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Treatment of Dental Root Fracture by
Medium Energy CO_2 Laser and DP-bioactive Glass Paste (I)

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Abstract

Sudden trauma or trauma associated with occlusal disharmonies or extreme clenching and gritting can produce vertical root fractures. The crack line usually appear near the development groove and can extend toward the root or horizontally across the tooth. The defect need not be a complete fracture, but may extend through part of the root or crown. When a vertical root fracture occurs, the tooth is extracted, endodontic treatment is completed extraorally, and the crack line is cemented with one of restoratives. However, the long-term prognosis are poor. Lasers were used to alternative treatment for cracked teeth. Results from the previous studies have not supported the findings that there was any fusion of the root fracture with either laser.

The research tried to use a medium energy continuous-wave CO_2 laser and a developed DP-bioactive glass paste to fuse or bridge the crack line. The DP-bioactive glass have a strong absorption band in wavelength of 10.6 «m. DP-bioactive glass and enamel/dentine are expected to be melted and fused together after expose to the CO_2 laser. The study was divided into three parts, 1. the compositional and structural changes in tooth enamel as well as dentine after the CO_2 laser irradiate; 2. the phase transformation and recrystallization of DP-bioactive glass paste during expose to the CO_2 laser; 3. the thermal interaction and bridging mechanism between DP-bioactive glass paste and enamel/dentine when they subject to the CO_2 laser.

The present report will be focused on the first part of the study to further analyze for changes in laser-irradiated human tooth enamel/dentine by means of x-ray diffractometer (XRD), scanning electron microscopy (SEM), differential thermal analysis/thermogravimetric analysis (DTA/TGA), and Fouries transforming infrared spectroscopy (FTIR).

After exposed to CO_2 laser, there were no significant difference in x-ray diffraction patterns of enamels compared to that of before laser treated. But a small peak belonging to ~-TCP appeared at the position of 2¯=30.78î. After treated with CO_2 laser, both powder dentine and block dentine showed much sharper in all the peaks of the diffraction patterns because of grain growth and better crystallinity. ~-TCP and -TCP were identified after laser treated. In FTIR analysis, a HPO_4^{-2} absorption band could be traced in the dentine without laser treatment but disappeared after exposed to laser. No significant change in the absorption band of HPO_4^{-2} in the FTIR curves of enamel before and after laser treatment. A crater with glass-like and melted structure would be formed both on the surface of dentine and enamel after exposed to medium energy CO_2 laser. We believe these thermal data should serve as a useful guide both to predict and to aid in the future studies for the thermal interaction and bridging mechanism between DP-bioactive glass paste and enamel/dentine when they subject to the CO_2 laser.

Keywords: DP-bioactive glass, CO_2 laser, phase transformation, thermal behavior

1. Introduction

A fracture tooth root is difficult to diagnosis accurately and almost impossible to treat effectively. A space in the apical area of a root canal that remains unfilled will cause infection with periapical complications. The treatments described in the literature are based on two facts: the necessity to hold the tooth structure around the crack line, and the necessity to fill the crack line to avoid any contact between the periodontium and the main canal [1-2].

When a vertical root fracture occurs, the tooth is extracted, endodontic treatment is completed extraorally, and the crack line is cemented with one of restoratives such as amalgam, composite resins, glass ionomers and cynocrylate. Although bonding, cementation, and replantation with ligation followed within 30 minutes, the long-term prognosis of the techniques are poor [2]. Lasers can represent an alternative treatment for cracked teeth. Results from the previous studies have not supported the findings that there was any fusion of the root fracture with either laser wavelength [3].

Stewart et al [4] reported on a technique using a CO_2 laser to fuse synthetic hydroxyapatite to enamel, formed by combining hydroxyapatite with a low fusing eutectic. Susan Arakawa [3] induced root fractures, irradiated them using an Nd:YAG laser with air/water surface cooling, and then filled the fractures with a paste of tricalcium phosphate. The results of the study suggested that fusion would not occur under such conditions caused by tissue dehydration and subsequent increased separation of the line of fracture [5-6].

In the study, the authors try to use a medium energy density continuous-wave CO_2 laser to fuse a developed DP-bioactive glass paste to the enamel/dentine, and then bridge the crack line. The DP-bioactive glass have a strong absorption band in wavelength of 10.6 μm. DP-bioactive glass and enamel/dentine are expected to be melted and fused after expose to the CO_2 laser. The study is divided into three parts, 1. the compositional and structural changes in tooth enamel as well as dentin after the CO_2 laser irradiate, 2. the phase transformations and recrystallization of DP-bioactive paste during expose to the CO_2 laser, 3. the thermal interactions and bridging mechanism between DP-bioactive glass paste and enamel/dentin when they subject to the CO_2 laser.

Although the possibility of phase changes has been expected, no additional studies have been reported to find new compounds or compositional and structural changes in tooth enamel/dentine subject to medium energy density laser irradiation [7-8]. Therefore, the present report will be focused on the first part of the study to further analyze for changes in laser-irradiated human tooth enamel/dentine by means of x-ray diffractometer (XRD), scanning electron microscopy (SEM), differential thermal analysis/thermogravimetric analysis (DTA/TGA), and Fouries transforming infrared spectroscopy (FTIR).

2. Materials and Methods

2-1 Specimens Preparation

Extracted sound human molars were removed from storage in alcohol, air dried at 25°C. 2 mm of the apical root of all the teeth was removed to facilitate easy removal of residual pulpal tissue by an endodontic braoch. The enamel and dentine of all the teeth were then separated at the enamel/dentine junction using a low-speed isomate. Enamel and dentine block with an area of 4x3 mm^2 were shaped by using a high-speed handpiece, respectively. The fragments of the enamel and dentine were pulverized into powder with an average particle size of 10.6 μm. The specimens were

divided into four groups of block enamel, powder enamel, block dentine, and powder dentine. Each group had 10 specimens. They were all prepared for CO_2 laser irradiation later.

2-2 Laser Treatment

The LUXAR LX-20 CO_2 laser (Luxar Corp., Bothell, WA) was operated at 5 W power setting using a focused (2 mm from target surface) continuous waveform beam delivered through an 0.8 mm diameter ceramic tip. For this model of CO_2 laser, the manufacturer has determined an 86% efficiency rate for the delivery of beam energy. The time interval for each exposure was 5 seconds. The total time for laser irradiation was 1 minutes. Thus, the calculated energy density using these parameters were 3000 J/cm^2. The specimen with powder type was suggested to compact into a disc (3 mm in diameter and 1mm in thickness) with applying a hydraulic force of 50 kg/cm^2, to prevent the powder from rising up or fluttering in the air during laser beam sputtering on the powder.

2-3 Materials Analysis

The crystalline phases of specimens before and after laser irradiated were determined by Rigaku X-ray powder diffractometer with CuK_α radiation and Ni filter at the speed of 4°/min. To determine phase contents, relative intensities of the main peaks of each phase were used. The FTIR spectra were recorded using KBr pellets (1 mg sample per 300 mg KBr) on a Jasco FTIR grating instrument with slow scan and normal slit width. The wavelength of the FTIR used in the experiment was in the range of 4000-400cm^{-1} to evaluate the functional group of the specimens. TA/SDT2960 was used to study the thermal behavior of dentine and enamel. The scanning temperature for the thermal analysis of the specimens was from room temperature up to 1500°C with a heating rate of 10°C/min and N_2 flow rate of 90ml/mim. The total weight of the specimen for each thermal analysis was 40mg and Al_2O_3 was as reference powder.

The morphology and microstructure of the specimens were observed under the scanning electron microscope (SEM). After laser treatment, the specimens were immersed in cold 2.5% glutaraldehyde fixative prepared in 0.1mol/L cacodylate buffer at pH 7.4 for 8 hrs. Subsequent to the initial fixation, specimens were rinsed in buffer and postfixed with 1% osmium tetorxide for 4 hrs. Specimens were then prepared for SEM examination by slow dehydration in a series of graded ethanol solutions (20 to 100%) at 45-min intervals, followed by immersion in hexamethydisilazane for 1 hr before overnight storage in a desiccator. Finally, all specimens were mounted on a aluminum stubs and sputer-coated with ~200Å of gold/palladium before being examined in a Jeol-840 They were then observed by SEM and analyzed using an energy-dispersive electron probe x-ray microanalyzer. P, Ca, and Na were analyzed across the grains and grain boundaries. An electron beam maintained at 2 x 10^{-10} amp was used and x-ray intensities in counts per second (cps) were recorded. The accelerating voltage was 12 kV.

3. Results and Discussions

3-1 XRD Analysis

Fig.1(a) and Fig.1(b) were XRD diffraction patterns of block enamel and powder enamel, respectively. Compared to standard JCPD card, they were all identified as a

hydroxyapatite and the peaks of the enamels were in agreement with that of the standard hydroxyapatite diffraction pattern. There were three reflected peaks of (002), (112), (411) much stronger than that of standard pattern in block enamel because of preferred orientation in these directions. H Warshawsky [9] showed the hydroxyapatite orientation almost paralleled to its c-axis in the surface part of enamel. It was tilted by about 40° and 60° to c-axis of the rhombohedral prism in the meddle part and inner part of the enamel. The crystal orientation for the whole enamel from outer to inner part was like a fan-out distribution along its rhombohedral prism.

After exposed to CO_2 laser, there were no significant difference in x-ray diffraction patterns of enamels compared to that without laser treatment. But a small peak belonging to α-TCP appeared in the position of 2θ=30.78° as shown in Fig.1(c). Since the laser irradiantly induced changes in tooth enamel are expected to primarily arise from localized heating, previously identified and reported thermal changes that occur in biological hydroxyapatite progressively heated to higher temperatures in conventional furnaces are similarly expected to occur in laser-irradiated tooth enamel.

Fig.2(a) and Fig.2(b) were the x-ray diffraction patterns of block dentine and powder dentine, respectively. They all identified as nonstoichiometric hydroxyapatite structure. There was a broaden peak in the position of 2θ=30°-50° because the particle size of hydroxyapatite in dentine was very small only about 300Å-600Å. The OH^- group of hydroxyapatite in the dentine replaced by the CO_3^{-2}, F^-, and Cl^- was also contributed to the broaden peak in those patterns [10].

After treated with CO_2 laser, the dentine showed much sharper in all the peaks of the x-ray diffraction pattern as shown in Fig.2(c). Four peaks other than hydroxyapatite could be traced at the positions of 2θ = 30.78°/34.21°, and 32.47°/33.05° in the diffraction patterns which were identified to be α-TCP and β-TCP, respectively.

3-2 FTIR Analysis

Fig.3(a) and (b) showed the FTIR patterns of enamel before and after CO_2 laser irradiation, respectively. The tooth enamel bands at 602 and 568 cm^{-1} (doublet) are well known to arise from the ν_4 phosphate mode. The tooth enamel band at 470 cm^{-1} arises from the ν_2 phosphate mode and the shoulder at about 3572 cm^{-1} arises from hydroxide "translation" by comparison with the assigned modes in hydroxyapatite. 1450, 1410, and 870 cm^{-1} in Fig.3(a) was the absorption bands of CO_3^{-2} in biological apatite structure, which proved that the mineral in enamel was carbonate-contained apatite. The spectra of the laser-irradiated tooth enamel showed (1) a minor phase of α-TCP by new bands of weak intensity at 502, 475 440, and the very weak shoulders at ~985 and ~940 cm^{-1}; and (2) the major phase was still hydroxyapatite (hydroxyapatite phopshate bands at ~1090, ~1040, 958, 602, 568, and 470 cm^{-1}); (3) The absorption bands of OH^- (1630 and 630 cm^{-1}) and CO_3^{-2} (1450 and 1410 cm^{-1}) decreased due to dehydration, proteins destruction, and carbonate evaporation [11-12].

The absorption band of OH^- at 1630 cm^{-1} of dentine (Fig.3(c)) was obviously higher than that of enamel due to higher water content in dentine. The strong- and medium-absorption pattern, although bands at 1040, 1093, 733, 692 cm^{-1} and so on confirmed the presence of the tetrahedral orthophosphate ion PO_4^{-3} in hydroxyapatite structure. The most intense bands associated with PO_4^{-3} vibrations in calcium phosphate materials were the antisymmetric stretching mode at 1100-1000 cm^{-1} (ν_2 band) and antisymmetric bending mode at 600-550 cm^{-1}(ν_4 band). The band at 1210

cm^{-1} was the absorption band of $HO\text{-}HPO_4^-$; 1133 cm^{-1} was the vibraing mode of HPO_4^{-2}; 870 cm^{-1} was the absorption band of P-O-(H); and 634 cm^{-1} belongs to OH^- vibration band [11]. After laser treatment (Fig.3(d)), dentine decreased in the absorption bands of OH^- (1630 and 630 cm^{-1}) and CO_3^{-2} (1450 and 1410 cm^{-1}) in FTIR pattern due to dehydration, proteins destruction, and carbonate evaporation. It was similar to that of laser irradiated enamel.

3-3 DTA/TGA Analysis

Fig.4(a) is the results of DTA analysis for tooth enamel where dotted line is the enamel after laser treated. An endothermic peak at 50-200°C is surface water and organically bound water evaporation on the enamel. The pyrolysis and volatilization of various organic constituents in the enamel appear in the temperature range of 250-350°C which is a continuous and broaden exothermic peak [13]. We can observe weight loss in the two temperatures (Fig.4(b)). The organic constituents in dentine (33%) is much higher than that of enamel (4%) which leads to dentine to have a larger endothermic peak, exothermic peak, and higher weight loss in the two temperatures (Fig.5). The maximum rate of oxidation and volatilization of the organic constituents of both enamel and dentine take place at 350°C.

The continuous endothermic reaction of both enamel (Fig.4(a))and dentine (Fig.5(a)) from 500-900°C appear to be the subsequent oxidation of carbon compounds from the inorganic phase [13-14]. It also reflects on the TGA curves of the enamel (Fig.4(b)) and dentine (Fig.5(b)). There is an exothermic reaction in the temperature of 1300-1400°C in the DTA curve of enamel (Fig.4) because hydroxyapatite thermally decomposes into α-TCP ($Ca_3(PO_4)_2$) and TTCP ($Ca_4P_2O_9$) [14]. The exothermic reaction of dentine at the temperature of 1300-1400°C in the DTA curve is more distinct than that of enamel because they are different in particle size and crystal structure. Though enamel and dentine are identified as hydroxyapatite lattice with XRD, they are different in ion-containing. Enamel is a carbonate-contained hydroxyapatite of $Ca_{10-x}(PO_4)_{6-3x/2}(CO_3)_{3x/2}(OH)_{2-x/2}x/2H_2O$ where CO_3^{-2} ions take the position of PO_4^{-3}. Dentine is a calcium-deficient hydroxyapatite of $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ ($0<x<2$) which includes HPO_4^{-2} group [14-15].

Except for the peak at 1300-1400°C, all the endothermic and exothermic peaks appear on the DTA curves both of laser treated enamel and dentine are much smaller than those of without laser treated. Enamel or dentine will lose some of water and organic constituents after expose to the CO_2 laser, which cause to the peaks of DTA curves decrease in scale. The TGA curves also have the same phenomenon that reflects the smaller amount of weight loss during heating after laser treatment.

3-4 Microstructure

Fig.6(a) shows a crater formed on the enamel surface by right-angled CO_2 laser beam. There are several cracks on the surface of the enamel which are resulted from rapid water evaporation and organic constituents decomposition during heated by CO_2 laser. Inside and around of the crater, glass-like mass is probably composed by a mass of melted hydroxyapatite of enamel (Fig.6(b)). Fig.7(a) shows the enamel microstructure without the laser treatment, where preferred orientation in three directions can be observed on the picture. (002) plane of hydroxyapatite prism parallels to the surface of enamel surface due to the higher hardness in the plane. (412) and (112) directions are crossover among the prisms parallel to (002) direction which

suppose to have a higher mechanical strength for the enamel. After treated with CO_2 laser, grain growth and recrystallization of hydroxyapatite in the enamel can be examined under SEM at a distance of the crater (Fig.7(b)). The thermal gradient generated from laser irradiation will cause hydroxyapatite grain around the crater sintering together and coalesce to be a larger grain.

Fig.8(a) is the dentine structure without laser treatment, where dentine tubules can be seen after etched with 37% H_3PO_4 solution for 1 minute. It have same microstructure after irradiation such as, grain growth, recrystallization, melting, and fusion (Fig.8(b)). Dentine tubules are closed by the CO_2 laser.

4. Discussions

A laser-irradiated tooth enamel and dentine surface will have a temperature gradient. High energy density laser-irradiant conditions (`10,000 J/cm^2) easily melt and penetrate tooth enamel and dentine. Even under lower energy density irradiant conditions (9-120 J/cm^2), slight surface melting has been detected which indicates very high temperature at the enamel and dentine surface [7,16-17]. From the melted surface inwards along this decreasing temperature gradient, different compositional, structural, and phase changes are expected under medium energy CO_2 laser irradiation in this study.

Biological hydroxyapatite has been heated in the conventional furnace. The heating history and its changes could be divided into three general temperature ranges [13-14, 17]: I 100-650°C; II 650-1100°C; and III >1100°C°C. Temperature range I (100-650°C): (1) The water content decreases with an abrupt decrease at 100-300°C of about 1/3 of the total. (2) An overall reduction in total CO_3^{-2} content and rearrangement of CO_3^{-2} ions occur; the major CO_3^{-2} component in “phosphate” positions progressively increases in 400-650°C. (3) The OH^- content progressively increase to a maximum of ~1.8 times the original in the ~300-500°C range. (4) Acid phosphate (HPO_4^{-2}) ions condense to form pyrophosphate ($P_2O_7^{-4}$) ions. (5) progressive uptake CO_2 and NCO^- occur in the range 500-600°C, and then both decrease with increasing temperature. (6) Protein decomposes at about 250-600°C.

In the study, most of the results of DTA/TGA analysis of enamel and dentine (Fig.4 and Fig.5) follow the previous description which occur in the temperature range I such as: water content decreases around 100-300°C and protein decomposes at about 250-600°C. There is an “saddle” in the TGA curves of dentine and enamel in the temperature of 500-800°C, which seems no weight loss to be observed. Although organic constituents gradually decompose that cause to weight decrease, some of ions such as CO_2, NCO^-, and OH^- will on the contrary progressively uptake in this temperature range that leads to a weight increase. It will be resulted to a dynamic balance in weight in the system. In FTIR analysis, a HPO_4^{-2} absorption band can be traced in dentine without laser treatment (Fig.3(c)). However, it is disappeared after expose to laser. As described, HPO_4^{-2} ions will condense to pyrophosphate ($P_2O_7^{-4}$) ions at the temperature of 500-600°C which will decrease the absorption band of HPO_4^{-2}[12, 17-18]. Hydroxyapatite of enamel contains no HPO_4^{-2} ions in the crystal structure. There is no significant change in the absorption band of HPO_4^{-2} in the FTIR curves of enamel before and after laser treatment.

Temperature range II (650-1100°C): (1) Thermal recrystallization and crystal size growth occur. Pyrophosphates reacts with apatite to form PO_4^{-3} at ~650°C, or lower, along with formation of a second phase of β-TCP. The beta-form of TCP normally

converts to the alpha-form at 1125°C. (2) The OH^- content changes from ~1.8 times the original to ~1.4 times the original at 600-650°C. (3) Additional water and CO_3^{-2} are lost from the apatite. (4) All trapped CO_2 and NCO^- are lost by 800°C.

It shows a decrease tendency in TGA curves both of enamel and dentine at the temperature of 500-800°C in the study because water, OH^-, trapped $CO_2$and NCO^- are lost by 800°C. We can also expect grain growth while temperature up to 650°C as shown in Fig.8. Enamel is a pure carbonate-contained hydroxyapatite. It will be not obvious phase transformation if heating temperature is lower than 1400°C. Dentine is an nonstoichiometric hydroxyapatite: $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ ($0<x<2$), where series of reactions will be happened as temperature increase [13-14, 18]:

(1) $2HPO_4^{-2} \Rightarrow P_2O_7^{-4} + H_2O$ (250-550°C)

(2) $P_2O_7^{-4} + 2OH^- \Rightarrow 2PO_4^{-3} + H_2O$ (600-700°C)

From the reaction, β-TCP will be formed in dentine once heating temperature is higher than 700°C. Dentine treated with CO_2 laser shows a β-TCP peaks at the position of 2θ = 32.47 and 33.05° (Fig.2) but enamel shows no beta-TCP formed after laser irradiation.

Temperature range III (over 1100°C): (1) The β-TCP converts to α-TCP at 1125°C and α-TCP converts at 1430°C to a higher temperature polymer designated $\underline{\alpha}$-TCP which melts at 1756°C (2) Remaining CO_3^{-2} and Cl^- are lost along with further OH^- reduction concomitant with O^{-2} incorporation in the apatite phase and then the oxyhydroxyapatite phase disproportionates at 1450°C to form $\underline{\alpha}$-TCP and TTCP whose mixture melts at 1600°C.

α-TCP could be traced both in the XRD curves of enamel and dentine after laser treated but no $\underline{\alpha}$-TCP appeared. Though α-TCP converts at 1430°C to a higher temperature polymer designated $\underline{\alpha}$-TCP; the $\underline{\alpha}$ form is not stable at room temperature. Glass-like and melted structure could be observed in the SEM photographs in the enamel and dentine after laser irradiated. We can speculate that the temperature on the surface of enamel and dentine should over than 1600°C.

5. Conclusion

After exposed to CO_2 laser, there were no significant difference in x-ray diffraction patterns of enamels compared to that of before laser treated. But a small peak belonging to α-TCP appeared in the position of 2θ=30.78°. After treated with CO_2 laser, the dentine showed much sharper in all the peaks of the x-ray diffraction patterns because of grain growth and better crystallinity. Four peaks other than hydroxyapatite could be traced at the positions of 2θ = 30.78°/34.21°, and 32.47°/33.05° in the diffraction patterns which were identified to be α-TCP and β-TCP, respectively. In FTIR analysis, a HPO_4^{-2} absorption band can be traced in dentine without laser treatment and it is disappeared after expose to laser because of HPO_4^{-2} ions condense into $P_2O_7^{-4}$ ions. Hydroxyapatite of enamel contains no HPO_4^{-2} ions in the crystal structure which cause to no significant change in the absorption band of HPO_4^{-2} in the FTIR curves of enamel before and after laser treatment. A crater with glass-like and melted structure will be formed both on the surface of dentine and enamel after expose to medium energy CO_2 laser, which is one of the evidence of temperature over than 1600°C. We believe these thermal data should serve as a useful guide both to predict and to aid in future studies for the thermal interaction and bridging mechanism between DP-bioactive glass paste and enamel/dentine when they subject to the CO_2 laser.

6. References

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7. Captions

Fig.1 X-ray diffraction patterns of (a) block enamel without CO_2 laser irradiation; (b) powder enamel without CO_2 laser irradiation; and (c) powder enamel with CO_2 laser

treatment.
H: hydroxyapatite, α: α-tricalcium phospahte

Fig.2 X-ray diffraction patterns of (a) block dentine without CO_2 laser irradiation; (b) powder dentine without CO_2 laser irradiation; and (c) powder dentine with CO_2 laser treatment.
H: hydroxyapatite, α: α-tricalcium phospahte, β: β-tricalcium phosphate

Fig.3 FTIR patterns of (a) enamel without CO_2 laser treatment, (b) enamel with CO_2 laser irradiation, (c) dentine before exposed to CO_2 laser, (d) dentine after CO_2 laser irradiated.

Fig.4 (a) DTA curves and (b) TGA curves for tooth enamel, where solid line is enamel before CO_2 laser treatment and dotted line is enamel without laser treated.

Fig.5 (a) DTA curves and (b) TGA curves for dentine, where solid line is the dentine before CO_2 laser treatment and dotted line is the dentine without laser treated.

Fig.6 (a) A crater formed on the enamel surface where exposed to CO_2 laser. (b) Inside and around of the crater, glass-like mass is composed by a mass of melted hydroxyapatite. Cr: crater, En: enamel, GM: glass-like and melted mass.

Fig.7 (a) The microstructure of enamel without laser irradiation, where preferred orientation in three directions can be observed on the picture. (b) After treated with CO_2 laser, grain growth and recrystallization of hydroxyapatite in the enamel can be examined under SEM at a distance of the crater.

Fig.8 (a) Microstructure of the dentine without laser treatment and (b) After laser irradiated, grain growth, recrystallization, melting, and fusion can also be examined. Dentine tubules are closed by the CO_2 laser. Dt: dentine tubules, GR: growth and recrystallization, GM: glass-like and melted mass.