Irradiation of Dental Enamel With Q-Switched $\lambda = 355$-nm Laser Pulses: Surface Morphology, Fluoride Adsorption, and Adhesion to Composite Resin

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Background and Objectives: Lasers can be used to modify the chemical composition of dental enamel to increase the bond strength to restorative materials and to render the mineral phase more resistant to acid dissolution. Previous studies have suggested a synergistic relationship between CO_2 laser irradiation and fluoride treatment on increased resistance to acid dissolution. In this study a near-UV laser operating with $\lambda = 355$-nm laser pulses of 3–5 nanoseconds duration was used to modify the surface morphology of dental enamel to increase the bond strength to restorative materials and increase the uptake of topical fluoride to render the surface more resistant to acid dissolution. We hypothesize that the short UV laser pulses are primarily absorbed by protein and lipid localized between the enamel prisms resulting in removal of intact mineral effectively etching the surface without thermal modification of the mineral phase. Such modification is likely to increase the permeability of the enamel surface and the subsequent absorption of fluoride. In addition, there is an increase in surface roughness without the formation of a layer of loosely adherent, thermally modified enamel that increases the bond strength to composite restorative materials.
Study Design/Materials and Methods: The surfaces of blocks of bovine enamel, 5×5 mm^2, were uniformly irradiated by 355-nm laser pulses and subsequently bonded to composite. The shear bond test was used to assess the bond strength of non-irradiated blocks (negative control), acid etched blocks (positive control), and laser irradiated blocks. The resistance to acid dissolution was evaluated using controlled surface dissolution experiments on irradiated samples, irradiated samples exposed to topical fluoride, and non-irradiated control samples with and without fluoride.
Results: The laser surface treatments significantly increased the shear-bond strength of enamel to composite, to a level exceeding 20 MPa which was significantly more than the non-irradiated control samples and significantly less than the acid etch. Laser irradiation alone and topical fluoride application alone did not significantly increase the resistance to acid dissolution. The laser treatment followed by topical application of fluoride significantly increased the resistance to acid dissolution to a level of over 50% versus the control samples.

Conclusions: We present a novel method for increasing bond strength to restorative materials and enhancing fluoride delivery to enamel surfaces and shed some light on the underlying mechanisms of caries inhibition via laser treatment and topical application of fluoride. Lasers Surg. Med. 32:310–317, 2003.   © 2003 Wiley-Liss, Inc.

Key words: dental enamel; UV-laser irradiation; caries inhibition; protein etching; bond strength; fluoride

INTRODUCTION

Several studies employing excimer lasers have demonstrated that UV photons can be used to selectively etch protein and lipid from enamel [1–5]. The two primary reasons for the surface modification of dental enamel are to increase the resistance to acid dissolution and to roughen the surface to enhance the bonding to composite. The purpose of this study was to evaluate the effects of laser irradiation at a wavelength that is selectively absorbed by the organic matrix of enamel on the microscopic surface morphology, the in vitro shear bond strength of resin bonded orthodontic attachments, and the in vitro caries resistance to acid challenge. In contrast to CO_2, Er:YAG and Er:YSGG laser wavelengths, IR measurements after irradiation with Q-switched 355-nm laser pulses have indicated that the ablation of enamel occurs without any spectral changes in the IR reflectance spectrum [6]. Therefore, we postulated that further studies using this laser system will shed light on both the mechanism of caries inhibition through laser irradiation and the bonding of laser treated surfaces to restorative materials.

High intensity laser radiation can be used to render dental enamel more resistant to acid dissolution [7–9].

Several studies over the past 20 years have advanced our understanding of the mechanism of inhibition. Thermal analysis studies of Holcomb and Young [10] and subsequent studies by Fowler and Kuroda [11] indicated that there was substantial loss of carbonate and water at temperatures between 100 and 400°C that were sufficient to change the crystallinity of the intrinsic mineral to form a purer phase more acid resistant form of hydroxyapatite. Kuroda and Fowler [12] observed a reduction in the carbonate content of enamel by 66% after irradiation with a continuous wave CO_2 laser. Heat treatment between 350°C and 650°C reduced the solubility of enamel to acid dissolution, [13−17] even though the permeability was increased. Featherstone et al. [18] correlated the carbonate loss from enamel measured with IR spectroscopy with the inhibition of the dissolution rate providing additional evidence that transformation of the mineral of enamel to a purer phase is the principal mechanism of inhibition. Therefore, the decreased solubility after IR irradiation can most likely be attributed to the thermal decomposition of the more soluble carbonated hydroxyapatite (CAP) into the less soluble hydroxyapatite (HAP) with corresponding changes in the crystallinity. Other studies have suggested that the production of pyrophosphate, permeability changes and modification of the protein matrix also play a role in inhibition [13,14,19,20]. Levels of inhibition exceeding 70% have been achieved with CO_2 laser irradiation [21]. Based on the observation that $\lambda = 355$-nm laser pulses etch the enamel surface without thermal modification of the mineral phase, i.e., without varying the carbonate content, we postulated that there should not be an increased resistance to acid dissolution if conversion to a purer phase hydroxyapatite is indeed the primary mechanism. This hypothesis is predicated on the assumption that the $\lambda = 355$-nm laser pulses preferentially interact with the protein and increase the permeability of the enamel. Therefore, we can ascertain whether or not modification of the protein is responsible for increased inhibition. This is important for two reasons; some previous studies have suggested that protein plays a key role in laser inhibition during laser irradiation [19, 22], and several studies have shown that laser irradiation followed by application of fluoride acts in a synergistic fashion to almost completely inhibit decay [23−25]. The influence on the uptake of topical fluoride after 355-nm laser irradiation application was also investigated in this study and the results provide insight into the synergistic mechanism of fluoride application and laser irradiation.

Reports of the effectiveness of laser irradiation on enhancing the bond strength of dental enamel to restorative materials vary widely in the literature [26−36]. Studies have shown that IR laser radiation can leave deposits of loosely attached enamel that compromise the bond between the enamel and the resin [32]. The bond strength increased significantly if a device such as an ultrasonic scaler was used to remove the "laser-generated" smear layer from the surface [32]. Previous studies have shown that non-apatite calcium phosphate phases of mineral can recondense on the tooth surface after ablation if water is not used [36−40]. No such deposits were observed on the surface of the enamel after ablation with the 355-nm laser pulses used in this study. Therefore, we also postulated that enamel surfaces modified by 355-nm laser pulses should yield high bond strengths, since the surface is free of such a laser-produced smear layer.

In a previous study, we found that laser pulses of the third harmonic of the Q-switched Nd:YAG (355-nm) can be used to completely remove composite from the surface of the tooth with no discernable damage to the underlying enamel [41]. Therefore, there is interest in using this particular laser system to remove residual composite from tooth surfaces and for the selective removal of composite from restorations during the replacement of failed composite restorations. This discovery was the primary motivation for the present investigation of the effect of these laser pulses at higher energy levels on the surface morphology of dental enamel.

MATERIALS AND METHODS

Sample Preparation

Polished blocks, $5 \times 5 \times 2$ mm^3 were prepared from the facial surfaces of gamma sterilized freshly extracted bovine incisors. Blocks were highly polished with sequential diamond abrasives of 6, 3, and 1 μm. The bovine blocks, with reproducible enamel surfaces, were stored until use in a 100% humidity environment with 0.01% thymol. Bovine tooth enamel has been shown to have similar results in adhesion tests with both composite resins and glass ionomer cements, when compared with human tooth enamel [42].

Laser Irradiation

A Q-switched Nd:YAG laser (New Wave Minilase III system; Sunnyvale, CA), operating at its third harmonic with a wavelength of 355 nm and a pulse duration of 3−5 nanoseconds, was used to irradiate the surface of the bovine blocks. There was no use of either air or water coolant during any of the laser irradiation procedures. The Minilase III laser beam was focused onto the surfaces of the samples using BaF_2 and fused silica lenses (focal length 50 mm) to generate a spot size (beam diameter) of 284 μm (e^{-2}) on the enamel surface. A pyroelectric energy meter, ED-200 (Gentec Ste. Foy, Que, Canada) was used to measure the beam energy.

Optical and Electron Microscopy

Representative samples were examined with optical and scanning electron microscopy (SEM). Samples were surface-sputtered with gold and examined with a Topcon SX-40A "wet" environmental SEM (Topcon Instruments, Pleasanton, CA) at up to $10,000\times$ magnification. Images were captured and stored in digital format. A sub-group of samples that were used in the shear bond strength tests were cross-sectioned and polished (same protocol as previously described up to 1 μm diamond slurry) to view the resin-enamel interface. All images cataloged for subsequent descriptive analysis of the imaged surfaces. A Model BX50 optical laboratory (Olympus, Melville, NY) microscope with integrated DVC 1300C digital camera

(Austin, TX) and Image Pro Plus image analysis software (Media Cybernetics, Silver Spring, MD) was used to acquire optical images of treated surfaces at up to $500\times$ magnification.

Shear Bond Strength Measurements

Four experimental sample groups were irradiated at fluences of 1.8, 4.2, 6.9, and 8.3 J/cm^2, (n = 8 each group). A pilot study of three samples was performed to determine the threshold for enamel modification and ablation. It was noted that the minimum fluence to cause surface modification was 1.3 J/cm^2. These findings are in agreement with the 1.3 J/cm^2 fluence threshold level reported by Alexander et al. [41]. The laser beam was focused to a spot diameter of $\sim$300 μm and the samples were scanned across the laser beam to uniformly cover the entire 5×5 mm^2 surface of each bovine block with overlapping laser spots using a ESP-300 motion control system incorporating two 850F stages (Newport, Irvine, CA). Ten pulses were delivered for each spot with a scan distance of 50 μm between spots. A repetition rate of 10 Hz was used for each sample, each pulse with a duration between 3 and 5 nanoseconds.

In order to access the suitability of laser treated surfaces for bonding, orthodontic brackets were attached to the center of the irradiated blocks and the shear bond test was employed to determine the shear bond strength. The modified single plane shear test assembly (SPSTA) was used according to the protocol developed by Watanabe et al. [43] in order to avoid the problems associated with shear tests using shearing knives or wire loops that produce shear-peel forces and not true shear forces. Flat orthodontic attachments (Ormco® Flat Lingual Pad with Button Attachment; Glendora, CA) affixed to the flat enamel surfaces were used to avoid the influence of tooth surface curvature. The orthodontic button used had a slightly larger diameter (3.25 mm) than the holes in the Delrin plates of the SPSTA testing assembly used in this study. Mesh bases of the orthodontic buttons were coated with a filled composite resin (3M Transbond XT Light Cure Adhesive Paste; 3M Unitek, Monrovia, CA) and affixed to the prepared enamel surface which was coated with a thin layer of unfilled resin adhesive layer (3M Transbond XT Light Cure Adhesive Primer; 3M Unitek). The SPSTA was attached to an Instron shearing machine with two aligning plates. The Instron was calibrated and set to record measurements in kilograms (Kg). A crosshead speed of 5 mm/min was used. The force level (measured in Kg) was recorded for each sample at the precise point when the two shear plates separate from each other. The recorded force-failure measurements were divided by the surface area of bonded region and multiplied by the conversion factor to convert the stress required for failure from Kg/cm^2 to Megapascals (MPa).

Surface Dissolution Measurements

A single fluence of 2.5 J/cm^2 was used for each of the laser treated samples studied. This fluence was selected because it was well above the minimum threshold for enamel modification, but below the fluence levels that cause frank ablation and tissue loss. After laser irradiation, samples were mounted on HDPE (high-density-polyethylene) disks and placed in a reactor vessel containing a solution of 0.1 M acetic acid buffered to a pH of 4.5 for surface dissolution rate measurements. Aliquots of the solution were collected for 20 minutes at 2-minute intervals after immersion. The aliquots were subsequently analyzed for calcium and phosphorus to determine the dissolution rate. Calcium concentration was determined using atomic absorption and the phosphate concentration was photometrically measured using an ammonium molybdate colored complex that absorbs light at 820 nm. The technique(s) for evaluating surface dissolution and carbonate content via reflectance IR spectroscopy have been discussed previously [44,18]. Linear dissolution plots of concentration of dissolved calcium and phosphate versus time were acquired for each sample, and the slope of each plot was recorded for subsequent statistical analysis. Descriptive statistics (mean, standard deviation, and standard error of the mean) and the Tukey−Kramer multiple comparison test were calculated using the INSTAT™ software program package (Graphpad Software, San Diego, CA).

Synchrotron Radiation Fourier Transform Infrared Spectra (SR-FTIR)

High-resolution IR spectra of laser-irradiated surfaces was obtained using a Nicolet Magna 760 Nic-Plan IR Microscope (Nicolet, Madison, WI) interfaced to Beamline 1.4 of the Advanced Light Source at Lawrence Berkeley National Laboratory. The high brightness provided by the synchrotron radiation source allows IR spectra to be acquired with a spatial resolution of 10-μm and is particularly advantageous for acquiring spectra from rough surfaces such as those produced after laser-irradiation. All spectra were acquired in reflectance mode from the surfaces of optically thick polished samples as described in our previous publication [6].

RESULTS

Surface Morphology

Above an incident fluence of 1.3 J/cm^2 there were surface changes in the sound enamel. Close examination with a scanning electron microscope at magnifications of 1000−5000×, indicate that the protein and lipid shealth are preferentially removed over the mineralized prismatic structures (Fig. 1). The prismatic structures can be resolved protruding from the irradiated areas. This is clearly evident in representative SEM micrographs of tracts etched into the surface of a polished enamel block at irradiation intensities of 4.2 and 8.3 J/cm^2 (Fig. 1). The surface morphology of the irradiated areas was similar in appearance for irradiation intensities ranging from 1.8 to 8.3 J/cm^2. In contrast to previous studies using carbon dioxide lasers there is no evidence of fusion of the enamel prisms.

SR-FTIR Spectra

SR-FTIR spectra of areas of the polished bovine enamel etched by Q-switched 355-nm lasers pulses manifest no
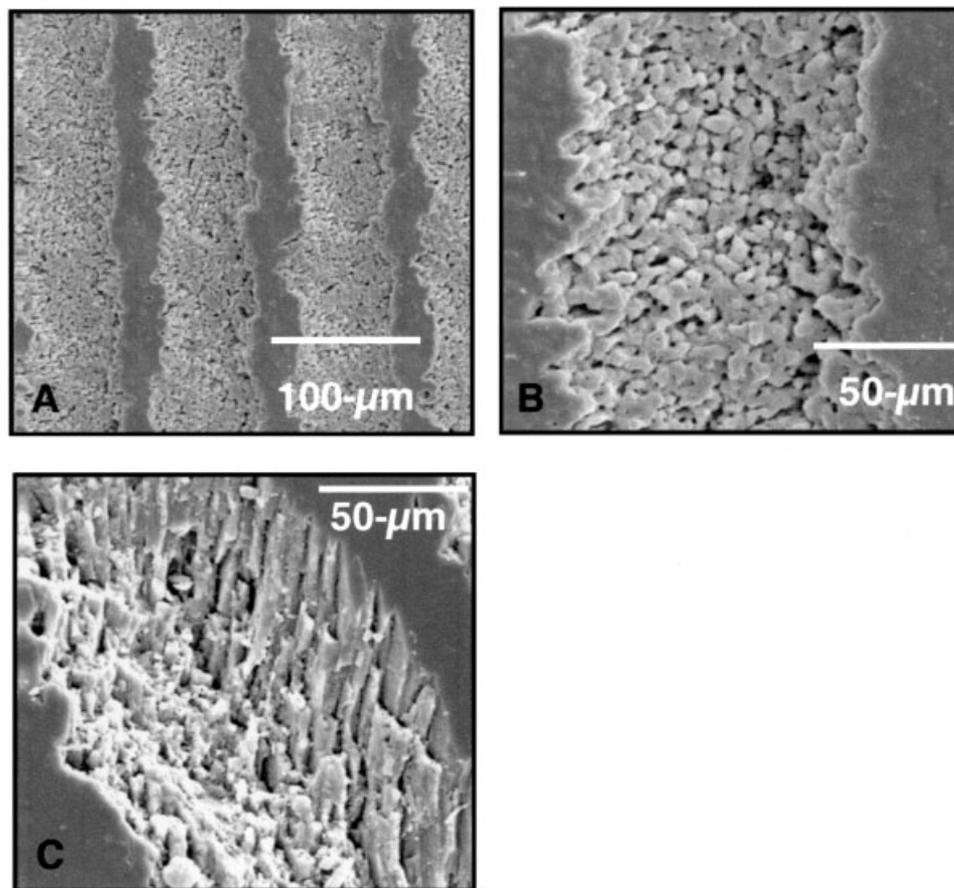
Fig. 1. Scanning electron micrographs of enamel irradiated at a fluence of 8 J/cm^2. **A**: Channels produced by scanning the sample by 50 μm increments along each channel with a center to center separation of 100 μm. **B**: Single channel of (a) shown at a magnification of 2000×. **C**: Channel produced at a fluence of 8 J/cm^2.

obvious chemical changes. In Figure 2, three SR-FTIR spectra of sound enamel, and enamel irradiated at 355-nm and 9.6-μm are displayed. Previous studies using carbon dioxide lasers have shown that pulsed and continuous laser irradiation result in melting and thermal decomposition of the mineral phase of enamel. This is most evident by a reduction in the 6.8 and the 7.1-μm carbonate (CO_3^{2-}) band intensities and changes in the intensity ratios of the three phosphate (PO_4^{3-}) bands between 9 and 11 μm. In Figure 2, there are no differences between the intensities of the molecular absorption bands between sound enamel and enamel irradiated at 355 nm. Unfortunately, we cannot determine using SR-FTIR whether or not the protein and lipid is eliminated, because the small relative quantity of these species in enamel along with their nominal extinction coefficients that preclude their measurement with SR-FTIR techniques.

Shear Bond Strength Measurements

The results of the shear bond measurements of orthodontic brackets bound to the enamel surface are shown in Table 1. There were six groups with eight samples per group. Four sample groups were irradiated at fluences of 1.8, 4.2, 6.9, and 8.3 J/cm^2, while one group was acid etched and the other was left untreated. Multiple comparisons were carried out using the Tukey–Kramer multiple comparison test. All the laser-irradiated groups manifested significantly higher bond strengths than the untreated control group. The acid etch group manifested a significantly higher bond strength than all the other groups. However, the bond strength of the two groups irradiated at intensities above 6 J/cm^2 exceeded 20 MPa which is considered sufficiently high to restrict the formation of gaps caused by curing shrinkage of composite resin [45].

Surface Dissolution Measurements

The effect of the laser etched surface on resistance to acid dissolution and the efficacy of topical fluoride delivery was evaluated using surface dissolution measurements on polished bovine enamel blocks. The mean dissolution rates determined by measuring the concentration of dissolved calcium and phosphate versus time of dissolution are tabulated in Table 2 in conjunction with the percent inhibition for each of the four groups, n = 10 per group. The
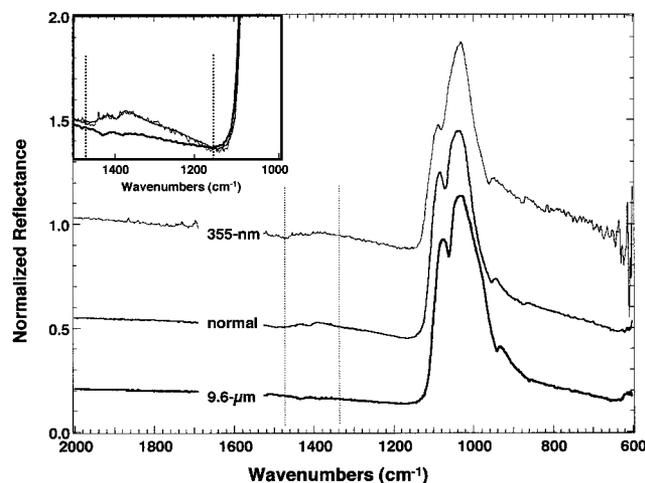
Fig. 2. SR-FTIR spectra of three representative samples, normal enamel, enamel irradiated at 355-nm with a fluence of 3 J/cm^2 and at 9.6 μm with a fluence of 1 J/cm^2. The inset shows the carbonate bands at 6.8 and 7.1 μm. The carbonate is eliminated after 9.6 μm due to thermal decomposition. The carbonate band intensity is undiminished after 355-nm irradiation.

laser treatment alone did not inhibit dissolution of the mineral and actually increased the dissolution rate by 14% as indicated by a percent inhibition of −14% in Table 2. Topical fluoride application alone did not significantly inhibit dissolution. The combination of laser treatment at 2.5 J/cm^2 followed by topical fluoride application inhibited decay by 52−53%, which was significantly greater than the other groups with $P < 0.001$.

DISCUSSION

In a previous study we demonstrated that $\lambda = 355$-nm laser radiation with a pulse duration of 3−5 nanoseconds was ideally suited for the removal of composite from the surface of dental hard tissues without modification of the underlying enamel [41]. In this study we have demonstrated that laser radiation incident at irradiation intensities that exceed the ablation threshold can beneficially modify the underlying enamel. Therefore the laser parameters

TABLE 1. Shear Bond Strength Measurements on Laser Irradiated Dental Enamel, n = 8

Irradiation conditions	Bond strength mean ± SD (MPa)
Untreated ctrl	2.1 (1.8)
1.8 J/cm^2	16.7 (2.7)[a,b]
4.2 J/cm^2	17.2 (1.5)[a,b]
6.9 J/cm^2	20.7 (1.7)[c,d]
8.3 J/cm^2	20.4 (2.1)[c,d]
Acid etch ctrl	29.5 (2.0)

[a,b,c,d]Significantly different ($P < 0.05$) from untreated and acid etch ctrl samples and other values in the same column not similarly marked.

examined in this study may be useful for several clinical applications. One can envisage using this laser system to pre-etch the enamel to enhance bonding to composite prior to adhesion of orthodontic brackets—followed by use of the same laser at a lower intensity to selectively remove the residual composite after debonding of the same brackets. Using the laser to pre-etch is advantageous since it provides a sufficient bond strength, ∼20 MPa [32] for bracket retention. Moreover, if topical fluoride is applied after laser irradiation it is likely to inhibit peripheral decay around the brackets.

This laser may also be well suited for the selective removal of failed composite restorations [41]. For this particular application, our results suggest that inadvertant removal of a small amount of enamel would actually be beneficial since restorative materials could be applied directly to the cavity and would likely be more resistant to secondary decay if topical fluoride was applied after removal of the composite. Finally, in a similar fashion we can speculate that the short 355-nm laser pulses are likely to be well suited for the selective and conservative removal of pit and fissure caries that contain an increased ratio of protein to mineral. In this final application etching the walls for retention of sealants would be of a particular advantage since the walls of fissures are sometimes difficult to etch due to the presence of prism-less enamel in these areas.

This study sheds light on the mechanisms by which laser irradiation influences both the bond strength to restorative materials and increases the resistance to dissolution by organic acids. Previous studies using IR spectroscopy and X-ray diffraction have shown that chemical and crystalline changes occur in enamel after IR laser irradiation suggesting that the primary mechanism of inhibition is the modification of the carbonated hydroxyapatite to the purer phase hydroxyapatite [12,18,25,46,47]. Thermal decomposition studies show that this transformation is initiated in enamel at temperatures exceeding 400°C [10]. Recently, Hsu et al. [19] proposed that removal of the organic matrix significantly decreases the ability of carbon dioxide laser irradiation to inhibit demineralization. In this study we show that irradiation at a laser wavelength that selectively etched the protein and lipid from the enamel surface does not either significantly increase or decrease the dissolution rate. Therefore, these results suggest that it is unlikely that the protein and lipid directly play a role in the mechanism of thermal transformation of enamel by laser irradiation, in contrast to the recent study by Hsu et al. [19]. Moreover, at the temperatures necessary for thermal decomposition of dental enamel there is complete pyrolysis of the lipid and protein components of enamel. The loss of organic components of enamel cannot be detected using FTIR since the volume fraction is very small. However, dentin contains a large volume fraction of collagen ∼40−50% and FTIR spectra show that there is complete pyrolysis of the protein at irradiation intensities below the threshold required for thermal decomposition of the mineral phase [48].

Several studies have shown that there is a synergistic effect between laser irradiation and topical fluoride application. Yamamoto and Sato [13] showed that Nd:YAG

TABLE 2. Surface Dissolution Rates of Laser and Fluoride Treated Specimens, n = 10

Treatment conditions	Dissolution rate[a] (Ca)	Dissolution rate[a] (PO$_4$)	% Inhibition[b] (Ca, PO$_4$)
Untreated	0.042 (0.0087)[c,d,e]	0.019 (0.0036)[c,d,e]	0, 0
Laser, 1.8 J/cm^2	0.049 (0.012)[c,d,e]	0.022 (0.0046)[c,d,e]	−14, −14
Topical fluoride	0.037 (0.011)[c,d,e]	0.018 (0.0041)[c,d,e]	12, 5
Laser and fluoride	0.020 (0.011)[f]	0.0089 (0.0058)[f]	52, 53

[a]The mean dissolution rate (ppm/min) ± SD represented by the slope of the Ca or phosphate concentration in ppm in the dissolution bath versus time in minutes.

[b]Percent inhibition is 100%-ratio of treated sample mean over the untreated sample mean, calculated for both Ca and phosphate dissolution data. Negative values indicate an increase in susceptibility to acid dissolution.

[c,d,f]Significantly different ($P < 0.05$) from other values in the same column not similarly marked.

laser (1064-nm) irradiation both thermally modified the enamel and increased the penetration depth of fluoride. Meurman et al. [49] and Phan et al. [50] proposed that the heat from the laser treatment transforms the hydroxyapatite to fluorapatite which is more resistant to acid dissolution. However, Tagomori et al. [23] showed that combined treatments were more effective if enamel was irradiated with the Nd:YAG laser before fluoride application, in effect contradicting the thermal transformation to fluoropatite hypothesis and supporting the hypothesis that there is an increase in permeability of the enamel surface. The results of this study strongly support the latter hypothesis that laser irradiation influences the permeability of the surface. In a recent study, Hsu et al. [19] extracted the protein and lipid from enamel before CO$_2$ laser irradiation and fluoride application. Exposure of the enamel surface to topical fluoride after the extractions inhibited the dissolution rate by a nominal amount, 17%, however that was not statistically significant from the control samples.

After irradiation with Q-switched 355-nm laser pulses there was no thermal transformation of the mineral phase by laser irradiation, nor were chemical treatments used to extract the protein and lipid, therefore this study is also important from a mechanistic standpoint. Based on the results presented in this article, we can postulate that laser irradiation at other laser wavelengths, such as CO$_2$ laser wavelengths, inhibit decay primarily through thermal transformation of the mineral phase of enamel. The protein and lipid are also removed increasing the permeability of the surface. Such changes in permeability most likely increase the efficacy of fluoride application, explaining the synergism between laser irradiation followed by topical fluoride application that has been observed for IR laser irradiation. In fact, the effectiveness of the laser irradiation at 355-nm followed by topical fluoride application was almost as effective as the laser irradiation at CO$_2$ laser wavelengths. Therefore, this approach presents an alternative mechanism of caries inhibition with laser irradiation. It is also important to note that the laser irradiation intensity required for the treatments using Q-switched 355-nm laser pulses was only 2.5 J/cm^2 which is not likely to result in excessive heat deposition in the tooth.

The enamel surfaces etched by Q-switched 355-nm laser pulses in this study did not manifest an associated smear layer and did not thermally transform the underlying mineral phase. Such surface morphology, yielded high shear bond strengths, therefore our results also support the hypothesis that the highly variable bond strengths associated with laser prepared surfaces in previous studies with Nd:YAG, Er:YAG, and CO$_2$ lasers is due to deposits of loosely attached modified mineral that compromise the bond between the enamel and the resin [32]. Previous studies have shown that non-apatite calcium phosphate phases of mineral can recondense on the tooth surface after ablation if a substantial layer of water is present during ablation to prevent the redeposition of non-apatite calcium phosphate phases [37–39].

Recently, several affordable flash-lamp pumped and diode-pumped 355-nm systems have become available operating at high repetition rates. Therefore, such systems are practical for implementation in clinical dentistry.

Near-UV, 355 nm photons lie within the UV-A band, which can potentially cause hyperpigmentation (tanning) and erythema at high exposure levels. The risk of skin cancers due to UV-A radiation exposure is generally several orders of magnitude less than for the shorter wavelength, UV-B, and the permitted exposure levels are relatively high compared to those of the shorter wavelength excimer lasers that fall within the UV-B and UV-C bands, respectively [51].

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