laser irradiation since laser energy was preferentially absorbed at defects. Fluences \(\leq 1.25\) J cm\(^{-2}\) were not high enough to induce catastrophic ablation in single-crystal Iceland spar. This differential behavior cannot be accounted for by the small differences in absorbance at 1064 nm between marble and Iceland spar single crystals. Other factors such as defect density, tensile strength, and grain-boundary effects seem to play a crucial role in laser-induced catastrophic ablation at subthreshold fluences.

It is concluded that much care should be taken when conventional Q-switched Nd:YAG lasers are used to clean marble artworks. Laser exposure conditions should therefore be adjusted to microstructure characteristics of each marble.

This is particularly important in the case of fine-grained marbles, the most common ornamental marbles.

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