An *ex vivo* investigation into the fluoride release and absorption profiles of three orthodontic adhesives

A. K. Coonar, S. P. Jones and G. J. Pearson*

Departments of Orthodontics and *Biomaterials Science, Eastman Dental Institute for Oral Health Care Sciences, University College London, UK

SUMMARY Prevention of peri-bracket decalcification is essentially mediated by effective oral hygiene, which is patient dependent. The potential to compensate for poor oral hygiene may be through the release of free fluoride ions from direct bonding agents. It is well established that glass ionomer cements (GICs) release free fluoride ions which may be replenished by exposure to fluoride containing solutions.

The aim of this *ex vivo* study was to compare the fluoride release and absorption profiles of a recently developed low fusion, monophase GIC, Limerick glass, with two materials in common clinical use, namely, Fuji-Ortho™ L.C. and Concise™. Ten test specimens of each material were fabricated and stored in deionized water at 37°C. The concentration of fluoride release was measured daily for the first 7 days after immersion and then weekly for 5 weeks. On day 42 the test specimens were recharged in 2 per cent sodium fluoride solution and fluoride release was measured initially after 24 hours and then every 48 hours. The recharge regimen was repeated for 3 weeks.

Both Limerick glass and Fuji-Ortho™ L.C. demonstrated the characteristic fluoride release pattern of GIC with a rapid elution of fluoride after the first 24 hours followed by a more gradual release profile over the following 2 weeks. Fuji-Ortho™ L.C. released the greatest quantity of fluoride but the release profile of Limerick glass was more sustained. Concise™ released negligible amounts of fluoride. Limerick glass and Fuji-Ortho™ L.C. showed an increase ($P < 0.01$) in fluoride release following exposure to 2 per cent sodium fluoride that decreased both with time and subsequent exposures to fluoride supplement.

Introduction

It is well established that the presence of fixed appliances reduces the efficacy of mechanical oral hygiene, increasing the incidence of demineralization of tooth surfaces that normally show a low prevalence of dental caries, such as the facial surfaces of both anterior and posterior teeth (Zachrisson and Zachrisson, 1971; Gorelick *et al*., 1982). Loss of calcified surface tooth mass results in clinically detectable white spots which are most pronounced at the gingival aspect of the teeth where a greater accumulation of plaque occurs (Gwinnett and Ceen, 1979).

Protective measures such as oral hygiene instruction, mechanical removal of plaque, and the application of topical fluoride agents are dependent upon patient co-operation and have proven to be of limited clinical significance in the reduction of decalcification (Kajander *et al.*, 1987; Mitchell, 1992). However, low doses of free fluoride sustained long-term are of great benefit in increasing the fluoroapatite concentration of enamel by promoting the re-growth of depleted crystals (Arends and Christoffersen, 1990).

At present, the most commonly used direct bonding agent is composite resin. Its popularity is based on bond strength and the technical ease

of application, but enamel decalcification in the peri-bracket area is a significant problem (Mitchell, 1992). Other disadvantages include enamel loss due to acid-etching and micro-fractures on debond. Attempts have been made to incorporate leachable fluoride into composite resins, but so far laboratory studies have shown that the quantity and duration of release is poor (Fox, 1990; Ghani *et al.*, 1994; Chadwick and Gordon, 1995).

The potential advantages of a method of delivering fluoride to the site most susceptible to demineralization which is independent of patient compliance has led to interest in orthodontic bonding materials which are capable of fluoride release. Glass ionomer cements (GICs) have been shown to be effective both *in vitro* and *in vivo* for fluoride release and reducing demineralization (O'Reilly and Featherstone, 1987; Valk and Davidson, 1987; Marcusson *et al.*, 1997), but have a weaker bond strength than composite resins.

The development of resin-modified glass ionomer cements (RMGICs) has heralded the potential to overcome this problem. Komori and Ishikawa (1997) found that the bond strength of RMGICs, in response to shear and tensile forces, was almost double that of conventional GICs and four times the minimum bond strength (8.5 MPa) suggested for successful orthodontic treatment (Maijer and Smith, 1981). Furthermore, the fluoride release capability of RMGICs has been shown to be comparable with conventional GICs in the long-term (McCabe, 1998).

GICs and their derivatives (RMGICs) are capable of absorbing fluoride from the local environment and subsequently releasing it at a greater concentration (Creanor *et al.*, 1995; Diaz-Arnold *et al.*, 1995) which highlights the potential of periodic fluoride application to boost peri-bracket protection in the clinical situation.

This investigation aimed to compare the fluoride release and re-absorption profiles of a recently developed monophase GIC, Limerick glass, with those of two bonding agents currently in clinical use, Fuji-Ortho™ L.C. and Concise™.

Materials and methods

Adhesives and mixing techniques

The bonding agents used in this study were:

(1) Concise™ (3M Dental Products, St Paul, MN, USA), a chemically activated composite resin. Polymerization occurs on manually mixing equal proportions of the two paste system.
(2) Fuji-Ortho™ L.C. (GC Corporation, Tokyo, Japan), a resin modified GIC. The setting reaction features both light activated polymerization corresponding to the resin component, and an acid–base chemical reaction by which the glass ionomer component sets. This cement was manually mixed with one level scoop of powder and two drops of liquid. The powder/liquid ratio was 3:1 by mass.
(3) Limerick glass (University of Limerick, Ireland), a conventional monophase GIC. The setting reaction is chemical (an acid–base reaction) and the cement is hand mixed. The powder/liquid ratio was 3.5:1.

Specimen preparation

Ten samples of each material were fabricated using split brass rings of 10 mm diameter and 1 mm height, placed in a dry incubator at 37ºC for 1 hour and weighed immediately before immersion in 20 ml deionized water. The specimens were then replaced in the incubator. All the specimens were fabricated by one operator (A.K.C.) during one session to maximize consistency.

Experimental procedure

The concentration of fluoride ions released by the test cements was measured by a differential electrode cell. A fluoride ion electrode and combination pH electrode were connected to an Orion Research Microprocessor Ionalyser/901 (Orion Research Inc., Cambridge, MA, USA). The analyser was calibrated against standard solutions of 1 and 10 parts per million (p.p.m.)

fluoride. Each test sample consisted of 0.5 ml storage solution combined with 1.5 ml 0.1 M hydrochloric acid, which acted as a decomplexing agent. The solution was contained in a small well in a block of poly(tetrafluoroethylene). Throughout measurement, the solution was agitated using a magnetic stirring rod. Fluoride concentration (p.p.m.) was recorded after 2 minutes. Following each reading, the specimen was carefully removed from the container using plastic tweezers, and rinsed with 10 ml of deionized water. It was then placed in a fresh container of 20 ml deionized water, and returned to the incubator. The Ionalyser was re-calibrated every 2 hours to account for fluctuations in temperature and humidity.

The concentration of fluoride released was measured daily for the first 7 days, and thereafter on a weekly basis for 5 weeks. On day 42, the specimen disc was immersed in 5 ml of 2 per cent sodium fluoride solution for 10 minutes. It was then rinsed twice with deionized water, placed in a fresh container of 20 ml storage solution and returned to the incubator. Fluoride ion release was initially measured after 24 hours and subsequently every 48 hours. This regimen was continued for three consecutive weeks. On day 63 the discs were removed from solution, air-dried and weighed.

Statistical analysis

Statistical analysis was carried out using SPSS version 7.5 for Windows 95.

The mean values of the 10 samples of each material were calculated and found to be normally distributed, for both the release and absorption studies. The sample population was small and as the variance of the means was different for each material, the relationship between the materials was investigated using a non-parametric testing system, the Mann–Whitney U-test, to compare the two independent samples.

The null hypothesis was that there is no difference in fluoride release between the three cements. A P value of less than 0.01 was established as indicative of a highly significant difference.

Results

Fluoride release study: day 0–42

The cumulative release of fluoride from the three cements is shown in Figure 1, which also indicates the kinetics of the release process. Both Limerick glass and Fuji-Ortho™ L.C. demonstrated the fluoride release profile typical of a GIC, with a profound release
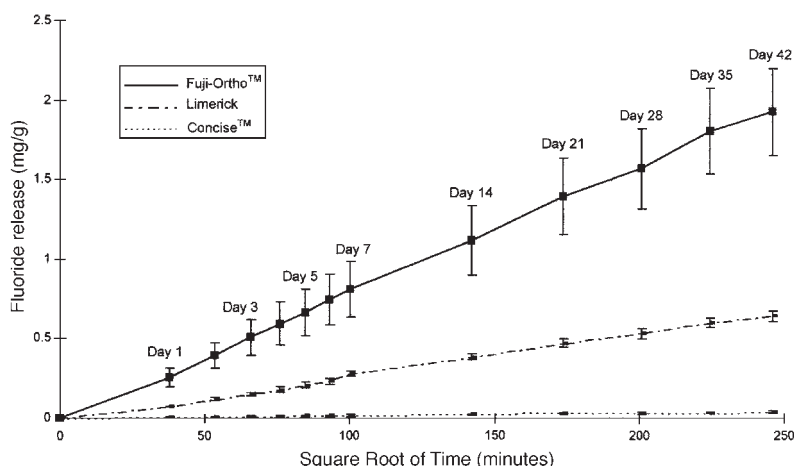

Figure 1 Mean cumulative fluoride release (mgF/g cement) and standard deviation over 42 days.

during the first 7 days, followed by a more gradual release profile declining to a low level plateau phase.

Maximal release occurred within the first 24 hours. The range for Limerick glass was 0.05–0.09 mgF/g. The range for Fuji-Ortho™ L.C. was 0.19–0.36 mgF/g, which was significantly higher. The concentration of fluoride on the second day fell sharply for Fuji-Ortho™ L.C. to a range of 0.08–0.17 mgF/g, and by day 7 the concentration had virtually plateaued. The release profile of Limerick glass also decreased on day 2, but the decrease was less dramatic, giving a range of 0.04–0.05 mgF/g. The level of release decreased only slightly until day 6, and then showed a rise in release on day 7. Days 15–28 showed a steady decrease in the fluoride release rate. An unexpected increase in both materials was noted at day 35, followed by a return to declining values. The release profile of Concise™ was negligible, recording values approximating 0 p.p.m. throughout the test period.

Figures 2 and 3 show the consistency of fluoride release amongst the individual samples of Limerick glass and Fuji-Ortho™ L.C. The parallel observations, particularly in the case of Limerick glass, are evident not only during the rapid elution phase, but also during the prolonged equilibration period. The release profile of Limerick glass was more sustained than that of Fuji-Ortho™ L.C. which may prove to be an asset in the clinical context.
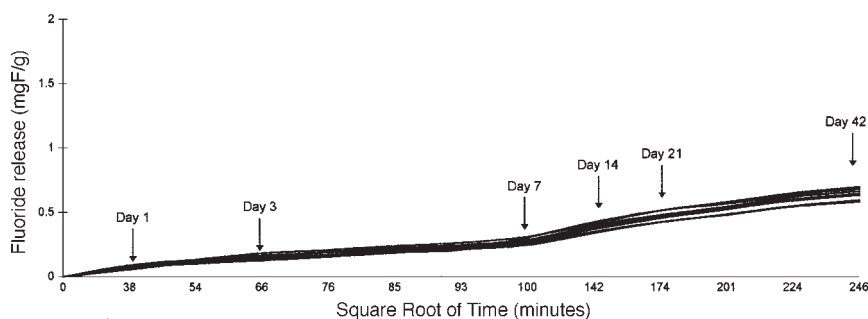

Figure 2   Cumulative fluoride release profile of each sample of Fuji-Ortho™ L.C.
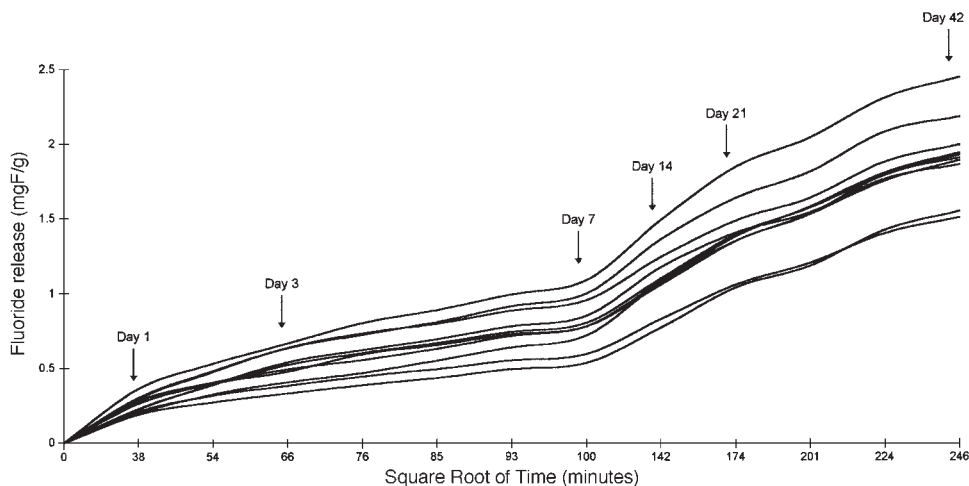

Figure 3   Cumulative fluoride release profile of each sample of Limerick glass.

Statistical analysis of the release study

The results of the Mann–Whitney *U*-test confirmed the visual differences in fluoride release depicted in Figure 1. Over the 42 day test period, the difference in the fluoride release pattern of Limerick glass compared with that of Fuji-Ortho™ L.C. was significantly different, and both the test materials showed a significant difference in fluoride release compared with Concise™ ($P < 0.01$).

Absorption and release study

Figure 4 shows the mean cumulative fluoride release following the weekly recharge regimen. During week 1, the fluoride released by Limerick glass increased from 0.0443 to 1.468 mgF/g; and that of Fuji-Ortho™ L.C from 0.12 to 1.7 mgF/g. The fluoride level released by Concise™ increased from 0.003 to 0.03 mgF/g.

By week 3, the fluoride released by Limerick glass had fallen to 0.18 mgF/g but at this level was still more than four times higher than the pre-immersion value of 0.0443 mgF/g. Fuji-Ortho™ L.C. by this stage was releasing fluoride at a mean value of 0.23 mgF/g which, although a declining value, was still almost double the pre-immersion value of 0.12 mgF/g. The mean

fluoride released by Concise™ returned to a near pre-immersion value of 0.004 mgF/g.

Statistical analysis of absorption and release study

Day 43–49: comparison of Limerick glass and Fuji-Ortho™ L.C. indicated no significant difference between the mean values ($P = 0.7$). As expected the test materials demonstrated a significant difference in fluoride release characteristics from Concise™ ($P < 0.01$).

Day 50–56: the fluoride release profiles of the three materials were significantly different from each other ($P < 0.01$).

Day 57–63: the differences in fluoride release profiles of the three test materials remained highly significant ($P < 0.01$).

Discussion

This was a comparative study to assess any differences between the three materials *ex vivo*. The use of standardized cylinders of material permitted comparison of fluoride release expressed as fluoride release per gram of cement (mgF/g). Whilst a valid method, this could be criticized
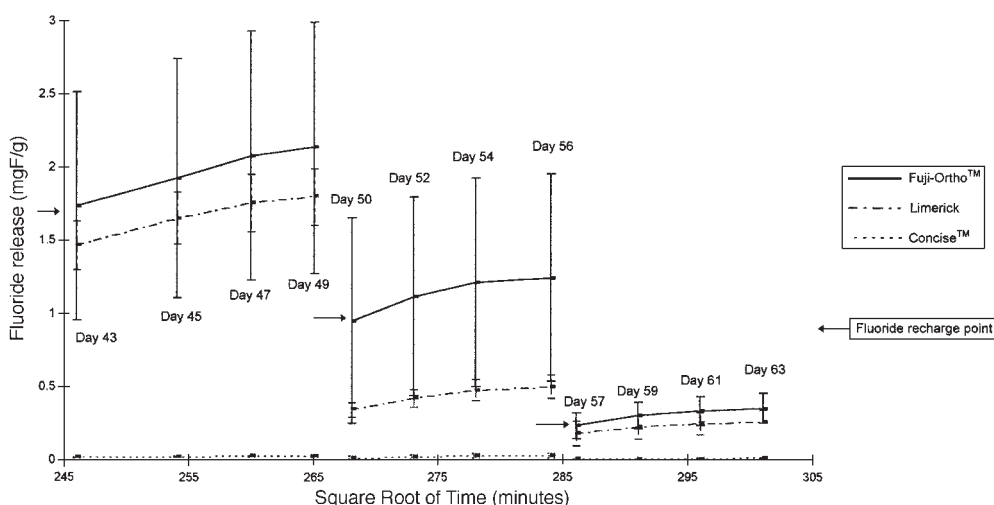

Figure 4 Mean cumulative release (mgF/g) and standard deviation for weekly recharge with 2 per cent sodium fluoride.

on the grounds of the increased surface area of material exposed to the environment compared with the *in vivo* situation of a cemented bracket. Hence, although the comparative behaviour of these materials is useful as an indicator of potential fluoride elution *in vivo*, the fluoride elution data cannot be directly extrapolated to the clinical situation.

In this study, Fuji-Ortho™ L.C. released four times the concentration of fluoride compared with Limerick glass over the first seven days of the experimental period. Factors affecting the concentration of fluoride release include:

(1) temperature
(2) timing of immersion into aqueous media
(3) pH of immersion media
(4) mixing time
(5) composition of the aluminosilicate glass and polyalkenoic acid used in the formulation.

The first four extrinsic variables were constant for both cements during disc fabrication. The difference in the fluoride concentration released was therefore a reflection of variations in formulation between the test cements. Resin-modified GICs have been found to release a lower fluoride ion concentration than non-hybrid cements of comparable formulation.

The pattern of fluoride release of both test cements was in keeping with that considered to be the classic profile of release demonstrated by other authors (Cranfield *et al.*, 1982; Wilson *et al.*, 1985). This early release of free fluoride ions has been attributed to the acid–base setting reaction between the fluoride containing aluminosilicate glass powder base and the polyacid liquid which results in the liberation of fluoride. Figure 1 graphically represents the mean cumulative fluoride release pattern over 42 days. Fluoride release commenced with an initial short-term rapid elution which stabilized after approximately 7 days. Maximum levels have been found to occur during the first 24 hours followed by plateau elution, characterized by long-term release of low levels of fluoride which follows $t^{1/2}$ dependence (Tay and Braden, 1988). The initial profound release is thought to relate to surface wash-off as the material sets

and the majority of the glass species react with the polyacid. The plateau phase corresponds to diffusion of fluoride ions through pores and cracks. Diffusion through the bulk of the material represents a long-term continuing reaction (Swartz *et al.*, 1984), which was beyond the time frame of this study.

The elution of free fluoride ions from GIC has been extensively investigated (Forsten, 1990; Hörsted-Bindslev and Larsen, 1990; De Schepper *et al.*, 1991), in order to establish reproducible evidence demonstrating a reduction in decalcification. However, a large variation exists amongst reported release profiles for a given glass ionomer, reflecting the complex nature of the elution process for which a physico-chemical model is yet to be fully established.

The overall finding that fluoride release increased following exposure to fluoride solution and the capacity to absorb and release fluoride decreased with time (Figure 4) is comparable with the findings of several other authors (Cook and Youngson, 1988; Hatibovic-Kofman *et al.*, 1997; McCabe, 1998). Detectable fluoride release by the Concise™ control material may have been due to diffusion into pores and cracks within the material, followed by subsequent release. As composite resins are the most commonly used direct bonding agent, the ability to take up and release low levels of fluoride after a 6 week maturation period indicates the possible benefit of topical fluoride application at this stage.

The precise mechanism of fluoride uptake by GICs is speculative (Damen *et al.*, 1996). Part of the water present in the cement can be evaporated and therefore has been defined as loosely bound (Wilson and McLean, 1988). The remaining water is associated with the matrix–cation complex and is tightly bound. The loosely bound water and solutes in the porosities of the cements are exchanged with the external aqueous medium by passive diffusion and fluoride uptake, and release is thought to be by this mechanism.

The concentration of fluoride released from re-fluoridated specimens was lower than that from the freshly mixed material. Therefore, exposure to fluoride solutions cannot restore the

initial fluoride release rate, but the amount absorbed and subsequently released was significant. Given that the immersion medium was deionized water i.e. fluoride free, this reduction reflects either a reduced capacity to absorb fluoride with time due to dissolution of the material with age, or concomitant binding of fluoride to matrix ions which could be released later. The environmental dependence of fluoride uptake and release potential demonstrated in this study might possibly be further exaggerated in the more hostile intra-oral environment where oral flora, temperature extremes, pH variation and mechanical stresses come into play. This is of potential importance in relation to long-term operator control of protection against demineralization.

In order to simulate *in vivo* conditions, fluoride release has also been measured following immersion in saliva. Rezk-Lega *et al.* (1991a,b) pre-incubated GIC in whole unstimulated saliva, and reported a markedly reduced fluoride release profile into water. This was later confirmed by the findings of Damen *et al.* (1996). Salivary proteins are known to form a thin film on enamel, the acquired pellicle (Baier and Glantz, 1978), but no data is available on salivary coatings on GICs. Indirect evidence from the studies of Rezk-Lega *et al.* (1991a,b) and Damen *et al.* (1996) have indicated that fluoride uptake and subsequent release from GICs would be reduced in the oral cavity, compared with the release profile into de-ionized water. One can extrapolate from the results of this study that less free fluoride might be liberated by the test cements *in vivo*.

GIC is in ubiquitous use for the placement of orthodontic bands, and is clinically proven to be associated with less decalcification than zinc phosphate (Mizrahi, 1988). At present, Limerick glass is not in clinical use and is currently undergoing investigation of its various properties. A crucial feature of its fluoride release pattern is that the concentration of fluoride released is more sustained after the initial rapid elution phase compared with Fuji-Ortho™ L.C. Therefore, Limerick glass could potentially offer clinical benefits such as optimum fluoride release capability, recharge capacity and favourable bond strength if it were developed into a resin-modified form.

Conclusions

This *ex vivo* study compared the fluoride release behaviour of a GIC (Limerick glass) and a resin-modified GIC (Fuji-Ortho™ L.C.) with a control of composite resin (Concise™). Both of the test materials exhibited the classic fluoride release curve of GICs with the Limerick glass showing a more sustained release over time. Both materials demonstrated an increase in fluoride release after re-charging with 2 per cent sodium fluoride but this re-charging potential appeared to diminish over time and with repeated exposure to fluoride supplement. This effect may influence the potential for fluoride release intra-orally and further studies are required to investigate this.

Address for correspondence

Mr S. P. Jones
Department of Orthodontics
Eastman Dental Institute for Oral Health Care Sciences
University College London
256 Gray's Inn Road
London WC1X 8LD
UK

References

Arends J, Christoffersen J 1990 Nature and role of loosely bound fluoride in dental caries. Journal of Dental Research 69 (Special Issue): 601–605

Baier R E, Glantz P O 1978 Characterization of oral and *in-vivo* films on different types of solid surfaces. Acta Odontologica Scandanavica 36: 289–301

Chadwick S M, Gordon P H 1995 An investigation into the fluoride release of a variety of orthodontic bonding agents. British Journal of Orthodontics 22: 29–33

Cook P A, Youngson C C 1988 An *in-vitro* study of a glass ionomer cement in the direct bonding of orthodontic brackets. British Journal of Orthodontics 15: 247–253

Cranfield M, Kuhn A T, Winter G B 1982 Factors relating to the rate of fluoride ion release from glass ionomer cement. Journal of Dentistry 10: 333–341

Creanor S L, Saunders W P, Carruthers L M C, Strang R, Foye R H 1995 Effect of extrinsic fluoride concentration on the uptake and release of fluoride from two glass ionomer cements. Caries Research 29: 424–426

Damen J J M, Bujs M J, Ten Cate J M 1996 Uptake and release of fluoride by saliva-coated glass ionomer cement. Caries Research 30: 454–457

De Schepper E J, Berry E A, Citleau J G, Tate W H 1991 A comparative study of fluoride release from glass ionomer cements. Quintessence International 22: 215–220

Diaz-Arnold A M, Holmes D C, Wistrom D W, Swift E J 1995 Short-term fluoride release/uptake of glass ionomer restoratives. Dental Materials 11: 96–101

Forsten L 1990 Short and long-term release from glass ionomers and other fluoride containing filling materials *in vitro*. Scandinavian Journal of Dental Research 98: 179–185

Fox N A 1990 Fluoride release from orthodontic bonding agents. An *in-vitro* study. British Dental Journal 17: 293–298

Ghani S H A, Creanor S L, Luffingham J K, Foye R H 1994 An *ex-vivo* investigation into the release of fluoride from fluoride containing orthodontic bonding composites. British Journal of Orthodontics 21: 239–243

Gorelick L, Geiger A M, Gwinnett A J 1982 Incidence of white spot formation after bonding and banding. American Journal of Orthodontics 81: 83–98

Gwinnett A J, Ceen R F 1979 Plaque distribution on bonded brackets: a scanning microscopic study. American Journal of Orthodontics 75: 667–677

Hatibovic-Kofman S, Koch G, Ekstrand J 1997 Remineralization of actual carious lesions with a glass ionomer cement. Swedish Dental Journal 21: 11–17

Hörsted-Bindslev P, Larsen M J 1990 Release of fluoride from conventional and metal-reinforced glass ionomer cements. Scandinavian Journal of Dental Research 98: 451–455

Kajander K C, Uhland R, Ophang R H, Sather A H 1987 Topical fluoride in orthodontic bonding. Angle Orthodontist 57: 70–76

Komori A, Ishikawa H 1997 Evaluation of a resin-reinforced glass-ionomer cement for use as an orthodontic bonding agent. Angle Orthodontist 67: 189–196

Maijer R, Smith D C 1981 Variables influencing the bond strength of metal orthodontic bracket bases. American Journal of Orthodontics 79: 20–24

Marcusson A, Norevall L-I, Persson S 1997 White spot reduction when using glass ionomer cement: a longitudinal and comparative study. European Journal of Orthodontics 19: 233–242

McCabe J F 1998 Resin-modified glass ionomers. Biomaterials 19: 521–527

Mitchell L 1992 Decalcification during orthodontic treatment with fixed appliances—an overview. British Journal of Orthodontics 19: 199–205

Mizrahi E 1988 Glass ionomer cements in orthodontics—an update. American Journal of Orthodontics and Dentofacial Orthopedics 94: 505–507

O'Reilly M M, Featherstone J D B 1987 Demineralization and remineralization around orthodontic appliances: an *in-vivo* study. American Journal of Orthodontics and Dentofacial Orthopedics 92: 33–40

Rezk-Lega F, Øgaard B, Arends J 1991a An *in-vivo* study on the merits of two glass ionomers for the cementation of orthodontic bands. American Journal of Orthodontics and Dentofacial Orthopedics 99: 162–167

Rezk-Lega F, Øgaard B, Rølla G 1991b Availability of fluoride from glass ionomer luting cements in human saliva. Scandanavian Journal of Dental Research 99: 60–63

Swartz M I, Phillips R W, Clark H E 1984 Long-term fluoride release from glass ionomer cements. Journal of Dental Research 63: 158–160

Tay W M, Braden M 1988 Fluoride ion diffusion from polyalkenoate (glass ionomer) cements. Biomaterials 9: 454–456

Valk J W P, Davidson C L 1987 The relevance of controlled fluoride release with bonded orthodontic appliances. Journal of Dentistry 15: 257–260

Wilson A D, Groffman D M, Kuhn A T 1985 The release of fluoride and other chemical species from a glass ionomer cement. Biomaterials 6: 431–433

Wilson A D, McLean J W 1988 Glass ionomer cement. Quintessence Publishing Co., Chicago.

Zachrisson B U, Zachrisson S 1971 Caries incidence and oral hygiene during orthodontic treatment. Scandanavian Journal of Dental Research 79: 394–401