Rapid and conservative ablation and modification of enamel, dentin, and alveolar bone using a high repetition rate transverse excited atmospheric pressure CO_2 laser operating at $\lambda = 9.3\ \mu m$

Kenneth Fan
Paul Bell
Daniel Fried
University of California at San Francisco
Preventative & Restorative Dental Sciences
707 Parnassus Ave.
San Francisco, California 94143

Abstract. Transverse excited atmospheric pressure (TEA) CO_2 lasers tuned to the strong mineral absorption of hydroxyapatite near $\lambda = 9\ \mu m$ are well suited for the efficient ablation of dental hard tissues if the laser pulse is stretched to greater than 5 to 10 μs to avoid plasma shielding phenomena. Such CO_2 lasers are capable of operating at high repetition rates for the rapid removal of dental hard tissues. The purpose of this study was to test the hypothesis that stretched $\lambda = 9.3$-μm TEA CO_2 laser pulses can produce lateral incisions in enamel, dentin, and alveolar bone for dental restorations and implants at repetition rates as high as 400 Hz without peripheral thermal damage. The single pulse ablation rates through enamel, dentin, and bone were determined for incident fluence ranging from (1 to 160 J/cm^2) for laser pulses from 5 to 18 μs in duration. Lateral incisions were produced in hard tissue samples using a computer-controlled scanning stage and water spray, and the crater morphology and chemical composition were measured using optical microscopy and high-resolution synchrotron radiation infrared spectromicroscopy. The residual energy remaining in tooth samples was measured to be 30 to 40% for enamel and 20 to 30% for dentin without water cooling, under optimum irradiation intensities, significantly lower than for longer CO_2 laser pulses. The transmission through 2-m length 300-, 500-, 750-, and 1000-μm silica hollow waveguides was measured and 80% transmission was achieved with 40 mJ per pulse. These results suggest that high repetition rate TEA CO_2 laser systems operating at $\lambda = 9.3\ \mu m$ with pulse durations of 10 to 20 μs are well suited for dental applications.
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Keywords: hard tissue ablation; enamel; dentin; bone; TEA CO_2 laser; dentistry; FTIR; thermal damage; hollow waveguides.

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1 Introduction

Previous measurements in our laboratory[1,2] suggest that transverse excited atmospheric pressure (TEA) CO_2 dental laser systems operating at 9.6 or 9.3 μm are ideally suited for dental hard tissue applications. Moreover, CO_2 lasers may be more versatile because they are suitable for soft tissue vaporization with hemostasis, precision removal of carious and noncarious dental hard tissue, caries inhibition treatments by localized surface heating, and surface conditioning for bonding. Although, the erbium:yttrium aluminum garnet (Er:YAG) and erbium:yttrium scandium gallium garnet (Er:YSGG) lasers can efficiently ablate dental hard tissue, they are expensive and somewhat limited in application, that is, they are not as well suited for caries prevention treatments as CO_2 lasers and are not applicable for soft tissue surgery due to poor hemostasis. The CO_2 laser is strongly absorbed by the mineral of dental hard tissues near $\lambda = 9\ \mu m$, due to the phosphate group of hydroxyapatite. The absorption coefficient of dental enamel has been determined to be approximately 8000 cm^{-1} at $\lambda = 9.6\ \mu m$ and 5250 at $\lambda = 9.3\ \mu m$,[3] which is approximately 10 times higher than for the conventional $\lambda = 10.6$-μm CO_2 laser wavelength used in medicine today

Address all correspondence to Daniel Fried, University of California at San Francisco, PRDS, 707 Parnassus Ave, San Francisco, CA 94143; Tel: 415–502–6641; Fax: 415–476–0858; E-mail: daniel.fried@ucsf.edu

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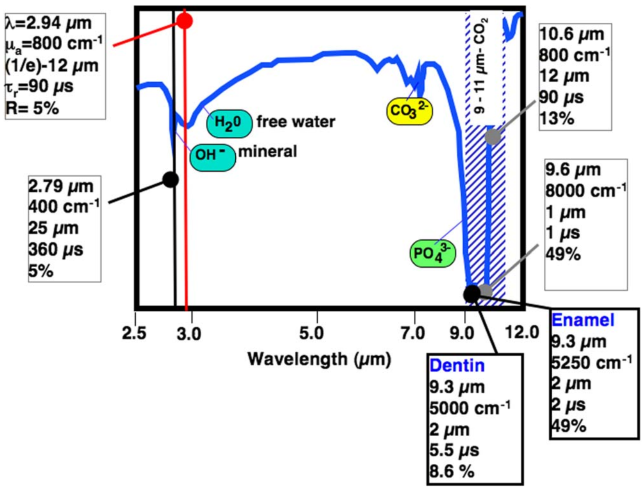

Fig. 1 Infrared transmission spectrum through KBr pellet with 1% enamel powder. The molecular groups responsible for absorption are indicated with the relevant laser wavelengths. The absorption coefficient (cm^{-1}), absorption depth ($1/e$), the thermal relaxation time (μs), and tissue Fresnel reflectance (%) for enamel are indicated in respective text boxes with relevant wavelength. The values for dentin at 9.3 μm are also shown.

and is markedly higher than for any other laser wavelengths throughout the visible and IR spectra (see Fig. 1).

Excessive deposition of heat in the tooth may lead to eventual loss of pulpal vitality, thus any viable laser-dental procedure has to minimize the accumulation of heat in the tooth. The accumulation of heat in the tooth can be minimized by using a laser wavelength tuned to the maximum absorption coefficient of the tissue irradiated and by judicious selection of the laser pulse duration.[4] The pulse duration should be on the order of the thermal relaxation time for axial heat conduction (τ_z) of the deposited energy in the tissue surface to minimize thermal diffusion during the laser pulse. For laser pulse durations greater than τ_z, the laser energy is conducted away from the enamel surface into the interior of the tooth during the laser pulse, resulting in inefficient surface heating and possible pulpal damage. The thermal relaxation time for enamel and dentin at 9.3 μm is 2 and 5.5 μs, respectively (see Fig. 1). If the pulse duration is too short, then the deposited power density may be too high, causing the generation of a plasma in the plume of ablated material that shields the surface and reduces the efficiency of ablation. This is what occurs with the conventional TEA CO_2 laser due to the 100- to 200-ns gain-switched spike.[1] As the ratio of N_2 to CO_2 is increased, more energy is shifted from the initial gain-switched spike to the nitrogen tail of the laser pulse temporally stretching it to achieve the desired length. In a previous study with a stretched 9.6-μm TEA laser, we observed an increase in the ablation rate from 1 to 2 μm per pulse to 10 to 20 μm per pulse after stretching the pulse length from 0.5 to 8 μs.[1]

Several studies have demonstrated that pulsed CO_2 lasers with pulse durations in the range of 0 to 100 μs can be used to efficiently ablate dental hard tissues with minimal heat deposition in the tooth.[5,6] Krapchev et al.[7] achieved ablation efficiencies of approximately 0.1 and 0.2 mm^3/J for enamel and dentin, respectively, using a CO_2 laser ($\lambda = 10.6$ μm) with a pulse duration of 20 μs.[3] Melcer[8] showed that the ablation rate of a 10.6-μm TEA CO_2 laser could be markedly increased by extending the pulse duration from 1 to 2 μs to approximately 10 μs. They measured an increase in the ablation rate at the saturation fluence from 1 to 2 μm to over 10 μm for enamel ablation. However, the thermal relaxation time for enamel at a wavelength of 10.6 μm is ~70 to 80 μs and it is not advantageous to operate with a pulse duration on the order of less than 20 μs as is the case for the 9.3- and 9.6-μm CO_2 laser wavelengths.

Featherstone and Nelson[9] demonstrated that TEA CO_2 lasers operating at the 9.3- to 10.6-μm wavelengths could be used effectively to inhibit enamel demineralization. Forrer et al.[10] found that the ablation efficiency of porcine rib bone was higher and the ablation thresholds markedly lower at $\lambda = 9.3$ and 9.6 μm than for the 10.6-μm wavelength. Ertl and Müller[6] reported similar results with enamel. Thus, for short TEA laser pulses, the ablation efficiency of enamel and dentin should be higher at $\lambda = 9.3$ and 9.6 μm than at the standard ($\lambda = 10.6$ μm) CO_2 wavelength resulting in reduced heat deposition in a tooth for similar irradiation conditions. Previous measurements showed that a TEA laser with a pulse duration of 2 μs reported took one-fifth the absorbed laser energy to melt enamel at 9.6 μm, than at 10.6 μm.[11]

Lasers can be highly effective for the processing of bone and dentin. It is well understood, that by matching the laser pulse duration to the thermal relaxation time of the deposited laser energy, peripheral thermal damage can also be minimized.[4] A major advantage the laser has over a bone saw is its inherent ability to cut more precisely. Lasers also have the potential to make precise cuts with very high aspect ratios (depth/diameter) and are well suited for endoscopic delivery and robotic control for selective ablation. In addition, lasers have been shown to leave a layer of chemically altered hard tissue that is more resistant to acid dissolution. A possible limitation of the laser is the potential for thermal damage to peripheral tissues near the site of irradiation that may inhibit or delay wound healing. It has been shown that excessive thermal damage to the underlying collagen matrix of dentin compromises bonding to restorative materials during cavity preparations. Determination of the laser parameters that minimize peripheral thermal damage is paramount for the safe and effective use of lasers on protein rich hard tissues such as dentin and bone.

In two previous studies, we investigated the use of nanosecond UV laser pulses at $\lambda = 355$-nm, Q-switched Er:YAG and Er:YSGG laser pulses at 2.94 and 2.79 μm, and short 9.6-μm TEA CO_2 laser pulses for minimizing thermal damage to dentin and bone during laser ablation.[12,13] The best results were attained for the Q-switched erbium laser pulses and the short highly absorbed CO_2 laser pulses. There have been several studies over the past 20 years concerning the ablation of dentin and bone with minimal thermal damage involving a wide range of lasers and some have utilized laser pulses that are shorter than the time constant for heat diffusion, so that the deposited laser energy is confined to the absorbed region during the laser pulse.[5,7,8,10,14–24] Although short Q-switched Er:YAG and Er:YSGG lasers are effective for the ablation of dentin and bone without peripheral thermal damage, such lasers can only be operated efficiently with fairly low repetition rates. UV lasers such as excimer lasers and femto- and picosecond lasers can be operated at high repetition rates; however, at most, only 1 to 2 μm of hard tissue are removed per pulse making them quite inefficient.[25,26] CO_2 lasers can be operated at very high repetition rates for the rapid removal of dental hard tissues and they can be operated with short pulses to minimize thermal damage. Ivanenko et al. used a Q-switched industrial CO_2 laser operating at $\lambda=10.6$ μm with a 300-Hz repetition rate and a pulse duration in the range of tens of nanoseconds for the rapid processing of bone.[27,28] More recent work by that group utilized longer $\lambda=10.6$-μm CO_2 laser pulses of 80-μs duration from an RF-excited laser for the processing of bone.[18,29]

We have calculated the thermal relaxation time for $\lambda=9.3$-, 9.6-, and 10.6-μm laser pulses absorbed by dentin to be 5.5, 3.3, and 210 μs, respectively, based on the absorption coefficients that we previously measured using time-resolved radiometry.[2] We expect similar time constants for bone due to its similar composition to dentin. Those data suggest that thermal damage to dentin and bone can be limited by using $\lambda=9.3$- and 9.6-μm CO_2 laser pulses with a pulse duration on the order of 5 to 20 μs. The purpose of this study was to determine whether enamel, dentin, and alveolar bone could be ablated efficiently at clinically relevant rates (i.e., 10 μm per pulse), without thermal damage at high repetition rates using $\lambda=9.3$-μm TEA laser pulses.

In summary, the purpose of this study is to demonstrate that TEA laser pulses at 9.3 μm with a duration of 10 to 20 μs can be used at high repetition rates for the ablation (cutting) of dental hard tissues with minimal peripheral thermal or mechanical damage and without excessive heat accumulation and that those laser pulses can be efficiently transmitted through hollow waveguides for clinical delivery.

2 Materials and Methods

2.1 *Laser Parameters*

An industrial marking laser, Impact 2500 from GSI Lumonics (Rugby, United Kingdom), operating at 9.3 μm, due to optical coatings on the resonator optics, which are capable of high repetition rates up to 500 Hz, was used for these experiments. The laser was modified for operation in a single-spatial mode optimized for the longer 5- to 20-μs laser pulses by LightMachinery (Ottawa, Canada) by installing an intercavity aperture and modified resonator optics. This laser also incorporates a solid-state switch for very stable and reliable high-voltage switching, solving the stability and heat dissipation problems encountered previously with thyratron-based systems. The laser gas handling system is sealed with an automatic gas exchange after 20-min of operation. Fluence ranging from 0.2 to 160 J/cm^2 and pulse energies of 0.1 to 45 mJ per pulse were used. The laser pulse temporal profiles shown in Fig. 2 were measured with a room temperature HgCdTe detector from Boston Electronics PD-10-6-3 (Boston, Massachusetts). The laser pulse was 18 μs in length for a 4% CO_2 gas mixture (20% N_2) and 15 μs for the 2% CO_2 gas mixture (22% N_2) with the use of a 75% reflectivity output coupler. Half the energy was contained in the initial 5 μs and 80% of the energy was in the first 10 μs. The laser pulse duration was approximately half the duration mentioned above, approximately 5 to 9 μs, with the same two gas mixtures if a higher reflectivity (85% reflectivity) output coupler was used. The laser energy was calibrated and measured using a laser energy and/or power meter, EPM 1000, Coherent-Molectron (Santa Clara, California) with a ED-200 Joulemeter from Gentec (Quebec, Canada). The laser was focused with a planoconvex ZnSe lens of 100-mm focal length to a beam diameter of approximately 200 μm. The laser beam diameter $(1/e^2)$ at the position of irradiation was determined by scanning with a razor blade across the beam. Two- and three-dimensional images of the laser spatial profile were acquired using a Spirocon Pyrocam III pyroelectric array (Logan, Utah). Both laser beam profile and spatial profile showed that the laser was operated in a single-spatial mode, Gaussian spatial beam (see Fig. 3). High spatial beam quality is a prerequisite for efficient coupling into hollow waveguide beam delivery systems.

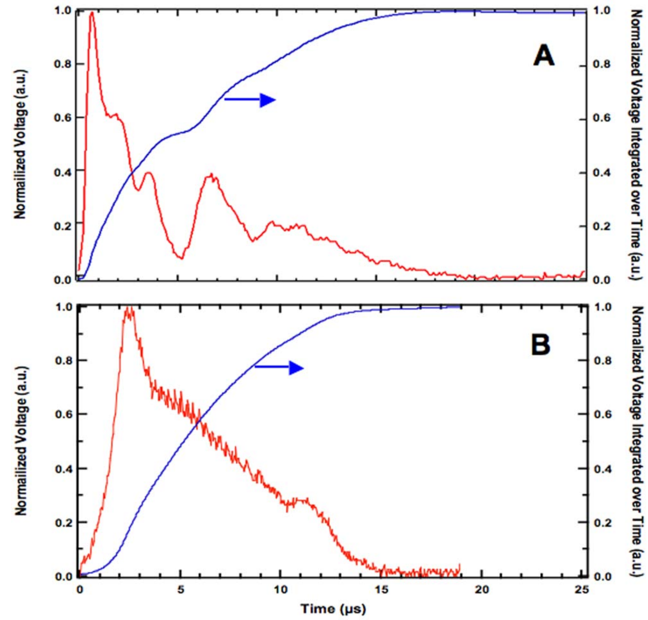

Fig. 2 The temporal profiles of the TEA CO_2 laser pulses for the two laser gas mixtures with varying CO_2 and N_2 concentration are shown: (a) 4.3% CO_2 and (b) 2% CO_2. The pulse durations were 15.4 and 18 μs, respectively, for each gas mixture. The temporal profiles (left axis) were integrated (right axis-arrow) to show that the laser pulses produced using the 4.3% CO_2 gas mixture had a greater fraction of the pulse energy in the initial few microseconds than that measured during the same time interval for the laser pulse produced with the 2% CO_2 gas mixture, that is, 50% of intensity in first 3.9 μs for the 4.3% CO_2 gas mixture versus 5.2 μs for the 2% CO_2 gas mixture.

2.2 *Laser Ablation Rate Determination*

Thin sections, approximately 200-μm thick, of human enamel and dentin from unerupted human molars and premolars and adult porcine alveolar bone were prepared using a MicroLux diamond band saw with water cooling from Micro-Mark (Berkeley Heights, New Jersey) and a Isomet 2000 precision saw from Buehler (Lake Bluff, Illinois). Each section was mounted over the edge of a glass slide and a ED-200

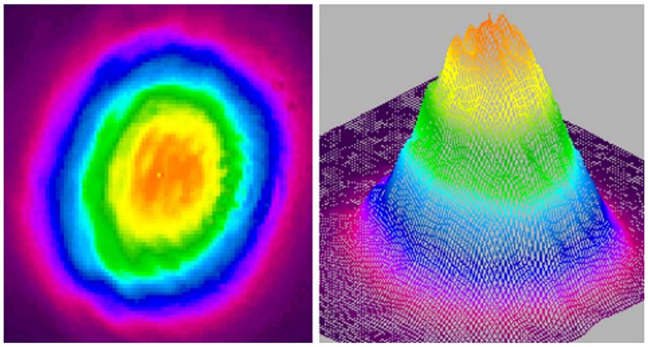

Fig. 3 Two- and three-dimensional images of the laser spatial profile acquired using a Pyrocam III pyroelectric beam analyzer.

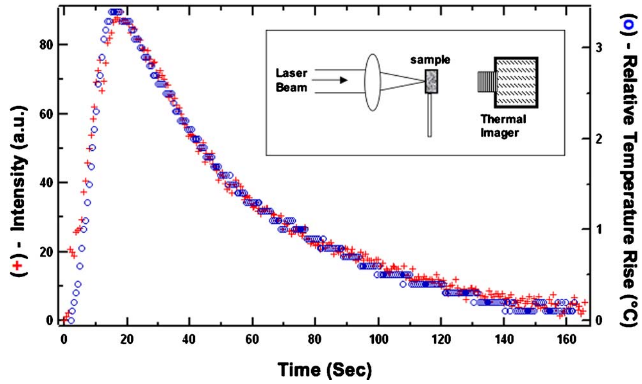

Fig. 4 (Inset) The experimental setup for residual heat deposition measurements on bovine enamel block samples. The thermal camera was placed behind the sample to record thermal radiation from the tissue sample throughout the laser ablation. Simultaneous thermal measurements using the thermal camera (+)-left-axis and a microthermocouple (o)-right axis for 3000 laser pulses delivered with a fluence of 0.28 J/cm^2 and a repetition rate of 300 Hz.

Joulemeter was placed directly behind each section to function as a perforation sensor. The number of pulses required to perforate each section was recorded to determine the ablation rate. It is important to point out that the single pulse ablation rate depends on the method of measurement with the highest rates measured for a single incident pulse on the tissue. However, such measurements require accurate measurement of the depth ablated. Sample perforation measurements are easier to carry out, however the ablation rate determined using this method is highly dependent on the sample thickness with the rate decreasing with increasing sample thickness. We have found that a 200-μm thickness works well for laser pulses that ablate 5 to 40 μm per pulse, requiring a minimum of several laser pulses to perforate the tissue samples.

2.3 *Laser Incisions in Human Enamel, Dentin and Porcine Bone*

Plano-parallel enamel blocks, 3×3 mm^2, approximately 2-mm thick, were prepared from human unerupted molars. Surfaces were polished with 1200 carbide grit, and smear layers produced from polishing on the sample surfaces were removed by sonication. Dentin and bone sections with a thickness of at least 2 mm were cut using diamond saws and samples were kept well hydrated before ablation and either cooled using a computer-controlled water spray or left dry during ablation. Bone samples were kept frozen before ablation. A low-volume and low-pressure air-actuated fluid spray delivery system consisting of a EFD 780S-SS spray valve, a Valvemate 7040 controller, and a fluid reservoir from EFD Inc. (East Providence, Rhode Island) controlled by a computer was used to provide a uniform spray of water on the tissue surface.

Lateral incisions 3 mm long were produced in our dentin and bone sections by scanning the laser in spots spaced at 50-μm intervals, each spot receiving 10 pulses. A computer-controlled stage was used to create controlled movement of the samples for the incisions. Three incisions were made for each frequency (10, 50, 100, 200, 300, and 400 Hz) for both wet and dry conditions in both dentin and bone. Figure 10 shows examples of the incisions in dentin and bone. After ablation, tissue sections and enamel blocks were embedded onto epoxy resin disks with LX-112 epoxy resin from Ladd Research (Williston, Vermont), that were subsequently serially polished with 1200 carbide grit, and 6, 3, 1, and 0.3 diamond suspensions, using Ecomet 2 and Fibromet polishers from Buehler.

2.4 *Residual Heat Measurements with Thermal Imaging Analysis*

Enamel blocks, 4×4 mm^2, $\sim$1-mm thick, were prepared from bovine incisors. Surfaces were polished with 1200 carbide grit and each block was glued onto the edge of a glass slide (Fig. 4). A thermal camera Omega, from Indigo System Corporation (Goleta, California), incorporating an uncooled microbolometer focal plane array with 14-bit digital output was placed behind the block to measure the thermal emission during laser ablation in the wavelength band from 7.5 to 13.5 μm.

The magnitude of the residual energy (E_R) remaining in the tooth as heat during enamel ablation was directly calculated by taking the ratio of the rise in signal due to thermal radiation on the opposite side of laser irradiated block for ablative versus nonablative laser pulses. Every image consisted of 164×129 pixels, and a region of interest, where the pixels correlate with the block surface, was selected before each series of measurements. The average value of all the 14-bit pixels within the region of interest was computed and recorded continuously throughout the laser treatment. The accuracy of this approach was validated and calibrated by comparison of the thermal emission from the block with simultaneous micro-thermocouple measurements. Figure 4 shows the temperature rise that was simultaneously measured using the thermal camera and a thermocouple cemented to the enamel surface. Nonablative laser pulses were delivered at a fluence of 0.28 J/cm^2 and a repetition rate of 300 Hz. The average residual heat deposition values were 71.2±5.0% for the thermocouple readings and 69.9±4.8% for the thermal camera readings.

In order to measure the residual energy remaining at each respective fluence of interest, each block was irradiated with two laser pulse trains: nonablative and ablative. The first train of pulses irradiated the surface of the block with 3000 low-

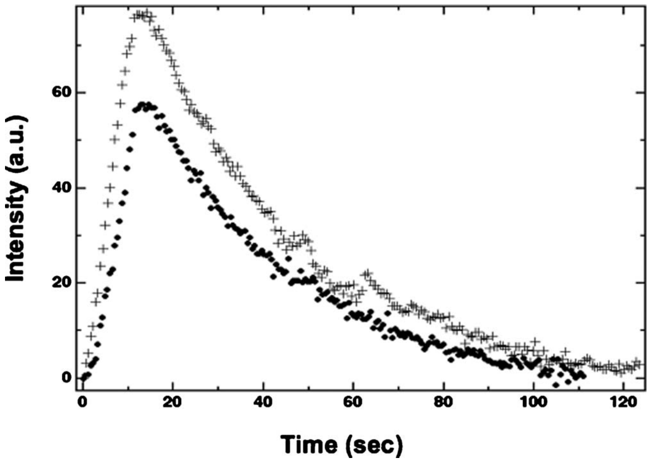

Fig. 5 Residual heat on the backside of a block of bovine enamel was monitored during irradiation with two series of ablative and nonablative CO_2 laser pulses. The repetition rate, fluence, and number of laser pulses were varied, but the total delivery time and cumulative energy was constant. The 3000 nonablative laser pulses (top crosses) were delivered at a repetition rate of 300 Hz and an incident fluence of 0.28 J/cm^2. The 90 ablative laser pulses (bottom trace filled) were delivered at a rate of 9 Hz and an incident intensity of 9.5 J/cm^2. The residual energy E_R was given by the ratio of the two peak intensities.

energy nonablative laser pulses delivered at a repetition of 300 Hz (Fig. 5). The measurements were repeated after the block had equilibrated (returned to room temperature), then a second train of ablative pulses were delivered to the surface of the block at the fluence of interest. In order to vary the fluence while keeping the total energy delivered and total delivery time, of 10 s, constant, the repetition rate, total number of laser pulses, energy per pulse, and the spot size were varied. These measurements are similar to those described in Ref. 30.

2.5 *Polarized Light Microscopy* (*PLM*)

Images of tissue surfaces were taken before and after laser irradiation with a Secolux BF/DF/DIC microscope manufactured by Leitz-Wetzlar (Germany). A low-volume and/or low-pressure air-actuated fluid spray delivery system consisting of a 780S spray valve, a Valvemate 7040 controller, and a fluid reservoir from EFD, Inc. was used to provide a uniform spray of fine water mist onto the enamel surfaces at 16 mL/min. Each incision, approximately 6-mm long and 700-μm wide, was prepared by scanning the laser beam, operating at 300 Hz, across the sample at 6 mm/s, with a 50-μm separation between each longitudinal scan.

Polarized light microscopy was used to determine the degree of thermal damage produced while creating our lateral incisions. Thermally damaged dentin and bone appears dark brown to black due to carbonization of protein (collagen). Under examination with a polarized microscope with crossed polarizers, thermal damage to the mineral and protein phases result in loss of birefringence. Thin sections were taken from each sample incision sectioning our samples using the Isomet 2000 diamond saw. Sections were made perpendicular to the direction of the lateral incisions to view them in cross section. After cutting, sections were imbibed with water and viewed in the optical microscope using crossed polarizers and a Red I wave plate. Thin sections were examined visually using a Westover Scientific Series 7 optical microscope (Westover Scientific, Mill Creek, Washington) with an integrated digital camera, Canon EOS Digital Rebel XT (Canon Inc., Tokyo, Japan) and IMAGE PRO PLUS software (Media Cybernetics, Silver Spring, Maryland). A moire ruling with 100 lines per millimeter was used to calibrate the length measurements on the images. Figure 11 shows images at 100× magnification of wet and dry dentin and bone.

The wave plate introduces a phase retardation of 530 nm so that addition and subtraction colors introduced by the tissue birefringence induce resolvable changes in color. In the case of thermal damage, increased attenuation of the illumination light causes altered tissue to appear black, which is easier to discern under polarized light. Subtle changes in birefringence should introduce resolvable color changes. However, we were unable to resolve such changes and there was a sharp demarcation between normal tissue and the thermal damage zone.[12,13] A complete loss in birefringence of dentin without any other changes in optical properties would have resulted in a subtle change in color around the rim of the crater. In cross section, the char layer appears as loosely attached debris along the crater walls, and some is probably lost during the sectioning procedure. The remaining layer is of uniform thickness and it most likely represents increased scattering and absorption due to denaturation and partial thermal decomposition of the collagen matrix.

2.6 *Synchrotron Radiation—Fourier Transform Infrared Spectromicroscopy* (*SR-FTIR*)

FTIR spectroscopy used in the specular reflectance mode is well suited for resolving thermally induced changes in dental hard tissue as a result of laser irradiation. Chemical changes in the mineral phase and loss of water and protein can be clearly seen as a result of thermal damage during laser irradiation. High spatial resolution (5 μm) is achievable with a high brightness synchrotron radiation source such as the advanced light source (ALS) at Lawrence Berkeley National Laboratory. IR spectra of laser treated dentin and bone in both wet and dry conditions were obtained at ALS. All samples had been irradiated at 400 Hz. A Nicolet Magna 760 FTIR interfaced to a Nic-Plan IR microscope, equipped with a motorized sample stage connected to beam line 1.4.3 of ALS at Lawrence Berkeley National Laboratory was used to acquire spectra of the incisions produced with the lasers.

Plano-parallel sections approximately 1-mm thick were cut at right angles to the laser incision. Each section was embedded onto 2 in. diameter LX-112 epoxy resin disks, which were subsequently serially polished with 1200 grit carbide and 3 and 1-μm diamond suspensions. Specular reflectance spectra were acquired with a spatial resolution of 5 μm by scanning the 5-μm spot imaged by the FTIR microscope across the laser intensity profile from the normal dentin to the resin outside the incision.

2.7 *Hollow Waveguide Transmission Measurements*

Quartz hollow waveguides, from Polymicro Technologies, LLC (Phoenix, Arizona), 2-m long and hollow-core diameters of 300, 500, 750, and 1000 μm were coupled to the laser using f=50 to 125 mm ZnSe lenses and a laser energy and/or power meter was used to measure and record the transmitted

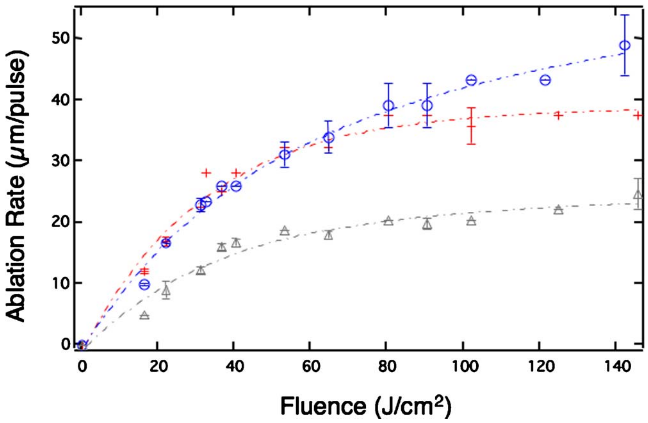

Fig. 6 Ablation rate versus fluence curves for porcine jaw bone (blue circle), human dentin (red cross), and enamel (gray triangle) carried out with the 4% CO_2 gas mixture with the 75% reflectivity output coupler. Each data point is the mean of three measurements±standard deviation. Curves are drawn as a visual aid to represent the expected increase in the ablation rate with increasing fluence, followed by saturation of the ablation rate above the plasma initiation threshold (color online only).

energy. The measured transmitted energy reflects losses due to both coupling in and out of the waveguide in addition to the attenuation of the 2-m length of the waveguide.

3 Results

3.1 *Laser Ablation Rate Determination*

Ablation studies were performed at $\lambda=9.3$ μm with TEA laser pulses of 18-μs duration (4% CO_2 gas mixture with 75% output coupler) for enamel, dentin, and alveolar bone. See Refs. 31 and 32 for measurements for the laser pulses of 15-μs duration (2% CO_2 gas mixture). The gain switched spike present in the beginning of the 18-μs pulse initiated the onset of a plasma, which reduced the ablation effectiveness at high fluence. Ablation rates as a function of the incident laser fluence are shown in Fig. 6 for all three tissues: enamel, dentin, and alveolar bone. These rates are for the perforation of 200-μm thick sections with no application of a water spray. The spot size was varied from 200 to 1080 μm by moving the sample away from the focal spot in order to achieve the targeted fluence, and the repetition rate was 1 Hz. The ablation rate of enamel saturated at a maximum rate of approximately 19 μm/pulse for irradiation intensities above 40 J/cm^2 for the 4% gas mixture. The ablation rate for dentin and bone was approximately twice as high, 30 to 50 μm per pulse.

3.2 *Residual Heat Deposition Measurements*

Figure 5 shows an example of the residual heat deposition measurements performed at a nonablative fluence of 0.28 J/cm^2 and an ablative fluence of 9.53 J/cm^2 with the 4% of CO_2 gas mixture. Ablative laser pulses have a lower residual heat deposition than nonablative pulses due to energy transformed into kinetic and internal energy of the ablated material.

The mean and individual values of the residual heat E_R that were measured for increasing irradiation intensities are plotted in Fig. 7 for enamel and dentin. For laser pulses near the threshold for ablation, the residual heat remaining in the tooth is high. Previous measurements have shown that ablation rapidly stalls after only a few laser pulses at irradiation intensities just above the ablation threshold.[33–35] The initial few laser pulses ablate some material before ablation stalls and subsequent laser pulses contribute significantly to heat accumulation. As the incident fluence increases, ablation proceeds without stalling and the E_R values converge to a minimum value due to plasma or debris shielding. The minimum E_R value represents the most efficient ablation attainable for this wavelength and pulse duration in bovine enamel. This value for enamel is approximately 34%, which indicates that over 66% of the deposited laser energy is carried away by the ablative laser pulses delivered at 33 J/cm^2. The magnitude of the fluence at which the residual heat reaches a minimum value, 34%, is closely correlated with the maximum ablation rate for enamel, which occurs near 40 to 60 J/cm^2 (Fig. 6). The ablation rate saturates because additional laser energy is absorbed or reflected by the highly opaque plasma, preventing further removal. The minimum E_R value for dentin is significantly lower than for enamel, below 20% most probably due to the more volatile water and collagen content.

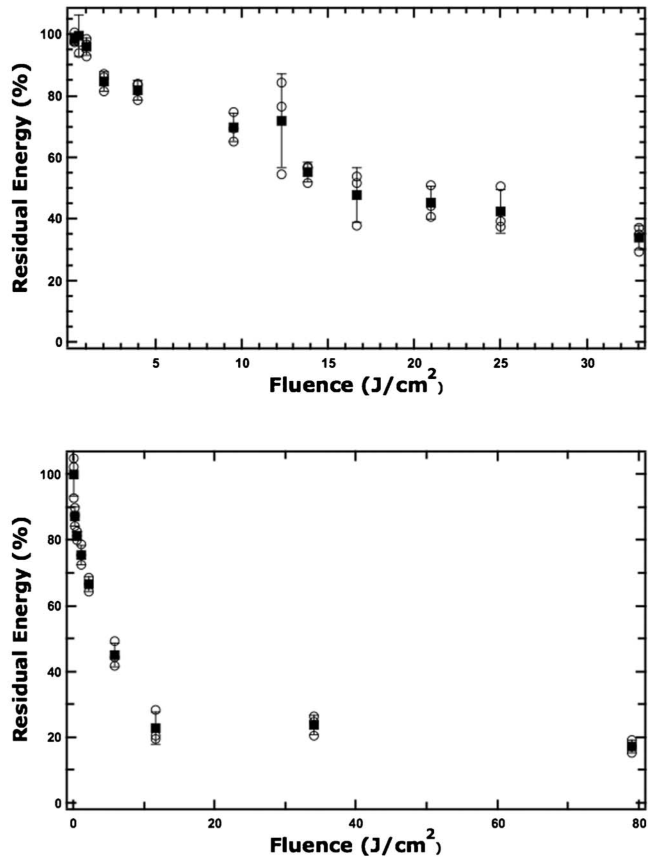

Fig. 7 The mean and individual values of the residual energy, $E_R\pm$ standard deviation ($n=3$) for the ablation enamel (top) and dentin (bottom) measured using CO_2 laser pulses delivered in varying irradiation intensity.

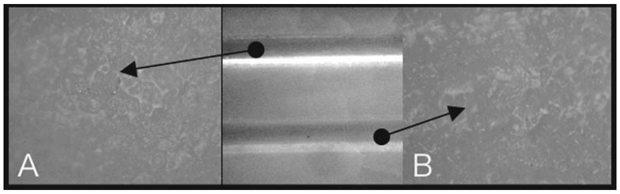

Fig. 8 Images of incisions in enamel produced without (a) and with (b) the water spray treatment (200× magnification). CO_2 laser pulses of 18-μs duration at a fluence of 31 J/cm^2, scanning at 6 mm/s.

3.3 *Peripheral Thermal Damage in Enamel, Dentin, and Bone* (*PLM and SR-FTIR*)

Figure 8 shows reflected light images of incisions produced in enamel at a repetition rate of 300-Hz scanning at 6 mm/s with and without the water spray at a fluence of 31 J/cm^2. The base of each incision appears to be uniformly melted. SR-FTIR spectra acquired in the area of the enamel in the melted region show that highly crystalline hydroxyapatite has been formed in that region even on the incisions produced with the water spray (Fig. 9). The loss of carbonate and narrowing of the phosphate peak near 1050 cm^{-1} are indicative of conversion to the more highly crystalline, pure phase hydroxyapatite that manifests a greater resistance to acid dissolution. Incisions produced at lower scanning speeds without water manifested greater thermal damage with the formation of chalky-white asperities that are most likely nonapatitic CaP phases formed due to disproportionation of hydroxyapatite at high temperature. SR-FTIR spectra of such asperities did not resemble spectra of hydroxyapatite.[36,37]

A comparison of incision depth in dentin for varying repetition rates showed no significant variation up to 400 Hz, the maximum repetition rate investigated. This demonstrates that high repetition rates can be employed without interference from ejected material in between pulses.

Minimal thermal damage to dentin and bone was observed in both wet and dry conditions for high scanning rates (6 mm/s) at the highest repetition rate (400 Hz). Figure 10 shows reflected light images of incisions produced in both

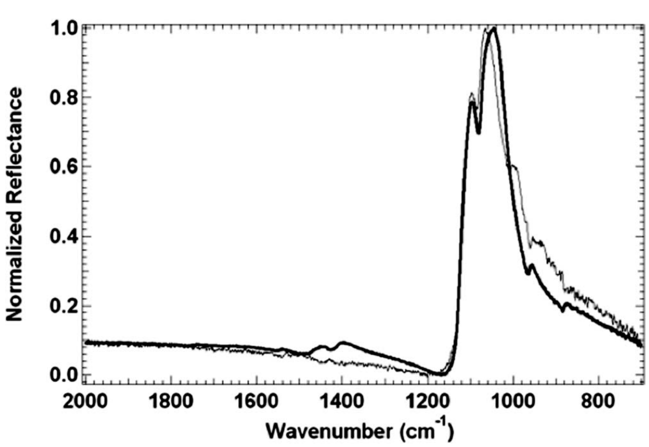

Fig. 9 Comparison of SR-FTIR spectrum of sound enamel (thick gray trace) versus spectrum of the incision area on the bovine enamel block produced scanned at 6 mm/s using a fluence of 31 J/cm^2 with the water spray (thin black trace).

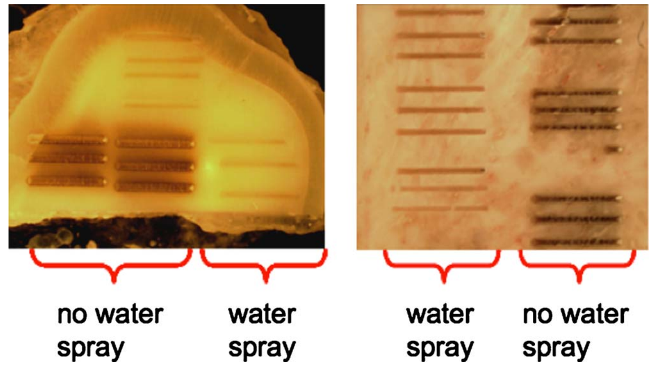

Fig. 10 Laser ablation in human dentin (left) and porcine bone (right) with and without the water spray at 400 Hz and 80 J/cm^2.

dentin and bone at 400 Hz at a fluence of 80 J/cm^2. Very clean uniform incisions without discoloration were produced with use of the water spray. Charring occurred without the water spray. Thin sections were cut across all the incisions in dentin and bone for examination with PLM (Fig. 11). PLM showed thermal damage zones of less than 22 μm for dry dentin and less than 16 μm for wet dentin for all repetition rates investigated up to 400 Hz. Thermal damage zones for bone were slightly higher: 27 μm for dry bone and 18 μm for wet bone. Thicker sections were embedded and examined with SR-FTIR with a spatial resolution of 5 μm. Incisions were produced at a fluence of 80 J/cm^2. Results were also compared for lower irradiation intensities of 40 and 20 J/cm^2. The thermal damage zones at 40 and 20 J/cm^2 were both smaller than those found at 80 J/cm^2 at 400 Hz. Graphs of the thermal damage in dentin and bone for irradiation intensities of 80, 40, and 20 J/cm^2 all at 400 Hz were reported in our SPIE proceedings paper.[32]

Figure 12 shows reflected light images of incisions produced in dentin at 40 J/cm^2 at a repetition rate of 400 Hz with 15.4 μs with and without the water spray. There is charring visible for the incisions produced without the water spray. The incisions produced with the water spray are much shallower than the dry incision pulses; however, they are clean without discoloration due to thermal damage.

SR-FTIR spectra were acquired across the edge of the incisions shown in Fig. 12. Spectra taken at 5-μm intervals across the incision wall as shown in Figs. 13 and 14 manifest few chemical changes due to peripheral thermal damage. These results show that within a resolution of 5 μm, minimal changes in the amide structure of the dentin could be detected. Therefore, FTIR showed no spectral changes within 5 μm around the periphery of the incisions of our samples in wet and dry conditions at 400 Hz.

3.4 *Hollow Waveguide Transmission Measurements*

The transmission rates through 2-m long 300-, 500-, 750-, and 1000-μm quartz hollow waveguides (Table 1) were measured. The bending diameter for the hollow waveguides was approximately 45 cm. The highest transmission was achieved for the 750-μm waveguide with a bending diameter of 45.5 cm.

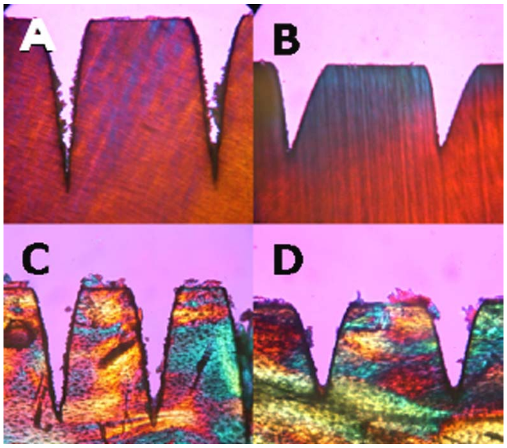

Fig. 11 PLM images under 100× magnification show dentin (a) irradiated at 200 Hz without the water spray and with the water spray at 100 Hz (b). Bone irradiated at 50 Hz without the water spray (c) shows bone irradiated at 50 Hz with the water spray in (d). Note thermal damage zones in (a) and (c).

4 DISCUSSION

These studies demonstrate that a $\lambda = 9.3$-μm pulsed TEA CO_2 laser operating at high repetition rates with a pulse duration of 15 to 18 μs can ablate dental hard tissues efficiently and at a practical rate to be used clinically with minimal peripheral thermal damage if a low-volume water spray is used. It was necessary to greatly reduce the fraction of energy disposed in the initial 100 to 200-ns gain-switched spike in the laser pulse to avoid plasma formation that restricts the ablation rate to 1 to 2 μm per pulse. The single pulse ablation rate varied from a maximum of 9 to 20 μm per pulse for enamel depending on the laser gas mixture and the reflectivity of the output coupler. The highest rate was obtained for the 2% CO_2 gas mixture with the 75% reflectivity output coupler (15-μs pulse duration). Dentin and bone ablation rates were typically twice as high than for enamel: 30 to 40 μm per pulse. Such $\lambda = 9.3$-μm laser pulses may be ideally suited for the irradiation of specific high risk areas of the dentition that are highly susceptible to tooth decay and early caries lesions to reverse or prevent the progression of tooth decay in those areas.

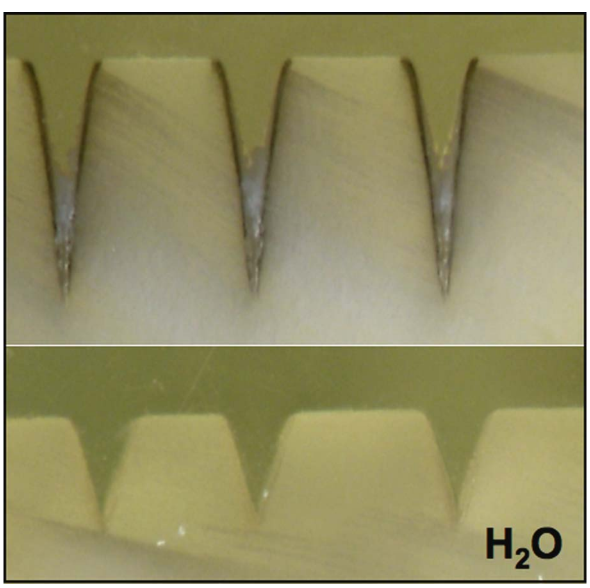

Fig. 12 Reflected light images of cross sections of human dentin produced with and without the water spray at 400 Hz and 80 J/cm^2.

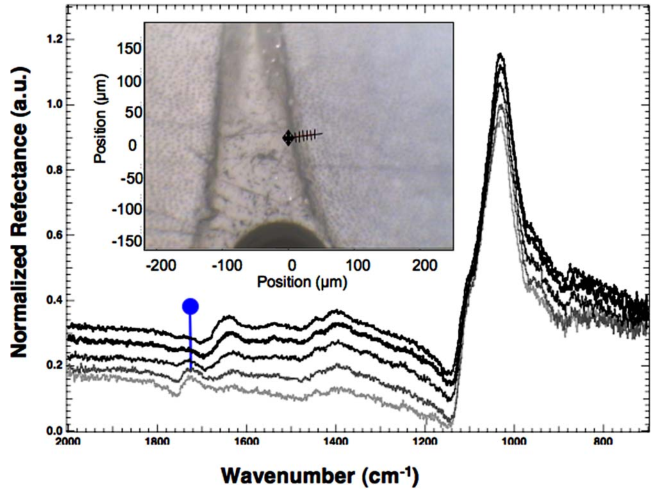

Fig. 13 Sequential SR-FTIR spectra taken at 5-μm intervals across the embedded dentin samples with incisions produced with the water spray, 400 Hz and 80 J/cm^2. The reflected light image contains a cross showing the position of each spectrum. The spectra are displayed progressing from the unmodified dentin (top spectrum) toward the center of the lesion. The peak near 1700 cm^{-1} marked by the gray line is due to the embedding resin and its rise indicates that the position is across the wall of the incision.

Measurements of the residual heat remaining in the tooth after each ablative laser pulse at the optimal irradiation intensities for efficient ablation indicate that only 34 and 20% of the energy remains in the tooth for enamel and dentin, respectively. In contrast, the energy remaining in the tooth after ablation using longer (100 to 200-μs) pulses from the more conventional $\lambda = 10.6$-μm CO_2 and free running Er:YAG and

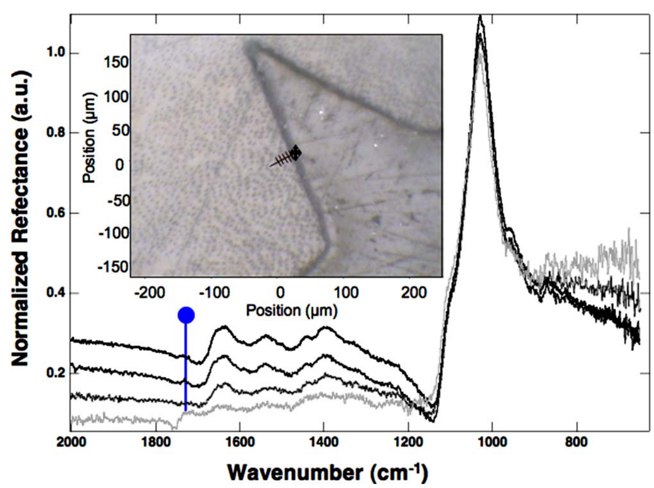

Fig. 14 Sequential SR-FTIR spectra taken at 5-μm intervals across the embedded dentin samples with incisions produced without the water spray, 400 Hz and 80 J/cm^2.

Table 1 The transmission properties of quartz hollow waveguides of 300-, 500-, 750-, and 1000-μm diameter, a length of 2 m, and a bending diameter of 45.5 cm for λ=9.3-μm laser pulses of 18-μs duration. The focal length of the lens used for coupling into the waveguide is indicated in the left column.

Lens Focal Length	Incident Energy	1000-μm Diameter Percent Energy Transmission (Trans. Energy)	750-μm Diameter Percent Energy Transmission (Trans. Energy)	500-μm Diameter Percent Energy Transmission (Trans. Energy)	300-μm Diameter Percent Energy Transmission (Trans. Energy)
125 mm	50 mJ	74% (37 mJ)	80% (40 mJ)	32% (16 mJ)	
70 mm	50 mJ			38% (19 mJ)	23% (12 mJ)
50 mm	52 mJ			20% (10 mJ)	29% (15 mJ)

Er:YSGG laser pulses is higher on the order of 50 to 60% based on our previous measurements.[30] The reflectivity is also much lower on the order of 5 to 13%.[34] Therefore the residual energy remaining in the tooth for those laser systems is twice as high, which increases the volume of water that is needed to offset heat accumulation.

This study also demonstrated that λ=9.3-μm TEA laser pulses are well suited for the precise removal of dentin and bone for dental restorations and implants at high repetition rates without peripheral thermal damage. PLM and SR-FTIR indicated that there was minimal peripheral thermal damage. As was observed in our previous studies,[12,13] there was negligible charring of dentin for CO_2 laser pulses of less than 10-μs duration, and that is comparable to the best results that have been previously reported in the literature for bone for free electron,[38,39] TEA CO_2,[14,10] excimer,[40] and Er:YAG[15,41–43] laser pulses used with water cooling. Although short Q-switched Er:YAG lasers also yield excellent results, they are expensive, difficult to operate without damaging the optics due to the high water absorption, and presently operate only at a few hertz. Moreover, recent studies indicate that they have the potential of causing peripheral mechanical tissue damage due to the large acoustic transients produced during ablation.[44–46] There was no mechanical damage observed for any of the CO_2 laser irradiation parameters. Additionally, the magnitude of the noise generated by both the conventional TEA CO_2 laser and the Q-switched Er:YAG is sufficient to be irritating and may exceed tolerable levels in the clinical environment.[6] Many of the current pulsed CO_2 lasers operating for industrial or medical application utilize RF power sources that are more expensive to produce. Moreover, such RF power supplies are not well suited for efficiently producing laser pulses with pulse durations as short as a few microseconds. Er:YAG and Er:YSGG lasers are inherently expensive due to the cost of the erbium laser rods. Moreover, the high single pulse energies are required for the drilling of enamel, typically greater than a 100 mJ. Another advantage of CO_2 laser technology in general over current erbium technology is that the peak repetition rate is not limited by the gain media to 10 to 50 Hz. The unfavorable lifetimes of the upper and lower laser levels limit the efficiency at higher repetition rates. Higher repetition rates have been achieved using diode pumping; however, longer pump pulse widths were required.[47] Rates up to 400 Hz were utilized in this study and rates above 1000 Hz are feasible. Thus, if improved cutting speeds are desired, the laser beam can always be rapidly scanned at a high repetition rate.

TEA laser technology utilizes DC power supplies that greatly reduce the intrinsic cost of these devices. This Lumonics TEA laser uses a solid-state high voltage switch instead of a thyratron, which reduces the cost, cooling requirements and increases stability and reliability of the laser system. Because the laser does not contain any very expensive components, such as a laser rod or thyratron, the laser can potentially be produced at a low price.

The single-pulse enamel ablation rates are not as high as the longer pulse λ=10.6-μm CO_2 laser and Er:YAG laser systems, which can ablate at rates exceeding 100 μm/pulse with higher fluence and energy; however, high repetition rates can be easily achieved with this TEA CO_2 laser to enhance the removal rate.

Previous studies of Ivanenko et al.[27,28,48] demonstrated that shorter Q-switched CO_2 laser of nanoseconds duration could be used for bone ablation with minimal thermal damage. However, the pulses were too short and plasma shielding restricted the ablation rate. In more recent studies by the same group, a high repetition rate, 40 W, RF-excited CO_2 laser operating at 10.6 μm was used with repetition rates 200 and 400 Hz to cut bone *in vivo* in an animal study.[18,29] The pulse duration was 80 μs and the single pulse energy was 68 mJ per pulse and high-speed galvanic mirrors were used to scan at a rate of 480 mm per second (6 mm/s was used in this study) to produce incisions without carbonization. Taking this approach the peripheral thermal damage should be similar to that achieved with running the laser in the same position at a repetition rate of 1 Hz. If we compare with peripheral thermal damage studies of Dela Rosa et al.[12] that were conducted at low repetition rates, there was a significant difference in the zone of peripheral thermal damage in dentin between the shorter λ=9.6 μm (8 μs) (less than 10 μm) and the longer (100-μs) pulses (20 to 30 μm) when a water spray was not used. The thermal damage zone for both pulse lengths was less than 10 μm for both pulses with the water spray. Even though a water spray is desired for the ablation of dentin and bone to lessen carbonization and to prevent the accumulation of nonapatitic asperites during the ablation of enamel, it is difficult gauge and control the amount of water at the ablation site. Moreover, a layer of water on the tissue reduces the ablation rate and the minimum amount of water needed to prevent carbonization should be used. The shorter and more highly absorbed laser pulses ($\lambda=9.3$ or 9.6 μm pulses of 5 to 20-μs duration) are likely to require less water cooling to prevent peripheral thermal damage as suggested by the results reported by Dela Rosa et al.[12] acquired without the water spray.

The wavelength also plays an important roll in reducing thermal damage because one cannot expect the zone of thermal damage to be less than the depth of absorption. The absorption depth of $\lambda=9.3$- or 9.6-μm photons in dentin is 1 to 2 μm—bone should be similar—while at 10.6 μm, the absorption depth is 12 μm. Therefore the utilization of the $\lambda=9.3$- or 9.6-μm wavelengths should also help reduce the zone of thermal damage. However, if pulses are on the order of 100 μs or longer, wavelength-dependent effects will be less evident as the thermal diffusion length approaches 10 μm or greater for longer pulses. The thermal diffusion length for 10- and 20-μs laser pulses in dentin is 2.5 and 4 μm, respectively. Therefore, the thermal damage zone in dentin and bone should not significantly increase by stretching the laser pulse from 1 to 2 μs to 10 to 20 μs. Moreover, most of the energy content in the laser pulse is in the first 5 μs for the more efficient 4% CO_2 gas mixture.

If it is necessary to increase the ablation rate, either the single pulse energy or the repetition rate can be increased. If the single pulse energy is to be increased, it is necessary to use IR laser pulses with a pulse duration greater than 50 to 100 μs to avoid plasma shielding effects and excessive acoustic effects. If the spot size for shorter pulses is increased, the loud acoustic recoil effects potentially increase markedly as well and the laser becomes prohibitively loud. Pulse energies exceeding 500 mJ per pulse have been explored for erbium pulses of 200-μs duration; however, for the higher single pulse energies, the mechanical-recoil effects increase to the point that they are disturbing to the patient and thermal injury may result.[49,50] Moreover, by increasing the spot size and increasing the single pulse ablation rates to more than 100 μm per pulse, precision and selectivity must be sacrificed and greater thermal and mechanical peripheral damage are likely.

CO_2 lasers can be operated with repetition rates in the kilohertz regime. Therefore, even though the shorter laser pulses employed in this study with a pulse duration on the order of the thermal relaxation time of the deposited energy in the outer layer of tissue (<20 μs) and a single pulse energy lower than the threshold for plasma formation have single pulse ablation rates about a factor 2 to 4 times lower than the free-running erbium laser pulses, the laser repetition rate can be easily increased to compensate for the lower ablation rate per pulse. The disadvantage of the later approach is that the laser beam must be scanned, which adds a further level of complexity to the ablation system and may increase the size of the hand piece and delivery system. However, scanning the laser beam can be advantageous for further reducing thermal and mechanical damage as has been clearly demonstrated in these measurements and by Frentzen et al.[18] Moreover, less water is required for cooling, effectively increasing the ablation rate. Future laser–hard tissue ablation systems are likely to be effectively coupled with optical diagnostic systems for selective caries removal and precise incision depth control. Kavo (Biberach, Germany)[51] has developed an integrated caries ablation–and caries fluorescence–based clinical laser system combining their Diagnodent Caries Detection and Er:YAG laser systems. However, a computer-controlled scanning-based system would be more desirable to implement such an approach. We have used this $\lambda=9.3$ TEA CO_2 laser integrated with a computer-controlled scanning system and a fiber-optic spectrometer to selectively remove composite from tooth surfaces.[52] Laser systems that operate with high repetition rates and have ablation rates on the order of 10–20 μm per pulse are ideally suited for this approach. If each laser pulse removes more than a 100 μm per pulse, selectivity would not be as feasible.

Acknowledgments

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