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XPS analysis of the dentin irradiated by Er:YAG laser

Masanori OMAE[1], Yasuo SHINNOU[1], Kumiko TANAKA[1], Tomoko ABO[1], Takashi NAKATA[1], Koichiro SUZUKI[2], Yoshinori HATSUOKA[2], Naohiro IWATA[2], Kazushi YOSHIKAWA[2], Yoshihiro NISHITANI[1], Kazuyo YAMAMOTO[2] and Masahiro YOSHIYAMA[1]

[1]Department of Operative Dentistry, Okayama University Graduate School of Medicine, Dentistry and Pharmaceutical Sciences, 2-5-1 Shikata-cho, Okayama 700-8525, Japan.
[2]Department of Operative Dentistry, Osaka Dental University, 8-1 Kuzuhahanazono-cho, Hirakata-shi, Osaka 573-1121, Japan.
Corresponding author, Masanori OMAE; E-mail: maemae.dds@kpb.biglobe.ne.jp

The aim of this study was to investigate the effect of Er:YAG laser irradiation on human dentin surface using X-ray photoelectron spectroscopy (XPS). 10 human dentin disks were prepared from extracted human molars for XPS analysis. These specimens were divided into two groups of five: a control group and group that were irradiated by an Er:YAG laser beam (100 mJ, 1Hz). All specimens were analyzed by XPS over a wide scanning range and narrow scanning ranges. The Ca/P ratio was calculated from the XPS results.
In the results, the binding energies of Ca, P, and N in the laser-irradiated group were higher than those in the control group. The Ca/P ratio of the Er:YAG laser irradiated group (1.24±0.05) was significantly lower than that of the control group (1.52±0.16).
This study showed that Er:YAG laser irradiation decreased Ca/P ratio and denatured the collagen of human dentin.

Keywords: XPS, Dentin, Er:YAG laser

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INTRODUCTION

Ever since Goldman first suggested the possibility of removing dental caries by using a ruby laser[1)], the efficacy of laser abrasion on removing caries has been studied. Studies have been performed using different kinds of lasers, including Er:YAG lasers and Nd:YAG lasers[2)], and CO_2 lasers[3,4)]. Attention has focused on Er:YAG lasers due to their high efficacies in removing dental hard tissue[5-7)].

Er:YAG lasers typically have an output wavelength of 2.94 μm, which corresponds to a strong absorption band of water. Absorbed laser pulses give rise to microexplosions on the dentin surface, so that dental hard tissue can be effectively removed[8,9)]. When irradiated by Er:YAG laser pulses, the dentin surface becomes microscopically rough, and dentinal tubules are opened without smear layers[8,10)]. Although these characteristics are considered to be advantageous for resin bonding, the bond strength of resin to Er:YAG laser-irradiated dentin is lower than that to conventionally ground dentin[11-17)]. The formation of a hybrid layer is thought to be necessary for excellent resin-dentin bonding. A hybrid layer is formed by intertwining of resins within the exposed dentin collagen fibril network[18)]. Thus, the strength of dentin bonds is influenced by the condition of the collagen fibrils on the dentin surface. Moreover, it has been reported that the loss of Ca on the dentin surface by acid treatment contribute to the strength of the dentin bonds[19)].

The dentin surface after Er:YAG laser irradiation has been found to be denatured containing a lot of microcracks[8,9,20-22)]. Collagen and Ca, which are considered to be important to adhesion between resin and dentin, are impaired by Er:YAG laser irradiation reducing the bonding strength between resin and dentin. This denaturation of collagen fibrils and Ca by Er:YAG laser irradiation is thus undesirable for resin-dentin bonding. Therefore, the null hypothesis of this study was that collagen fibrils and Ca in the Er:YAG-irradiated dentin are denatured.

MATERIALD AND METHODS

Five extracted human molars that had been stored at –40°C after extraction were defrosted immediately prior to use and cleaned using a scaler. The teeth were mesiodistally cut with a low-speed diamond disk (Isomet Low-Speed Saw, Buehler, Lake Bluff, Illinois, USA) and were then divided into two groups: those on the buccal side formed the (1) control group and those on the palatal/lingual side as (2) Er:YAG laser irradiated group (n=5×2 groups).

Cylindrical tooth samples (3 mm in diameter) were prepared using a cylindrical diamond drill (Fig.1-a), and embedded with acrylic resin (Unifast II Clear, GC Co., Tokyo, Japan) in an acrylic-resin cylindrical mold (an outer diameter of 5 mm and an inner diameter of 4 mm, Fig.1-b). After polymerization of the embedding resin, the samples were ground with a diamond disk (Model Trimmer MT-7D, Morita Co., Tokyo, Japan) under running water to expose the dentin. The dentin surfaces were polished with SiC paper up to #4000 and a 0.5-μm-grain alumina paste (Gamma Micropolish® Alumina B, Buehler, Illinois, USA, Fig.1-c). Acrylic-resin molds were cut off horizontally to produce 2-mm-thick dentin specimens (Fig.1-d).

The dentin surfaces of specimens in the Er:YAG laser irradiated group, were irradiated with an Er:YAG

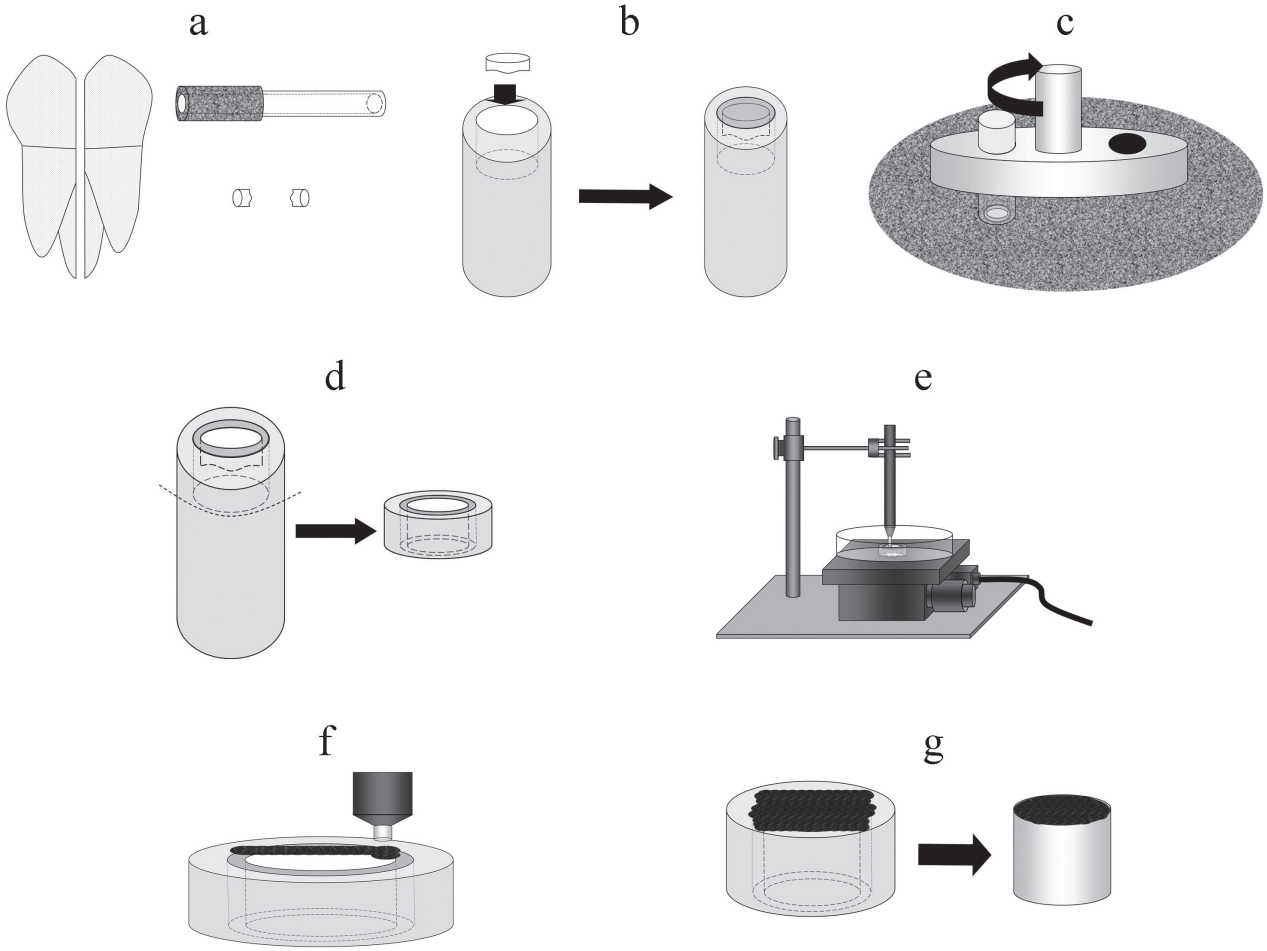

Fig. 1 The construction of dentin disks and irradiation of Er:YAG laser
a : The dentin disk were prepared with a cylindrical diamonds drill as 5 mm of outer diameter and 3 mm of inner diameter.
b : The dentin disks were embedded with acrylic resin in acrylic-resin molds (5 mm of outer diameter and 4 mm of inner diameter).
c : The specimens were polished with SiC-paper up to grid #4000, and polished with a 0.5 micrometer - grained alumina paste.
d : Acrylic-resin mold was cut 2 mm under polished surface.
e,f : Er:YAG laser irradiation to dentin surface was performed. The specimens were placed on the moving stage which moved horizontally 0.3 mm/sec and the Er:YAG laser was irradiated uniformly.
g : The dentin disks irradiated with Er:YAG laser were removed from the acrylic-resin cylinder.

laser (Erwin, Morita Co., Tokyo, Japan). The following parameters were used: wavelength of 2.94 μm, pulse energy of 100 mJ at a pulse repetition rate of 1 Hz, pulse counts of 1024 pulses, pulse duration of 200 μs. The Er:YAG laser was irradiated on the specimens without contact and with water coolant flowing at a flow rate of 3 mL/min. The laser beam spot size was 0.6 mm. A removable tip (TS-15, Morita Co., Tokyo, Japan) was connected to a handpiece used to position the laser beam. The beam power was measured and controlled using a power meter (LabMaster, Coherent Inc., Santa Clara, California, USA). The specimens were mounted on a translation stage (Model MINI60XY, Intelligent Driver CSG-522R, Sigma Koki Co., Tokyo, Japan) and translated horizontally at a rate of 0.3 mm per 1 s; the translation range of the stage was 5×5 mm. The irradiation distance was standardized by using a holder to fix the laser handpiece, and the working distance from the dentin surface was 1 mm. The Er:YAG laser beam irradiated the dentin surface uniformly (Fig. 1-e,f). The specimens irradiated with the Er:YAG laser beam were first removed from the acrylic-resin mold (Fig. 1-g).

After Ar-ion etching at 10 kV for 10 min, the specimens were qualitatively analyzed by the electron spectroscopy for chemical analysis (ESCA, ESCA-Type

Table 1 Scanning parameters for qualitative analysis (eV)

	Wide Scanning	Narrow Scanning				
		P_{2p}	C_{1S}	Ca_{2p}	N_{1S}	O_{1S}
Start Energy	800	146	294	360	410	542
Stop Energy	0	126	280	340	392	526
Repeat Time	5	10	10	10	10	10

XPS analysis conditions: Pressure: 5×10^{-5} Pa; X-ray source: MgK*á*; potential: 8 kV, current: 30 mA; wide scanning interval: 0.5 eV; narrow scanning interval: 0.05 eV; sampling time: 200 ms

750, Shimadzu Seisakusho, Kyoto, Japan).

Table 1 shows the scanning parameters for qualitative analysis.

After performing qualitative analysis by ESCA, the spectral data of the specimens were calculated and the binding energy of each element was computed. Furthermore, the Ca/P ratios of both groups were calculated. Statistical analysis for all data of binding energy of each element was performed using one-way ANOVA and Tukey's test ($p<0.01$).

RESULTS

Representative wide-scanned XPS spectra of the control group and the Er:YAG laser irradiated group are shown in Fig. 2. The height of peaks Ca, N, O and P occurred at lower energies for the Er:YAG laser irradiated group than for the control group.

The narrow-scanned XPS spectra of the P, C, Ca, N and O peaks for both groups are shown in Fig. 3 (a-e), and the binding energy of each element is presented in Table 2.

The binding energies of Ca and P in the Er:YAG laser irradiated group were shifted remarkably towards higher energies relative to those in the control group (Figs. 3-b,c). In the spectrum of C, the spectra profile for the Er:YAG laser irradiated group differed from that of the control group. In particular, the peaks due to -COO- (288.5 eV) disappeared in the Er:YAG laser irradiated group. There was no observable difference between the binding energy of O between the two groups.

The Ca/P ratio of the control group was 1.52±0.16, while that for the Er:YAG laser irradiated group was 1.24±0.05. There was a significant difference between these two groups ($p<0.01$, Tukey's test) (Table 3).

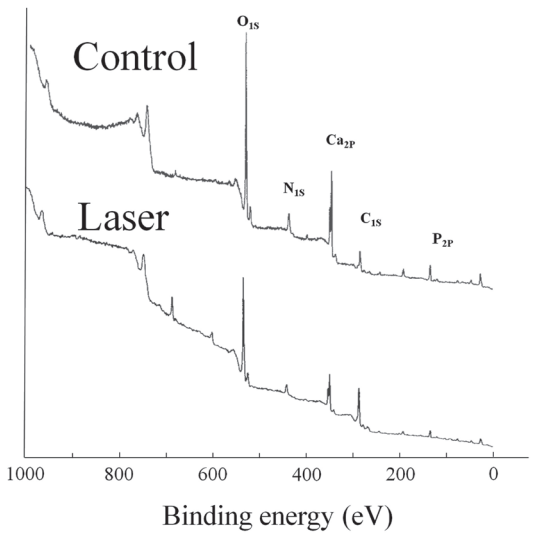

Fig. 2 Spectra of a wide scanning of control group (Control) and Er:YAG laser irradiation group (Laser).
Peaks of the elements P, C, Ca, N and O were observed. Spectra of P, Ca, N and O in Er:YAG laser irradiation group showed lower peaks comparing with the spectra in the control group.

DISCUSSION

The bonding strength of adhesives to Er:YAG laser-irradiated dentine is lower than that to bur-cut dentine[11-13]. Dentine after Er:YAG laser-irradiation had a denatured surface structure[21,22]. A hybrid layer was rarely detected at the resin-dentine interface when adhesives were applied to Er:YAG-irradiated dentine [23,24]. These results imply that the denatured dentine layer produced by Er:YAG laser irradiation has an adverse effect on dentine bonding.

Er:YAG laser irradiation is generally considered to produce less thermal damage of organic tissue is lower than irradiation by other lasers[8,9]. However, the results of the present study indicate that Er:YAG laser irradiation causes chemical changes to the dentin surface[25-27], and that the dentin surface is denatured. The denatured dentin surface typically exhibited a scaly surface and the collagen fibrils were melted. Raman spectroscopy analysis showed that the mineral and organic dentin contents were affected little by Er:YAG irradiation at low energies, but that high-energy Er:YAG laser irradiation deteriorated Type I collagen on dentin[25]. A previous report demonstrated that chemical changes on Er:YAG laser irradiated dentin surface depend on the duration of the laser pulse[28]. When the duration of the laser pulse was short, the cooling time was reduced, so that thermal damage accumulated in the dentin surface. This suggests that

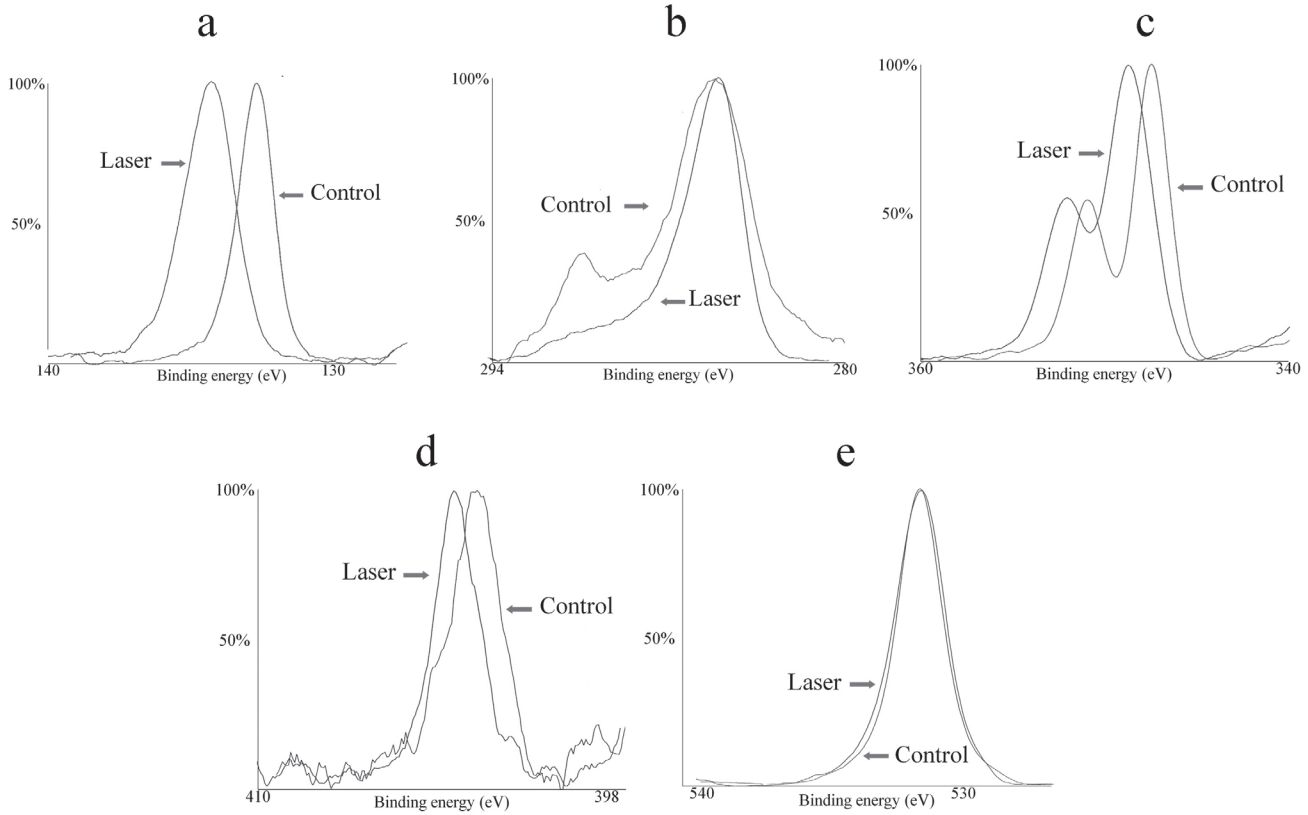

Fig. 3 The narrow-scanned XPS spectra of the P, C, Ca, N and O peaks for control group and Er:YAG laser irradaiation group.

a : Spectra of a P in control group and Er:YAG laser irradiation group.
The peaks of a P in the Er:YAG laser irradiation group were similar to the control group. However the binding energy of the Er:YAG laser irradiation group was higher than that of control group.

b : Spectra of a C in control group and Er:YAG laser irradiation group.
The peaks of a C in Er:YAG laser irradiation group were different from the control group.

c : Spectra of a Ca in control group and Er:YAG laser irradiation group.
The peaks of a Ca in the Er:YAG laser irradiation group were similar to the control group. However the binding energy of the Er:YAG laser irradiation group was higher than that of control group.

d : Spectra of a N in control group and Er:YAG laser irradiation group.
The peaks of a N in the Er:YAG laser irradiation group were similar to the control group. However the binding energy of Er:YAG laser irradiation group was higher than that of the control group.

e : Spectra of a O in Control group and Er:YAG laser irradiation group.
The peaks of O in the Er:YAG laser irradiation group were similar to Control group.

Table 2 Binding energy of elements (eV)

	P_{2p}	C_{1S}	Ca_{2p}	N_{1S}	O_{1S}
Control group	133.0±0.32*	284.9±0.06	347.5±0.3*	399.5±0.36*	531.8±0.2
			351.0±0.2*		
Er:YAG laser irradiated group	134.6±0.32*	285.0±0.06	348.9±0.12*	400.1±0.12*	532.1±0.41
			352.2±0.15*		

*: $p<0.01$ Tukey's test

The binding energies of Ca_{2p}, P_{2p} and N_{1S} in the laser irradiated group were significantly different from those in the control group ($p<0.01$, Tukey's test).

Table 3 Ca/P ratio of the control group and the Er:YAG laser irradiated group

	Ca/P ratio
Control group	1.52±0.16*
Er:YAG laser irradiated group	1.24±0.05*

* $p<0.01$ Tukey's test

There was a statistical difference between the Ca/p ratios of the control and the laser irradiated groups.

the denaturation of dentin irradiated by an Er:YAG laser beam is caused by thermal damage with laser energy.

In this study, the binding energies of Ca and P in the Er:YAG laser irradiated dentin were significantly higher than for the ground dentin. In addition, the spectra of the C peak differed significantly between the Er:YAG laser irradiated group and the control group. The peak due to -COO- (288.5 eV) was not present in the Er:YAG laser irradiated group spectrum. *Mine et al.* reported that the binding energies of Ca and P of laser irradiated human enamel were differed slightly from those of polished enamel, and that the Ca/P ratio of lased enamel was significantly different from that of polished enamel[29]. Moreover, the spectral profiles of the C and N peaks of the Er:YAG laser irradiated dentin differed from those of unirradiated dentin. The low protrusion at about 290 eV in the C spectrum was not present and the spectrum of the N peak was rough for Er:YAG laser irradiated dentin. On the other hand, in this study we found no significant difference between the binding energies of C and O of unirradiated dentin and those of Er:YAG laser irradiated dentin. These results suggested that the crystal formation of Ca, P and N on the dentin were affected by Er:YAG laser irradiation, therefore the binding energy of these elements changed. Irradiation by an Er:YAG laser beam significantly changes the absorption bands of dentin[30]. This is probably due to alteration of spectra and binding energies of the Ca, P and N on dentin irradiated by an Er:YAG laser beam.

On the other hand, Bakary *et al.* reported that no significant chemical changes were observed when dentin was irradiated by Er:YAG laser pulses having a pulse energy of 100 mJ under water irrigation. In addition, as the energy of the Er:YAG laser was increased, the intensity of the amide II peak weakened. Furthermore, indications of thermal damage increased gradually with laser energy[27]. In our study, we found alteration of the peak profiles and binding energies of the elements that make up dentin when using a pulse energy of 100 mJ with water irrigation. The study by Bakary *et al.* was based on FT-IR and XRD analyses, whereas our study was performed using XPS. This explains the different observations between Bakary *et al.*'s study and our study despite the experimental conditions being the same in both studies (i.e., 100 mJ/pulse with water irrigation).

The organic material of dentin is destroyed in the temperature range 100°C - 400°C[31]. The denaturation of dentin commences at 100°C, and becomes stronger at 700°C[32]. The denaturation of dentin irradiated by an Er:YAG laser beam may be related to thermal injury. The denatured dentin irradiated by an Er:YAG laser beam has a similar structure to that of dentin heat-treated at 500°C and 800°C and analyzed by XRD analysis[20]. The root temperature was elevated to 66.5°C when subjected to Er:YAG laser irradiation with a pulse energy of 30 mJ at a repetition rate of 10 Hz under dry conditions, while under wet conditions it was elevated to 28.6°C[33]. Changes in the components of dentin are not expected to occur at these temperatures. It seems that Er:YAG laser irradiation produces locally high elevation of the temperature on the dentin surface, but the temperature falls abruptly, so that the measured temperature of dentin irradiated by an Er:YAG laser beam might be lower than its actual temperature.

In this study, the Ca/P ratio of the control group was similar to theoretical value for hydroxyapatite (1.67), whereas the ratio of the Er:YAG laser irradiated group was significantly lower than theoretical value for hydroxyapatite. This reduction in the Ca/P ratio indicates a decline in the concentration of Ca, and this phenomenon is similar to decalcification of the tooth. These considerations reveal that the organic tissue of dentin was denatured by Er:YAG laser irradiation. The character of Ca on the dentin surface and the dentin collagen fibril network is important for achieving excellent dentin bonding[18,19], although the elements Ca, P and N of dentin are affected by Er:YAG laser irradiation. Thus, the bond strength of dentin irradiated by a Er:YAG laser beam may be less than that of bur-cut dentin.

Although Er:YAG laser irradiation is known to produce lower thermal damage than irradiation by other lasers, this study shows that Er:YAG laser irradiation causes denaturation of the organic components of dentin.

CONCLUSION

The organic components of dentin irradiated by an Er:YAG laser beam were denatured. The binding energies of Ca and P shifted and the peak profiles of C and N changed compared to those of ground dentin.

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