Structural modifications induced in dentin by femtosecond laser

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Abstract. The structural and chemical modifications induced in dentin by ultrafast laser ablation were studied. The laser experiments were performed with a Yb:KYW chirped-pulse-regenerative amplification laser system (560-fs pulse duration, 1030-nm radiation wavelength), fluences in the range 2 to 14 J/cm², 1-kHz pulse repetition rate, and 5-mm/s scanning speed. The ablation surfaces were characterized by scanning electron microscopy and Fourier transform infrared spectroscopy. The ablation surfaces produced with 2 J/cm² presented an irregular morphology with exposed dentinal tubules and no evidence of thermal effects. For 7 and 14 J/cm², the ablation surfaces were covered by a layer of redeposited ablation debris, consisting mainly of amorphous calcium phosphate. This layer is weakly adherent to the underlying tissue and can be easily removed by ultrasonication, revealing a surface with a morphology similar to the one obtained with 2 J/cm². The constitution of the dentin ablation surfaces is similar to the constitution of pristine dentin, showing that, within this fluence range, the laser treatment does not significantly modify the structure and constitution of dentin. The results achieved suggest an ablation mechanism where collagen is preferentially decomposed by the laser radiation, reducing the tissue cohesive strength and leading, ultimately, to its ablation.

Keywords: femtosecond laser; dentin; surface modification; ablation.

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1 Introduction

Since their introduction to commercial use in the 1960s, lasers have been investigated as an alternative to mechanical drills for dental caries removal. The first investigations, based on CO₂ (wavelength ranging from 9.3 to 10.6 μm)3-4 or Nd:YAG (wavelength 1064 nm)5,6 lasers working in the CW regime or in the pulsed regime with pulse durations in the microsecond to millisecond range, showed that the laser treatment could be accompanied by undesirable thermal effects, such as melting, carbonization, thermomechanical cracking of dentin, and, in extreme cases, tooth pulp necrosis.7 These phenomena are due to the thermal nature of the radiation–material interaction mechanisms for those lasers and their long interaction time, which lead to excessive heat transfer to the tooth. The use of Nd:YAG lasers with shorter pulse duration (in the 10⁻⁷ to 10⁻⁹ s range) allowed reducing thermal effects to some extent, but heating remained significant, leading to decomposition of hydroxyapatite, melting, denaturation of collagen, and thermomechanical cracking.1,3,5,9

The accumulation of heat in the tooth during the laser treatment can be reduced by water cooling, but signs of melting are still observed, as reported by Fried et al.10 for the ablation of enamel with a CO₂ laser with 8-μs pulse duration, 30-J/cm² fluence, and 300-Hz pulse repetition rate and by Zhang et al.11 for the ablation of bone with a CO₂ laser with 100-μs pulse duration, 50-J/cm² fluence, and 50-Hz pulse repetition rate, the surface being covered by a water layer 1-mm thick.

Er,Cr:YSGG and Er:YAG lasers allow reducing the thermal degradation of dental tissues and, due to this advantage, became the main types of laser sources used in dentistry.12,13 This is due to the particular ablation mechanism of dentin with these lasers. Their radiation wavelengths (2.78 and 2.94 μm, respectively) are within a strong absorption band of water.14,15 Consequently, radiation is efficiently absorbed by the water contained in the tissue, which warms up and boils explosively, leading to the formation of a shockwave that disrupts the tissue.16-18 This ablation mechanism reduces heat transfer to the tooth, but the shockwave created by the rapid water evaporation may lead to the formation of cracks.19,20 Cracking can, however, be minimized by proper selection of the processing parameters.21

Thermal degradation of dental tissues can also be significantly reduced by using UV lasers.22-26 Turkmen et al.26 reported that the temperature increase in the tooth pulpal chamber during a laser treatment with an ArF excimer laser with 193-nm radiation wavelength and 15-ns pulse duration was significantly lower than the temperature increase produced during the same period of time with a 1064-nm radiation wavelength Nd:YAG laser with 150-μs pulse duration. This result was explained by Eugenio et al.24 and Sivakumar et al.,25 who showed that the ablation of intubular dentin, which forms the bulk of the tooth, by a KrF excimer laser with 248-nm radiation wavelength and 30-ns pulse duration occurs predominantly by a photochemical mechanism, contrary to the photothermal ablation mechanism associated with CO₂ and Nd:YAG lasers,16,27,28 leading to a significant reduction of thermal effects. However, despite their advantages, excimer lasers are not particularly suited for clinical use, because their ablation rate is low and the potential health hazard caused by exposure to intense UV radiation.
A more effective method to reduce thermal effects is by using ultrafast lasers. Femtosecond lasers allow ablating dentin efficiently and with negligible thermal degradation of the remaining tissue.\(^3\) Alves et al.\(^4\) showed that the surface of dentin specimens treated with fluences in the range 1 to 3 J/cm\(^2\) were flat, with opened dentinal tubules, and showed no traces of melting or structural or compositional alterations of the underlying tissue. The ablation of enamel with a similar laser is accompanied by melting but the thickness of the molten layer is <1 \(\mu\)m and the tissue underneath remained unaltered.\(^5\) This reduction of thermal effects is due to the fact that the pulse duration of these lasers is shorter than the electron-lattice energy transfer and the heat conduction characteristic times.\(^6\) As a result, most of the energy absorbed by the electrons in the material is spent in the ablation process and carried away by the ablated material before significant heat transfer to the lattice may occur. However, ultrafast lasers can only be used clinically if material removal rates comparable to or higher than those obtained with conventional lasers are achieved and, for this to occur, high pulse repetition rates and high fluences must be used, increasing the risk of thermal damage. In this paper, the structural and compositional changes induced in dentin by ultrafast laser ablation with fluences up to 14 J/cm\(^2\) at a pulse repetition rate of 1 kHz were investigated.

2 Materials and Methods

2.1 Sample Preparation

The experiments were performed using recently extracted human third molars. Tooth extraction was performed according to a protocol approved by the local Ethics Committee (process DC 2014/04) and with informed consent of the patients. Nineteen disks of dentin about 1.5-mm thick were cut parallel to the occlusal plane using a low-speed diamond saw (model Accutom-50, Struers, Denmark). The samples were stored in distilled water at 4°C. Less than 3 days before the laser experiments, one of the faces of these disks was polished under flowing water with a 600- to 2500-grit sequence of SiC abrasive papers. Prior to the laser treatment, the specimens were gently wiped with a clean paper tissue to remove the excess water.

The laser surface treatment was performed in ambient atmosphere using a Yb:KYW chirped-pulse-regenerative amplification laser system with a Gaussian beam, 560-fs pulse duration, 1030-nm radiation wavelength (model s-Pulse HP, Amplitude Systemes, France). The pulse repetition rate was 1 kHz. The laser beam was incident perpendicularly to the specimen surface and focused with a 100-mm focal length lens. In order to achieve the required radiation intensity, the specimen surface was located at a distance of 3 mm from the local plane, leading to a laser spot diameter, calculated by the D\(^2\)-method,\(^7\) of \(\sim71\ \mu\)m. The pulse energy was varied with an attenuator to obtain average fluences in the range 2 to 14 J/cm\(^2\). The average laser beam power, measured with a power meter (model 10ASHV1.1, Ophir Photonics, Israel), varied in the range 80 to 560 mW. The pulse energy, calculated from the average laser beam power and the pulse repetition rate, took values from 80 to 560 \(\mu\)J. The specimens were moved under the stationary laser with a scanning velocity of 5 mm/s using a computer-controlled XY-stage (model LS-110, PI micos, Germany).

In order to measure the ablation rate, linear tracks were created with fluences between 2 and 14 J/cm\(^2\), 5-mm/s scanning speed, and 1-kHz pulse repetition rate. With these parameters, each surface spot receives 14 laser pulses, but the average fluence varies from pulse to pulse due to the Gaussian energy distribution in the laser beam. The ablation rate was calculated from the ablation volume using the following equation:

\[
r_a = v \cdot \frac{V_a}{f \cdot L},
\]

where \(v\) is the scanning speed, \(f\) is the repetition rate, \(V_a\) is the ablated volume, and \(L\) is the length of the linear track. The ablation volume was calculated by integration of the three-dimensional surface profiles of the tracks, measured using a white light interferometer (model WYKO NT1100, Veeco). The values of the ablation rate presented are the average of three measurements performed in different regions of the tracks.

The morphology and the chemical constitution of the ablation surfaces were studied on specimens submitted to large area laser treatments with fluences of 2, 7, and 14 J/cm\(^2\). These laser treatments were performed by overlapping individual tracks. Each track was created by moving the specimen in the X-direction at a velocity of 5 mm/s while pulsing the laser beam at 1 kHz. After completing the track, the specimen was returned to the origin of the movement, moved 0.01 mm in the Y-direction and another linear scan was performed in the X-direction. These steps were repeated until reaching complete surface coverage. With these parameters, overlap between consecutive tracks is 86% of the track width and each point of the surface received ~100 laser pulses, but the fluence varies from pulse to pulse due to the Gaussian energy distribution in the laser beam. Six specimens were tested for each value of the fluence. After the laser treatment, the specimens were rinsed in copious flowing water.

2.2 Sample Characterization

From the six dentin disks treated with each fluence, two were randomly chosen for the surface morphological analysis. Surfaces were observed by scanning electron microscopy (SEM), in the secondary electron imaging mode, with a field-emission gun scanning electron microscopy (JSM-7001F, JEOL, Japan) operated at an acceleration voltage of 10 kV. To avoid charging, the samples were coated with a conductive Pd/Au film prior to observation. The surfaces were observed in the laser-treated condition and after elimination of the ablation debris by ultrasonication. For cross-sectional SEM observation, the specimens were immersed in liquid N\(_2\) and broken with a sharp hammer blow from the back side. The remaining specimens were analyzed by Fourier transform infrared (FTIR) spectroscopy in the attenuated total reflection mode with a Nicolet 5700 FTIR spectrometer (Thermo Electron Corporation) equipped with a solid-substrate beam splitter and a deuterated triglycine sulfate thermoelectrically cooled detector. The FTIR analysis was performed in the as-treated condition and after the elimination of the ablation debris layer by ultrasonication.

3 Results

3.1 Ablation Rate

The variation of average ablation rate with the radiation fluence is depicted in Fig. 1(a). The average ablation rate increases with fluence and reaches a value of $44 \times 10^2 \mu\text{m}^2$/pulse for 14 J/cm\(^2\), corresponding to a material removal rate of...
0.44 \times 10^{-2} \text{ mm}^3/\text{s}. The evolution of the ablation efficiency, defined as the ablation volume per unit of laser pulse energy, with the fluence is depicted in Fig. 1(b). The ablation efficiency reaches a maximum of 0.015 mm$^3$/J for 2 J/cm$^2$ and decreases with increasing fluence.

### 3.2 Surface Morphology

The surface morphology of specimens treated with 2, 7, and 14 J/cm$^2$ is depicted in the SEM micrographs of Fig. 2. The surface treated with 2 J/cm$^2$ is flat and presents an irregular morphology with open tubules and a very small amount of redeposited ablation debris [Fig. 2(a)]. The amount of ablation debris increases with fluence and the surfaces prepared with 7 and 14 J/cm$^2$ are covered by a continuous layer of ablation debris, aggregated in relatively large clusters [Figs. 2(c) and 2(e)]. The thickness of this layer and the size of the clusters increase with fluence. The layer of ablation debris is poorly adherent to the surface and can be removed by ultrasonication. The surface morphology after ultrasonication is presented in the micrographs of

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**Fig. 1** (a) The evolution of the ablation rate and (b) ablation efficiency of dentin with radiation fluence.

**Fig. 2** Morphology of laser treated dentin surfaces before and after ultrasonication. Fluences (a) and (b) 2 J/cm$^2$, (c) and (d) 7 J/cm$^2$, and (e) and (f) 14 J/cm$^2$. 

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Figs. 2(b), 2(d), and 2(f). The dentinal structure is now clearly exposed and the tubules are open. The observation of the transverse cross section of the laser treated specimens (Fig. 3) shows that no significant laser-induced damage occurred below the ablation surface and the tissue preserves its original morphology even in the specimens treated with a fluence of $14 \text{ J/cm}^2$.

3.3 Surface Constitution

The IR spectra of polished and laser-treated specimens, normalized to the largest amplitude peak, are shown in Fig. 4. This peak, located at 1005 cm$^{-1}$, corresponds to the $\nu_3$ vibrational mode of the phosphate group of hydroxyapatite, whereas the peak at 960 cm$^{-1}$ can be assigned to the $\nu_1$ vibrational mode of the same anion. The peak at 875 cm$^{-1}$ corresponds to the $\nu_2$ vibrational mode of the carbonate anion and the peaks at 1415 and 1450 cm$^{-1}$ to the $\nu_3$ vibrational mode of the same anion substituted in B-type $\text{PO}_4^{3-}$ and A-type $\text{OH}^-$ anionic sites, respectively. The bands between 1680 and 1600 cm$^{-1}$, and 1580 and 1510 cm$^{-1}$ correspond to the vibrational modes of amide I ($\text{C}=\text{O}$ stretching) and amide II ($\text{C}−\text{N}$ stretching and $\text{N}−\text{H}$ deformation modes) groups of collagen, respectively. The FTIR spectrum of the specimen treated with $2 \text{ J/cm}^2$ is similar to the spectrum of the polished specimen, showing that laser ablation with this low fluence does not significantly change the constitution of dentin. On the contrary, the spectra of the specimens treated with 7 and $14 \text{ J/cm}^2$ exhibit some differences as compared to untreated dentin. On the one hand, the amplitude of the peaks corresponding to vibrational modes of $\text{CO}_2^{3-}$ and of the amides decreases after a laser treatment with $7 \text{ J/cm}^2$ and these peaks disappear when the surface treatment is performed with $14 \text{ J/cm}^2$. On the other hand, the width of the phosphate band at 1005 cm$^{-1}$ increases and the well-defined phosphate peak at 960 cm$^{-1}$, which appears in the spectra of the polished specimen and of the specimens treated with 2 and $7 \text{ J/cm}^2$, is replaced by a broad band at 950 cm$^{-1}$ in the spectrum of the specimen treated at $14 \text{ J/cm}^2$. Interestingly, the FTIR spectrum of the specimen treated with $14 \text{ J/cm}^2$ is similar to the spectrum of amorphous calcium phosphate (ACP), indicating that this compound is the main constituent of the dentin surface after laser treatment with this fluence. ACP peaks are also observed in the spectra of the specimens treated with $7 \text{ J/cm}^2$, but their amplitudes are lower, indicating that the proportion of this compound in the surface layer decreased.

After removing the ablation debris with ultrasonication, the spectra of the specimens treated with 7 and $14 \text{ J/cm}^2$ become similar to the spectrum of the polished specimen (Fig. 5), indicating that the ACP exists mainly in the ablation debris and that the tissue underneath is unaffected by the ablation process. It should be emphasized that the depth of sampling of the FTIR spectroscopy method used, estimated assuming that the refractive index of dentin is 1.4 (Ref. 39) for the IR absorption spectral region of collagen (1650 cm$^{-1}$), is $\sim0.6 \mu\text{m}$. Therefore, the thickness of the laser-induced damaged layer is $<0.6 \mu\text{m}$.
4 Discussion

The results obtained in this work can be directly compared to those obtained by Alves et al.30 with the same laser system and applying similar laser processing methods but lower fluences, in the range 1 to 3 J/cm². The surface morphology and constitution of the specimen treated with 2 J/cm² are in good agreement with the results of Alves et al.,30 showing that the differences in behavior observed in this work for higher fluences are not due to sample variations, as may happen in biological tissues.39 The main difference between the specimens treated with 2 J/cm² and those treated with higher fluences is the formation of a dense layer of ablation debris aggregated in clusters for the higher fluences. The size of the clusters and the thickness of the ablation debris layer increase with fluence. This evolution can be explained by the corresponding increase of the ablation rate (25 × 10² and 44 × 10³ μm²/pulse for 7 and 14 J/cm², respectively, as compared to 14 μm²/pulse for 2 J/cm²), which leads to an increase of the particles’ collision probability in the plume and favors their coalescence into larger aggregates.41 A similar variation of the cluster dimensions with fluence was observed by Trelenberg et al.42 for GaAs. The FTIR analysis showed that the redeposited ablation debris consist mainly of ACP, the organic matter existing in dentin being decomposed at the high temperatures existing in the plume and in the redeposited debris. On the other hand, the extremely high cooling rates prevailing during the collapse of the plume explain why the calcium phosphate particles that redeposit on the surface present an amorphous structure.37 After the removal of the ablation debris with ultrasonication, the underlying tissue morphology and constitution are similar, independent of the fluence used in the range of 2 to 14 J/cm². No traces of thermal degradation of the dental tissue are observed.

In a previous study,13 the present authors showed that the ablation of human dental enamel in the same fluence range that was used in this work is accompanied by melting, leading to the formation of a continuous layer of resolidified calcium phosphate as well as by the projection of a large quantity of liquid droplets. These observation lead the authors to suggest that the predominant ablation mechanism of enamel in this fluence range is liquid spallation.43,44 On the contrary, the ablation of dentin in the same fluence range is not accompanied by melting, even though the predominant phase in dentin and enamel is the same (hydroxyapatite). This difference in ablation behavior shows that the ablation mechanisms of dentin and enamel are different due to the different microstructures of both tissues. Dentin is a composite material consisting of hydroxyapatite nanocrystals dispersed in a network of collagen fibrils. Despite the fact that the predominant phase is hydroxyapatite (~70 wt.% in average), contrary to enamel, this phase is not continuous and the cohesive strength of dentin is ensured by the collagen fibrils.33 These fibrils consist of long molecules where the atoms are bonded by covalent bonds, connected to one another by weak Van der Waals forces. As a result, collagen presents low thermal stability40 and the ablation threshold for femtosecond laser radiation is also low (0.06 J/cm²) as compared to enamel, which consists entirely of hydroxyapatite (3.3 J/cm²).32 Collagen is degraded for relatively low radiation intensities, leading to a significant decrease of the strength of dentin and facilitating its ablation for radiation intensities lower than those required for hydroxyapatite-rich enamel and hydroxyapatite, which are ablated by liquid spallation or phase explosion depending on the laser processing parameters.33,34,48 The present results support the ablation mechanism proposed by Alves et al.30 for dentin. The authors observed that for fluences only slightly higher than the ablation threshold, the morphology of dentin surfaces treated with a femtosecond laser are very similar to brittle fracture surfaces and suggested that these surfaces should result from an ablation mechanism dominated by photomechanical fracture, with only very limited melting, a proposal that was supported by the results of the pump-probe experiments reported recently by Domke et al.49 The authors observed extensive cracking around the ablation regions, but these cracks are due to dentin embrittlement by dehydration40 and can be attenuated with water irrigation.51 The contribution of solid spallation on the ablation of dentin was also demonstrated in this work by the angular shape of the ablation debris for the specimen treated with 2 J/cm². However, the proportion of resolidified droplets in the ablation debris increased with fluence, indicating that ablation mechanisms such as liquid spallation and phase explosion43,44 play an increasingly important role in the ablation process as fluence increases, but these mechanisms are not the predominant dentin ablation mechanisms in the fluence range tested.

The results achieved in this work can be compared to those achieved with Er:YAG and Er:Cr:YSGG lasers. Ceballo et al.53 observed a 3- to 5-μm-thick surface layer depleted in collagen followed by a 1-μm-thick layer where collagen was partially denatured in dentin surfaces treated with Er:YAG (23 J/cm² and 2 Hz) and similar observations were reported by Moretto et al.20 for dentin treated with an Er, Cr:YSGG laser at 90 J/cm² and 20 Hz. The removal of collagen from these surfaces may explain the lower strength of the bonds between restorative adhesives and dentin surfaces prepared with Er:YAG and Er, Cr:YSGG lasers compared to surfaces prepared by mechanical methods,8,13,15 because this bonding depends on the formation of a hybrid layer resulting from the impregnation of collagen by the adhesive,53 which cannot occur if collagen is decomposed or denatured. This study shows that surface collagen is relatively well preserved when a femtosecond laser is used for the ablation of dentin. Moreover, after the removal of the ablation debris, a well-preserved dentin surface with open dentinal tubules, free of resolidified material and subsurface cracks exists. These characteristics are all favorable for the formation of a strong bond between dentin and dental restorative adhesives.

The maximum ablation efficiency achieved in this work was 0.015 mm²/J for 2 J/cm², similar to the value obtained for a laser with 1025-nm radiation wavelength and 400-fs pulse
duration at a fluence of 4.69 J/cm² (0.018 mm³/J) \(^{54}\) and lower than the value achieved for an Er:YAG laser (0.025 mm³/J for 203.7 J/cm²).\(^{55}\) The ablation efficiency decreases with increasing fluence for fluences higher than 2.8 J/cm², in contradiction with the trend observed by Chen et al.\(^{56}\) (an increase of the ablation efficiency with fluence in the range 1 to 6 J/cm² followed by a decrease between 6 and 11 J/cm²). This difference in behavior can be explained by the different average number of pulses per surface spot used in the two works (14 and 1.6, respectively). Neuenschwander et al.\(^{57}\) showed that the ablation efficiency depends on the ratio \(F/F_{th}\), where \(F\) is the radiation fluence and \(F_{th}\) is the material ablation threshold. The ablation threshold of hard tissues such as enamel,\(^{35}\) cortical bone,\(^{32}\) and dentin\(^{30}\) decreases with increasing number of laser pulses, a dependence that was explained by Jee et al.\(^{60}\) assuming that laser irradiation of materials at fluences lower than the ablation threshold create defects in the material that lead to an increase of its absorption coefficient. The corresponding effect on the ablation threshold can be expressed by

\[
F_{th}(N) = F_{th}(1) \times N^{S-1},
\]

where \(F_{th}(1)\) and \(F_{th}(N)\) and \(S\) are the ablation thresholds for a single pulse and for \(N\) pulses and the incubation coefficient, respectively. Assuming that the incubation coefficient of dentin is similar to the incubation factor of cortical bone (0.8) and that its single-pulse ablation threshold is 0.6 J/cm²,\(^{30}\) the average ablation threshold values for 14 in this work, and 1.6, in the work by Chen et al.\(^{54}\) laser pulses, calculated by Eq. (2), are 0.35 and 0.55 J/cm², respectively. If expressed in terms of \(F/F_{th}\) as suggested by Neuenschwander et al.\(^{57}\) instead of \(F\), in the fluence range used by Chen et al.\(^{54}\) (2.75 < \(F/F_{th}\) < 14.30) the ablation efficiency increases first, passes through a maximum for \(F/F_{th} \sim 8.58\), then decreases. In the fluence range used in this work (5.65 < \(F/F_{th}\) < 39.56), the decrease of the ablation efficiency with fluence can be clearly observed for \(F/F_{th} > 7.9\) (\(F > 2.8\) J/cm²), showing good agreement between the two works.

The maximum material removal rate found in this work (0.44 x 10⁻³ mm²/s for 14 J/cm²) is significantly lower than the removal rate obtained with mechanical drilling (~1 mm²/s).\(^{35}\) This value shows that femtosecond lasers can only be applied for carious dentin removal with higher fluences and higher repetition rates to achieve high caries removal rates.

## 5 Conclusion

This study shows that the structure and constitution of dentin are preserved when the tissue is ablated using 560-fs laser pulses of 1030-nm radiation, fluences in the range 2 to 14 J/cm², and 1-kHz repetition rate. The ablation surface obtained with a fluence of 2 J/cm² shows a scaly appearance and is free of melting, carbonization, or cracking. For higher fluences, a loosely attached layer of redeposited ablation debris covers the ablation surfaces, but this layer can be easily removed with ultrasonication, revealing a surface morphology similar to the one found for 2 J/cm². The ablation debris consists mainly of ACP. The absence of surface melting, the morphology of the dentin ablation surfaces, and the shape of the ablation debris suggest that the ablation on dentin in the fluence range used in this work occurs predominantly by a photomechanical mechanism (solid spallation) instead of the photothermal mechanisms reported for enamel and hydroxyapatite.

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**Disclosures**

The authors confirm that there are no conflicts of interest.

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Biographies for the authors are not available.