Original Article

Acid Resistance of Erbium-doped Yttrium Aluminum Garnet Laser–Treated and Phosphoric Acid–Etched Enamels

Jung-Ho Kim[a]; Oh-Won Kwon[b]; Hyung-Il Kim[c]; Yong Hoon Kwon[d]

ABSTRACT

Objective: To compare the effects of erbium-doped yttrium aluminum garnet (Er:YAG) laser ablation and of phosphoric acid etching on the in vitro acid resistance of bovine enamel.

Materials and Methods: Teeth were polished to make the surface flat. The polished enamel was either etched with 37% phosphoric acid for 30 seconds or ablated with a single 33 J/cm^2 pulse from an Er:YAG laser. The control specimens were free from acid etching and laser ablation. Changes in crystal structure, dissolved mineral (calcium [Ca] and phosphorus [P]) contents, and calcium distribution in the enamel subsurface after a pH-cycling process were evaluated.

Results: After laser treatment, poor crystal structures improved without forming any new phases, such as tricalcium phosphates. Among the tested enamels, dissolved mineral contents were significantly different ($P < .05$). Er:YAG laser–treated enamels had the lowest mineral dissolution (Ca, 13.78 ppm; P, 6.33 ppm), whereas phosphoric acid–etched enamels had the highest (Ca, 15.90 ppm; P, 7.33 ppm). The reduction rate and reduced depth of calcium content along the subsurface were lowest in Er:YAG laser–treated enamels.

Conclusion: The Er:YAG laser–treated enamels are more acid resistant to acid attack than phosphoric acid–etched enamels.

KEY WORDS: Er:YAG laser; Phosphoric acid; XRD; ICP-AES; pH-cycling; EPMA

INTRODUCTION

The use of acid to increase microscopic roughness, by selectively removing mineral crystals, to improve the retention of composite restoratives has become a standard process for dental preparation since the report of Buonocuore.[1–4] Among the various proposed methods, etching with 37% phosphoric acid is the most widely used. As long as the enamel surface is clean and sustains enough etching to separate enamel crystallites, an optimal enamel-resin bond can be achieved.[3]

[a] Private practice, Daegu, Korea.

[b] Professor, Department of Orthodontics, College of Dentistry, Kyungpook National University, Daegu, Korea.

[c] Professor, Department of Dental Materials, College of Dentistry, Pusan National University, Pusan, Korea.

[d] Assistant Professor, Department of Dental Materials, College of Dentistry and Medical Research Institute, Pusan National University, Pusan, Korea.

Corresponding author: Yong Hoon Kwon, PhD, Department of Dental Materials, College of Dentistry, Pusan National University, 1-10 Ami-dong Seo-gu, Pusan 602-739, Korea (e-mail: y0k0916@pusan.ac.kr)

However, because of the weak correlation between the depth of etching and strength of the enamel-resin bond, the total strength of the enamel-resin bond might not vary with depth. As a result, recent studies suggest a shorter duration of acid etching.[5,6] The advantage of etching with phosphoric acid is the high level of bracket bond strength achieved. On the other hand, the loss of mineral crystals, essentially the acid-protecting barrier, is inevitable. Because of this mineral loss, the acid-etched region may be vulnerable to successive acid attacks in the oral environment.

For many years, the erbium-doped yttrium aluminum garnet (Er:YAG) laser has been applied in dentistry for carious lesion removal, cavity preparation, endodontic procedures, and surface conditioning.[7–11] The Er:YAG laser is able to handle dental hard tissue with high efficiency because of the high absorbability of the 2.94 μm wavelength by water and dental enamel.[12–14] The absorbed laser energy is converted to heat that boils water in the tooth, forming high-pressure steam. The successive explosive vaporization of water modifies the smooth tooth surface, creating an irregularly serrated and microfissured morphology.

To use this morphological modification for orthodontic treatment, recently, the Er:YAG laser has been in-

troduced into practice.[10,15,16] Compared with other lasers, the Er:YAG laser has a greater ability to roughen tooth surface and produce the microretentive structure needed for monomer infiltration to seal the tooth surface with a bonding agent. However, in spite of these favorable structural modifications, similar to those of an acid-etched surface, the bracket tensile bond strength achieved was lower than that for the phosphoric acid–etched case, and this was common for most laser-treated cases.[17–19]

Unlike acid etching, Er:YAG laser etching is accompanied by a complex thermomechanical process. In addition to the morphological modifications, heat-induced structural or physical property modifications of dental enamel need further investigation to find a way to compensate for the lower bracket bond strength before the Er:YAG laser can be considered an alternative to conventional acid etching.

The purpose of this study was to compare Er:YAG laser–ablated dental and phosphoric acid–etched dental enamels by evaluating their acid resistance. The dissolved mineral content and calcium distribution in the enamel subsurface after a pH-cycling process were investigated.

MATERIALS AND METHODS

Sound and noncarious bovine incisors were obtained and stored in 0.1% thymol solution at 4°C until the experiments. The labial side of the selected teeth was gradually polished with silicon carbide (SiC) papers and diamond pastes. Then the teeth were ultrasonicated in distilled water several times.

The polished specimens (n = 47) were divided into three groups: group 1, control (no acid etching or laser ablation); group 2, phosphoric acid etching; and group 3, laser ablation. For acid etching, 37% phosphoric acid (ORTHO-ONE etchant, Bisco, Schaumberg, IL) was applied to the enamel surface, rinsed with running water and gently dried with dryer. Each procedure was done for 30 seconds. For laser treatment, the enamel surface was ablated with an Er:YAG laser (Twinlight, Fotona, Ljubljana, Slovenia) at 2.94 μm wavelength. The pulsed laser beam was scanned across the surface in a noncontact mode. The diameter of the treated spot was about 1.2 mm. Each spot was irradiated with only one laser pulse to minimize surface damage. The irradiation energy was 380 mJ/pulse (33 J/cm^2 per pulse) with a repetition rate of 2 Hz. During laser ablation, water was sprayed. After ablation, to clear tooth particles and dust, the surface of laser-treated specimens was cleaned with running water without brushing and dried in air.

For analysis of their x-ray diffraction (XRD) patterns, specimens were polished (n = 5) and made into slabs.

The x-ray diffraction patterns were obtained from the control and laser-ablated enamels. The x-ray diffractometer (X'Pert-APD, Philips, Eindhoven, Netherlands) was operated at 30 kV/20 mA. A reference spectrum was obtained before the laser treatment using the same specimens.

To evaluate the mineral dissolution of the treated enamel surface, an ion coupled plasma atomic emission spectrometer (ICP-AES) (Optima 4300DV, PerkinElmer, Boston, MA) was used. Specimens analyzed were control (n = 7), phosphoric acid-etched (n = 7), and laser-ablated (n = 7) enamels. Each specimen was cut to 5.5 × 7 × 0.5 mm and ultrasonicated with distilled water for 1 minute. The rear side of each slab was coated with nail varnish to prevent reaction with the demineralization solution. The demineralization solution contained 0.1 M lactic acid and 0.2 mM methylene diphosphonic acid at pH 4.8. Each slab was put into a separate container and attached to the bottom of the container, and then 3 mL of demineralization solution was poured in. The container was stored at 37°C for 24 hours. The next day, the solution was diluted 100-fold, and the dissolved calcium (Ca) and phosphorus (P) concentrations (ppm) were measured. Three measurements were performed on each element for each diluted solution.

To test the acid resistance of the treated specimens, a 4-day pH-cycling process was followed. The control, phosphoric acid-etched, and laser-ablated specimens were demineralized for 18 hours and then remineralized for 6 hours each day to form artificial caries-like lesions. The demineralizing solution, at pH 4.6, contained 0.05 M acetic acid, 2.2 mM calcium, and 2.2 mM phosphate ions. The remineralizing solution, at pH 7.0, contained 0.15 M potassium chloride, 1.5 mM calcium, and 0.9 mM phosphate. The pH-cycling process started with the demineralizing phase. A 5-minute wash with distilled and deionized water was done between the demineralizing and remineralizing phases and at the end of the process. Each solution was unchanged during the 4-day process.

To evaluate the calcium distribution, specimens were washed in distilled water after the 4-day pH-cycling process, cut longitudinally from the labial side, and imbedded into resin with the cut surface at the top. The cut surface was gradually polished with SiC papers and diamond pastes, washed in distilled water for 3 minutes twice, and dried in a vacuum dryer for 2 days. Five specimens from each group were selected. The distribution of calcium in each specimen was evaluated from the surface to subsurface by an electron probe microanalyzer equipped with a wavelength dispersive spectrometer (EPMA1600, Shimadzu, Japan) operated in the line analysis mode. The examination beam was 1 μm with a 20-kV acceleration voltage.
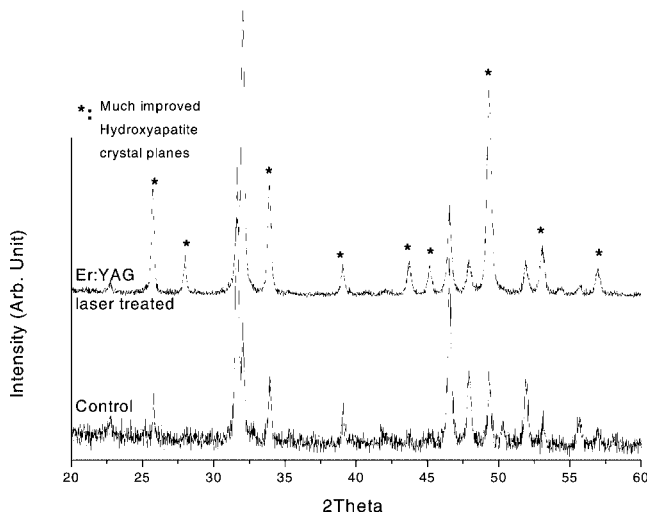
Figure 1. The x-ray diffraction pattern of control (unlased) and laser-ablated specimens. Slightly amorphous crystal structure of the control specimen has improved after laser treatment.

Table 1. Dissolved calcium and phosphorus contents from the different specimens[a]

Specimen	Ca, ppm*	P, ppm*
Control	15.37 (0.36) a	7.09 (0.23) a
Phosphoric acid-etched	15.90 (0.52) b	7.33 (0.29) b
Er:YAG laser-ablated	13.78 (0.53) c	6.33 (0.24) c

[a] Ca indicates calcium; P, phosphorus; Er:YAG, erbium-doped yttrium aluminum garnet.

* Significantly different (one-way ANOVA, $P < .05$). Within each column, values marked with different letters were significantly different (Tukey's studentized range test, $P < .0001$).

Two random measurements on each specimen were performed.

The data acquired from the ICP-AES measurements were analyzed by one-way ANOVA (P value of .05), followed by Tukey's studentized range test for variables (P value of .0001).

RESULTS

The XRD patterns of control and laser-ablated specimens are shown in Figure 1. Laser-ablated specimens had improved crystalline structures compared with the pool crystalline structures in the control specimens. The starred (*) crystal planes show the improved crystalline structure after laser treatment. However, new phases, such as TCPs (tricalcium phosphates), were not observed after the laser ablation.
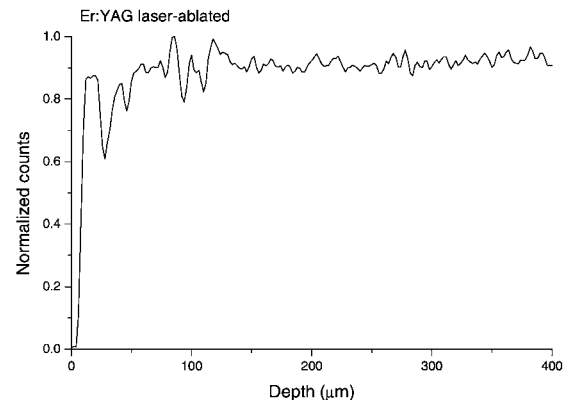
The mineral (Ca and P) contents in the demineralization solution are listed in Table 1. The dissolved Ca and P contents among the three groups were significantly different ($P < .05$). Among the groups, phosphoric acid–etched specimens had the highest Ca and P dissolution (15.90 and 7.33 ppm, respectively) and
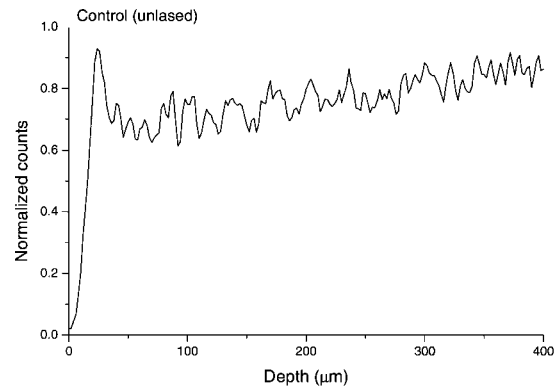
a
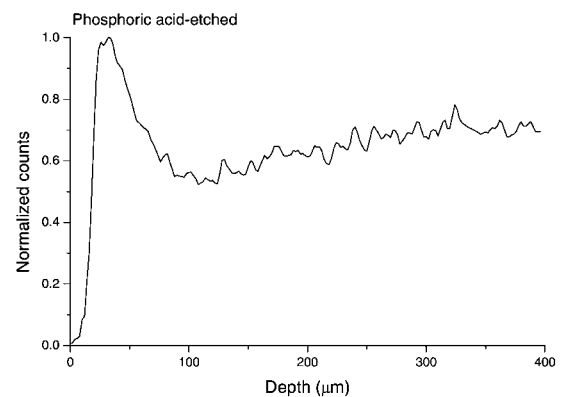
b

c

Figure 2. Calcium distribution in the specimens along the subsurface after pH-cycling process: (a) control, (b) phosphoric acid–etched, and (c) laser–ablated.

Er:YAG laser-ablated specimens had the lowest dissolution (13.78 and 6.33 ppm, respectively).

Figures 2a–c show the calcium distribution in the specimens along the subsurface after the pH-cycling process. Significantly different calcium distributions were found in the unlased (control and phosphoric

acid-etched) and laser-ablated specimens. The subsurface calcium loss of the unlased enamels was much higher than that of the laser-ablated enamels. The calcium content was mainly lost from the subsurface in the unlased enamels; however, in the laser-ablated enamels, the calcium content decreased from the surface to the subsurface. And the reduction rate and reduced depth of the calcium content along the subsurface were much lower in the laser-ablated enamels than in the unlased enamels.

DISCUSSION

The Er:YAG laser ablation is the result of an explosive vaporization of water within the tooth. The Er:YAG laser wavelength is coincident with the main absorption band of water, so the light is absorbed well by hydroxyl ions. Light of this wavelength is also absorbed well by enamel.[12–14] Enamel consists of 85% mineral by volume. The remaining 15% consists of free water and equal amounts of protein and lipid.[20] The strongly absorbed laser energy in the enamel is converted to heat that boils water abruptly. The boiled water forms high-pressure steam that leads to the ablation process when the pressure exceeds the ultimate strength of the tooth. During the ablation process, water evaporates explosively with tooth particles. The ablated materials and their successive recoil force create craters on the surface. And the irradiated surface becomes a flaky structure with an irregularly serrated and microfissured morphology.

The temperature rise in the enamel induces modifications in the enamel structure: water is lost at 80–120°C, protein decomposes at about 350–400°C and completely decomposes above 400°C, β-tricalcium phosphate (β-TCP) forms above 600°C with the loss of carbonate, enamel melts above 1000°C in an air atmosphere, and β-TCP converts to αTCP above 1100°C.[21–24] The decomposed protein and other organic matrix products melt and swell and probably lead to a blockage of the interprismatic and intraprismatic spaces, which act as ion diffusion channels, and eventually result in the decrease of calcium loss.[25] Furthermore, the enamel crystalline structure improves with the decrease of enamel solubility in acid at temperatures of 250°C to ~400°C.[23,26,27] In the range of 600°C to ~1000°C, the possibility of the optimal caries inhibition has been suggested.[28,29] However, because any new phases (β-TCP and αTCP) formed in this range are more soluble than hydroxyapatite, even though still less soluble than enamel, temperatures increased above 600°C may not be beneficial.

Interpretation of the XRD pattern after the Er:YAG laser ablation revealed improved crystallinity. The improvement did not occur in all crystal planes, but selectively in some crystal planes. That no new phases (βTCP) were found can imply that the temperature during the laser irradiation may not rise above 600°C. According to the ICP-AES study, the improved crystalline structure may be related to the decrease of enamel solubility against acidic environment.

With a single laser pulse on each spot, approximately 10% and 13% inhibition of mineral (Ca and P) dissolution was achieved, relative to the control and the phosphoric acid–etched specimens, respectively. The inhibition of mineral dissolution may be partially ascribed to the decomposed organic matrix. The decomposed organic matrix may have blocked the ion diffusion channels and retarded both the permeation of external acid solution and the dissolution of mineral.[30]

Among the unlased and laser-ablated specimens, probably as a result of the improved crystallinity and the blocking effect of organic matrix, the calcium distribution in the subsurface had a different nature after the pH-cycling process. In the unlased specimens, the mineral loss occurred from the subsurface, whereas in the laser-ablated specimens, the mineral loss occurred from the surface.

Because the Er:YAG laser-ablated surface can be easily characterized by the flaky with irregularly serrated and microfissured morphology, these microfissures can work as open channels for acid to reach the subsurface. Ironically, these microfissures and microspaces in the laser-ablated region are believed to trap the free ions essential for remineralization. However, such morphological changes must be vulnerable to acid attack and mineral loss.[27] Such irregularly serrated and microfissured morphology can increase the mechanical retention important for bond strength, but such laser ablation may cause a problem in the recovery of the original tooth morphology after debonding. To get the original tooth state, control of the laser conditions is important to make the polishing of a tooth surface easy. On the basis of these findings, it may be possible to insist that Er:YAG laser ablation effectively induces acid resistance in enamel, probably by crystalline improvement and the blocking effect of the organic matrix, with reasonable laser conditions.

Unlike laser ablation, phosphoric acid etching modifies the surface morphology by selective removal of interprismatic mineral structure. The organic materials are less affected by acid etching than by laser ablation. The smooth and solid surface is modified to a regularly rough and extensively microfissured structure. These structures are very useful to increase the retention of resin composites for adhesion.[1–4] On the other hand, these structures are more vulnerable to acid attack. Acid etching does not improve crystalline structure and does not induce blocking of ion diffusion

channels. However, acid etching also removes the acid-protecting superficial enamel layer and increases microfissures on the surface, with a subsequent increase in mineral loss in acid-etched enamel compared with control and laser-ablated enamels. The use of phosphoric acid is conventional in orthodontic preparation. However, for treating teeth that are exceptionally vulnerable to acid, Er:YAG laser may be a reasonable alternative to phosphoric acid treatment. In these circumstances, to take full advantage of the acid resistance provided with this technique, researchers should work on increasing bond strength with proper laser ablation conditions and bonding procedures.

CONCLUSIONS

• The bovine enamel treated with a single Er:YAG laser pulse had improved crystallinity without forming any TCP phases.
• As a result of laser treatment, enamels had less mineral loss than the phosphoric acid–etched enamels against acid attack.
• The Er:YAG laser treatment can be proposed as a possible alternative for the conventional phosphoric acid etching in orthodontic preparation.

REFERENCES

1. Buonocore MG. Simple method of increasing the adhesion of acrylic filling materials to enamel surfaces. *J Dent Res.* 1955;50:125.
2. Jassem HA, Retief DH, Jamison HC. Tensile and shear strengths of bonded and rebounded orthodontic attachments. *Am J Orthod.* 1981;79:661–668.
3. Retief DH, Busscher HJ, de Boer P, Jangebloed WL, Arends J. A laboratory evaluation of three etching solutions. *Dent Mater.* 1986;2:202–206.
4. Rux W, Cooley RL, Hicks JL. Evaluation of a phosphonate BIS-GMA resin as a bracket adhesive. *Quintessence Int.* 1991;22:57–60.
5. Legler LR, Retief DH, Bradley EL. Effects of phosphoric acid concentration and etch duration on enamel depth of etch: an in vitro study. *Am J Orthod Dentofac Orthop.* 1990;98:154–160.
6. Gunadi G, Nakabayashi N. Preparation of an effective light-cured bonding agent for orthodontic application. *Dent Mater.* 1997;13:7–12.
7. Visuri SR, Gilbert JL, Wright DD, Wigdor HA, Walsh JT, Jr. Shear strength of composite bonded to Er:YAG laser-prepared dentin. *J Dent Res.* 1996;75:599–605.
8. Cozean C, Arcoria CJ, Pelagalli J, Powell GL. Dentistry for the 21st century? Erbium:YAG laser for teeth. *J Am Dent Assoc.* 1997;128:1080–1087.
9. Aoki A, Ishikawa I, Yamada T, Otsuki M, Watanabe H, Tagami J, Ando Y, Yamamoto H. Comparison between Er:YAG laser and conventional technique for root caries treatment in vitro. *J Dent Res.* 1998;77:1404–1414.
10. Martinez-Insua A, Dominguez LS, Rivera FG, Santana-Penin UA. Differences in bonding to acid-etched or Er:YAG-laser-treated enamel and dentin surfaces. *J Prosthet Dent.* 2000;84:280–288.
11. Apel C, Meister J, Schmitt N, Graber HG, Gutknecht N. Calcium solubility of dental enamel following sub-ablative Er:YAG and Er:YSGG laser irradiation in vitro. *Lasers Surg Med.* 2002;30:337–341.
12. Robertson CW, Williams D. Lambert absorption coefficients of water in the infrared. *J Opt Soc Am.* 1971;61:1316–1320.
13. Hale GM, Querry MR. Optical constants of water in the 200 nm to 200 μm region. *Applied Optics* 1973;12:555–563.
14. Zuerlein M, Fried D, Featherstone J, Seka W. Optical properties of dental enamel at 9–11 μm derived from time-resolved radiometry. *Special Topics IEEE J Quant Electr* 1999;5:1083–1089.
15. Usumez S, Orhan M, Usumez A. Laser etching of enamel for direct bonding with an Er, Cr:YSGG hydrokinetic laser system. *Am J Orthod Dentofacial Orthop.* 2002;122:649–656.
16. Otsuki M, Eguro T, Maeda T, Tanaka H. Comparison of the bond strength of composite resin to Er:YAG laser irradiated human enamel pre-treated with various methods in vitro. *Lasers Surg Med.* 2002;30:351–359.
17. Walsh LJ, Abood D, Brockhurst PJ. Bonding of resin composite to carbon dioxide laser modified human enamel. *Dent Mater.* 1994;10:162–166.
18. Corpas-Pastor L, Villalba Moreno J, de Dios Lopez-Gonzalez Garrido J, Pedraza Muriel V, Moore K, Elias A. Comparing the tensile strength of brackets adhered to laser etched enamel vs. acid-etched enamel. *J Am Dent Assoc.* 1997;128:732–737.
19. Ariyaratnam MT, Wilson MA, Mackie IC, Blinkhorn AS. A comparison of surface roughness and composite/enamel bond strength of human enamel following the application of the Nd:YAG laser and etching with phosphoric acid. *Dent Mater.* 1997;13:51–55.
20. Odutuga AA, Prout RES. Lipid analysis of human enamel and dentine. *Arch Oral Biol.* 1974;19:729–731.
21. Fowler BO, Moreno EC, Brown WE. Infrared spectra of hydroxyapatite, octacalcium phosphate and pyrolyzed octacalcium phosphate. *Arch Oral Biol.* 1966;11:477–492.
22. Corcia JT, Moody WE. Thermal analysis of human dental enamel. *J Dent Res.* 1974;53:571580.
23. Holcomb DW, Young RA. Thermal decomposition of human tooth enamel. *Calcif Tissue Int.* 1980;31:189–201.
24. Kuroda S, Fowler BO. Compositional, structural, and phase changes in in vitro laser-irradiated human tooth enamel. *Calcif Tissue Int.* 1984;36:361–369.
25. Sato K. Relation between acid dissolution and histological alteration of heated tooth enamel. *Caries Res.* 1983;17:490–495.
26. Fowler BO, Kuroda S. Changes in heated and in laser-irradiated human tooth enamel and their probable effects on solubility. *Calcif Tissue Int.* 1986;38:197–208.
27. Oho T, Morioka T. A possible mechanism of acquired acid resistance of human dental enamel by laser irradiation. *Caries Res.* 1990;24:86–92.
28. Featherstone JB, Barrett-Vespone NA, Fried D, Kantorowitz Z, Lofthouse J, Seka W. Rational choice of laser conditions for inhibition of caries progression. *SPIE.* 1995;2394:57–67.
29. Featherstone JB, Fried D, McCormack SM, Seka W. Effect of pulse duration and repetition on CO_2 laser inhibition of caries progression. *SPIE.* 1996;2672:79–87.
30. Hsu CY, Jordan TH, Dederich DN, Wefel JS. Effects of low-energy CO_2 laser interaction and the organic matrix on inhibition of enamel demineralization. *J Dent Res.* 2000;79:1725–1730.