Spectroscopic Characterization of Sound and Carious Ablated Dental Tissue after Er:YAG Laser Interaction

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KEY WORDS: Er:YAG laser, tooth ablation, spectroscopy, temperature, protein, demineralization

ABSTRACT

Yttrium–aluminum–oxide doted with erbium^{3+} ions (Er:YAG) laser light emission at 2.94 μm is strongly absorbed by water in dental structure, leading to a volumetric expansion and microexplosions that result in hard tissue ablation. By means of infrared radiation (IR) spectroscopy, the teeth ablation mechanism by this laser has been determined and investigated in sound and carious teeth. In vitro human-ablated ejected dental material was deposited on IR windows and the absorption spectra were measured in the range 2,000 to 20,000 nm (5,000–500 cm^{-1}). Sound and natural carious teeth were used, and the corresponding film spectra were compared with spectra obtained by traditional methods. The film spectra obtained did not differ appreciably from those obtained by the traditional method for either sound or carious teeth, indicating that the material ejected by an Er:YAG represents the tooth condition. The results confirm that spectroscopic analysis of a tooth treated with an Er:YAG laser can be performed by measuring the absorbance spectrum of a film consisting of ejected material without the need to slice the tooth. In addition, it was determined that laser absorption occurs mainly by interstitial water, and the temperature elevation of the ejected material does not exceed 60°C.

INTRODUCTION

There is a broad range of lasers for use in dentistry today, including excimer, ion gas, helium–neon, copper vapor, carbon dioxide, neodymium lasers (first and second harmonics), titanium:sapphire, chromium-doped lithium–strontium–aluminum fluoride (Cr:LiSAF), holmium, and erbium lasers, among others.[1] These lasers can act as high-precision tools in numerous applications for soft and hard dental tissues (e.g., gum treatment, decay removal, sealant application, teeth whitening, drilling).[2] Using the laser, it is possible to treat teeth in a variety of new conditions that reduce pain, mechanical stress, noise, and post-operative problems, without anesthesia in most cases. In recent years, lasers have become attractive and affordable for clinical use in removal of dental tissue by ablative processes, due to recent developments in the diode laser and solid-

state laser technology.[3,4] Two main mechanisms of dental laser ablation exist. The first nonresonant ultrashort laser, uses pulses with a duration of a few femtoseconds.[4,5] The second mechanism, which uses erbium lasers, relies on the use of long laser pulses ranging from microseconds to milliseconds, resonant with dental absorptions originating from the hydroxyapatite and water inside of the structural micropores.[6]

The solid-state laser system is based on yttrium–aluminum–oxide (Er:YAG), doted with erbium^{3+} ions as the lasing material and emits at a wavelength of 2.94 μm, which coincides with the absorption peak of the stretching mode of the water molecule, thus being strongly absorbed.[7] This intense absorption within micropores heats the water instantaneously, changing its phase to vapor, increasing the pressure inside the micropore. This effect breaks the hydroxyapatite structure leading to microexplosions that eject dental tissue away from the laser interacting volume.[8,9] As a result, an erbium laser pulse focused on the tooth is drastically absorbed, and the thermal effect is therefore highly localized and is restricted to a region near the tooth surface.

Erbium lasers are more appropriate than those of neodymium or holmium due to the strong absorption of the Er:YAG, which leads to much less energy required for dental tissue ablation. The lower energy deposited for ablation reduces the thermal effect, which is desirable to prevent irreversible damages in the dental pulp that occur if the tooth temperature rises by more than 5.5°C during the laser irradiation.[10]

The plume created during the Er:YAG laser ablation of dental tissue consists of ejected material. Its formation mechanism and the eventual presence of potentially toxic materials being created in the ablation process are beginning to be understood.[11] Hard dental tissue consists mainly of enamel, dentine, and water in proportions that depend on the type and local structure of the sample and also on its health. Due to the microexplosions, the ablation is not a vaporization process, but is produced by the pressure build-up inside the micropores of the tissue. When this pressure exceeds the tensile strength of the tissue, ablation occurs by means of localized microexplosions. A higher plume velocity due to higher pressures inside the tissue can be produced by increasing the energy density of laser irradiation. In previous work,[12] the (plume) material ablated from a sound tooth by an Er:YAG laser retained the spectroscopic characteristics of the tooth, and the absorption spectrum of the tooth was determined by measuring the absorption spectrum of a film formed by the ablated material over an adequate substrate.

Dental caries are formed when an exposed dental surface is covered by acidogenic bacteria that metabolize fermentable carbohydrates (e.g., glucose, sucrose, fructose) producing acids (lactic, acetic, propionic, and formic) that diffuse through the tooth pores, dissolving its crystals and liberating calcium and phosphorus according to the demineralization reaction[13,14]:

$$Ca_{10}(PO_4)_6(OH)_2 + 8H^+ \rightarrow 10Ca^{2+} + 6HPO_4^{2-} + 2H_2O$$

If this process is not reversed, the lesions evolve to cavitation, resulting in porous enamel with a permeable structure. Because of this demineralization, dental caries have a whitish aspect, and therefore can be detected by optical techniques.

The aim of this study was to determine whether the ablation mechanism induced by Er:YAG laser in sound teeth is similar to that for carious teeth, using infrared radiation (IR) spectroscopy to characterize the ablation plume material ejected from dental tissue by pulsed Er:YAG laser irradiation at 2.94 μm. This spectroscopic differentiation between carious and sound, ejected material is most likely being reported in the literature for the first time.

MATERIALS AND METHODS

The study was conducted in vitro using sound and typical carious teeth. The teeth

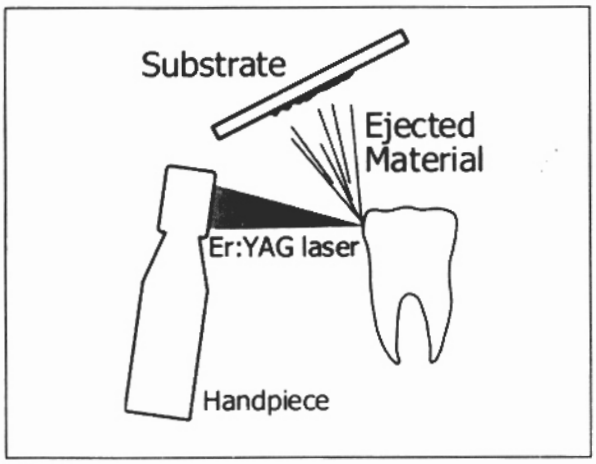

Figure 1. Experimental design for evaluation of ablation mechanism induced by Er:YAG laser in sound teeth compared with that for carious teeth.

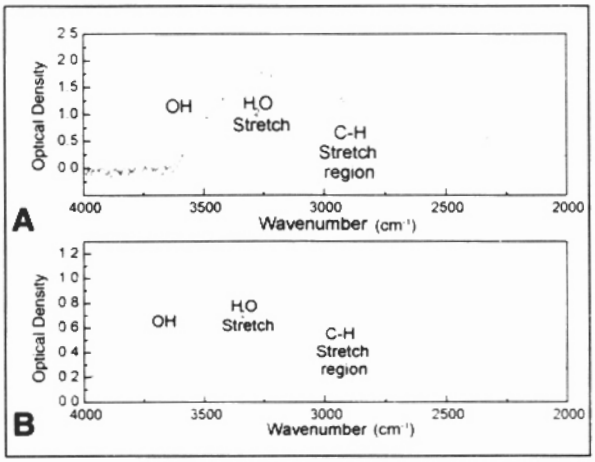

Figure 2. FT-IR spectra for sound teeth, showing absorption spectrum for a film of sound tooth ejected ablated dental material (**A**) and absorption spectrum for a dehydrated tooth slice (**B**).[17]

were extracted human molars obtained from the Faculdade de Odontologia da USP (University of São Paulo School of Dentistry), and were conserved in physiologic serum to avoid cracking due to dryness.

The teeth were irradiated by a commercial Er:YAG laser (KEY Laser; KaVo) operating at 2.94 μm without water spray as coolant, with a flexible optical fiber to a handpiece for the beam delivery. This system allowed selection of pulse energy from 60 to 500 mJ and a repetition rate from 1 to 15 Hz. All evaluations used a pulse energy of 300 mJ at 10 Hz repetition rate for 1-minute irradiations.

The erbium laser pulses were focalized on the tooth, and the ejected ablated material was deposited on an Irtran substrate, which is transparent in the optical range from 725 to 10,000 cm^{-1}. This substrate was positioned at approximately 2 cm from the laser focus point (Figure 1). The ejected dental plume formed a uniform film of the ablated material on the substrate with a good adherence to its surface, being removed only by mechanical abrasion. The ablation point was constantly changed by moving the tooth sample to avoid carbonization. The absorption spectra of the films of the ablated materials were measured in the visible and infrared using double-beam spectrophotometers.

The absorption spectra of the films were measured by a Cary 17D spectrophotometer in the range of 1,000 to 2,500 nm (5,000 to 4,000 cm^{-1}) and a Nicolet 740 FT-IR in the range of 2,500 to 20,000 nm (4,000 to 500 cm^{-1}).

RESULTS AND DISCUSSION

The optical spectra of the deposited film of ejected hard dental tissue material was studied after ablation by an Er:YAG laser in sound and carious teeth in the near- and far-infrared regions. The IR absorption spectra for sound teeth from previous work is presented in Figure 2.[17] The spectrum from the earlier study conducted by the authors is from the Er:YAG-ablated dental tissue, and a second one is from a dehydrated human tooth reported the literature by Harris et al.[15] Similarities between the two spectra can be observed. The spectrum reported by Harris et al[15] was obtained by cutting thin slices (100 and 200 μm in thickness) from the tooth, therefore destroying it.

Details of the absorption spectra of the deposited films of sound and carious teeth in the range of 1,800 to 600 cm^{-1} can be observed in Figure 3, along with spectra reported by Kawasaki et al.[16] This spectral region is particularly important in the present work because it contains the absorption bands of minerals and proteins that compose

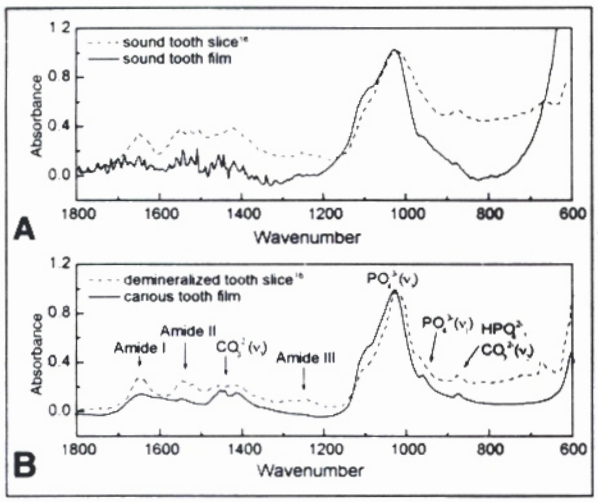

Figure 3. Absorption spectra of hard dental structure in the range 4,000-500 cm^{-1}. Dotted lines represent the spectra taken from the literature,[16] from teeth slices, and the continuous lines of the spectra measured in the present study from the deposited films of ablated material under Er:YAG pumping. Results are for sound (**A**), carious (**B**) and demineralized (**B**) teeth.

the tooth and also because the absorption spectra of slices of sound and demineralized teeth are available in the literature for comparison.[16] The absorption spectrum measured from the film of an ablated sound tooth and the absorption spectrum of a sound tooth slice are compared in Figure 3. There is remarkable similarity between these spectral structures. The same similarity can be observed for the absorption spectra of carious teeth measured in the present study and those for demineralized teeth previously reported (Figure 3). This result corroborates findings in an earlier study that Er:YAG laser ablation does not alter the spectroscopic and chemical characteristics of the ablated material in a significant way. However, in both spectra (Figure 3), the absorption bands of PO_4^{-3} (approximately 1,030 cm^{-1}) are much more resolved and narrow in comparison with the spectra of the teeth slices, which are more comparable to demineralized samples. This effect is probably caused by the reduction of Ca^{2+}–(PO_4^{-3}) bonds, which is responsible for the band enlargement and its asymmetry. In addition, the major protein absorption bands at 1,650 to

Table 1. Infrared Absorption Peaks for the Species Present in Teeth

Species	Absorption Peaks (cm^{-1})
Amide I	1,650
Amide II	1,540
Amide III	1,240
CO_3^{-2} (ν_2)	870–960
CO_3^{-2} (ν_3)	1,450–1,550
PO_4^{-3} (ν_1)	960
PO_4^{-3} (ν_3)	1,030
HPO_4^{-2}	880

1,700 cm^{-1} (amide I, due to C=O bond stretching), 1,550 cm^{-1} (amide II, due to N–H and C–N), and at 1,240 cm^{-1} (amide III, C–N and N–H) are observed to be present in the films of the laser ablated material.[16,17] All absorption peaks of organic and inorganic species found in the films of ablated material are listed in Table 1.

Absorption spectra of films of ablated material from sound and carious measured in the near infrared region from 2,000 to 2,500 nm (5,000–4,000 cm^{-1}) are shown in Figure 4. Since the absorption spectrum of a film composed of ejected tooth material was shown to match the absorption spectrum of the tooth (Figures 2 and 3), the spectra shown in Figure 4 are believed to represent sound and carious teeth.

In the spectra in Figure 4, the existence of an absorption band centered at 4,527 cm^{-1} (2,209 nm) for both the sound and carious teeth can be observed. The observation of these bands would be very difficult in tooth slices due to the strong interstitial water absorption band at 2,700 cm^{-1} shown in Figure 2. The wing of this band is observed around 2,500 nm (4,000 cm^{-1}), and obscures other bands in this range. The presence of this absorption band in sound and carious teeth is noted, with no observable difference in its shape. It is proposed that this band corresponds to the first overtone of the fundamental N–H frequency (approximately 2,263 cm^{-1}), indicating there is some nitro-

gen incorporation in the laser-ablated tooth material.

CONCLUSIONS

Results of this study show there is similarity between the absorption spectrum of a film of deposited dental material ablated by an Er:YAG laser at 2.94 μm and the absorption spectrum of tooth slices. The spectral similarities are present for both sound and carious teeth, demonstrating that the Er:YAG laser irradiation does not alter the chemical composition of the ablated material. In addition, the health condition of a localized ablated portion from a tooth can be determined spectroscopically, aiding the characterization of the surgical procedure.

From the data shown, it is assumed that two main processes occur during the Er:YAG laser interaction with the tooth. One of the processes involves the interaction of the laser with the structural OH group present in the hydroxyapatite and the other one with the interstitial water.

It is proposed that a chemical reaction mechanism resulting from the interaction of the laser with the hydroxyapatite structural OH –resonant absorption band. This interaction breaks the OH bond, liberating H^+ free ions, which start the demineralization process described by the formula of Featherstone[14], liberating Ca^{2+} ions that can stabilize as carbonate. This carbonate creation explains the increase of the absorption below 600 cm^{-1} in the film's spectra.

The other process in which the Er:YAG laser interacts with the interstitial water is the main one causing the ablation. If the interaction occurred with the hydroxyapatite structural OH, the dental characteristics would be absent from the spectra of the films. Additionally, these microexplosions does not elevate the temperature of the ejected material by more than 60°C, as evidenced by the presence of protein lines on the absorption spectra of the films. The temperature elevation appears to be greater in the carious tooth, as judged by the greater decrease in protein bands, indicating greater protein losses.

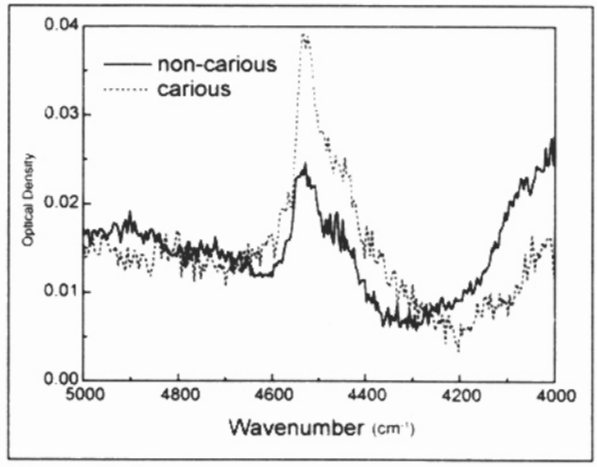

Figure 4. Absorption spectra of films of ablated material from sound and carious measured in the near infrared region.

The study provides strong evidence that the main ablation mechanism in sound and carious teeth is the same and is due to absorption by interstitial water, preserving the particular characteristics of each tooth. In addition, the presented method introduces a simple, nondestructive and reliable method to obtain a tooth spectrum.

ACKNOWLEDGMENTS

The authors thank the administration of LELO (Laser in Dentistry Experimental Laboratory) at the University of São Paulo and Patricia Lerros de Paula Eduardo for donating and operating the KaVo Er:YAG laser and for donating the teeth used in this study. The authors also acknowledge Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support.

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