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Aluminium and fluoride release into artificial saliva from dental restoratives placed in teeth

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Abstract This study examined the release of aluminium and fluoride from restorative materials placed in either deciduous or young permanent immature teeth stored in artificial saliva for 1 month. Cavities were prepared in extracted teeth, then filled with a fluoride releasing restorative (glass-ionomer, compomer or composite resin), with and without conditioning as appropriate. The teeth were then stored in artificial saliva for 1 month, after which the amount of aluminium and fluoride released was determined spectrophotometrically. With all materials tested, both aluminium and fluoride were released in all cases. Young immature teeth were associated with lower level of ion release which was attributed to the absorption of ions by the enamel. However, unconditioned samples were usually associated with similar ion release to conditioned ones, suggesting that the loss of mineral phase on conditioning has only a marginal effect on the capacity for ion uptake. The ratio of aluminium to fluoride released varied with the type of tooth, deciduous conditioned teeth generally absorbing proportionately less aluminium than young immature teeth. The overall conclusion is that interaction with ions released by restorative materials is influenced by type of tooth.

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1 Introduction

Fluoride-releasing restorative materials are widely used in dentistry [1]. The most important of these are the glass-ionomer cements and their derivatives, i.e. the resin modified glass-ionomers and compomers. Fluoride-releasing composite resins are also available [2].

These materials contribute to caries reduction by two basic mechanisms, one physicochemical, the other biological. From the physicochemical point of view, low concentrations of fluoride in saliva reduce the ability of the saliva to dissolve the mineral phase of the tooth, thus shifting the demineralization/remineralization equilibrium towards remineralization. Fluoride also replaces a small fraction of hydroxyl groups in the upper layers of the hydroxypatite crystals, thus reducing the acid-solubility of the mineral phase [1–3].

Fluoride ions may also have a biological effect. At high doses they alter the ability of microflora in the plaque to metabolise carbohydrates by inhibiting the magnesium-containing enzymes that catalyse the process. This leads *inter alia* to decreased acid production. High fluoride concentrations may also eliminate sensitive bacteria and thus change the overall acid tolerance of populations. This has been shown in *Streptococcus mutans*, and this has the potential to lead to a lower pathogenicity of the plaque micro-flora in vivo [4].

Glass ionomer cements are one of the most effective fluoride-releasing dental restorative materials [5], and are known to be capable of releasing fluoride for several years. In addition to fluoride, glass-ionomers release other ions [6, 7], namely aluminium, calcium, sodium and silicon [8, 9]. Most studies have examined the release of fluoride only from glass-ionomer cements [10–15], and neglected the fact that aluminium ions (Al^{3+}) can form stable complexes with fluoride ions. There are several possible aluminium fluoride complexes with different F/Al atomic ratio that may occur, i.e. AlF_6^{3-}, AlF_3, AlF_2^{+} and AlF^{2+}. This means that the presence of one aluminium ion can eliminate up to six free fluoride ions from solution, though the significance of this in vivo is not clear [16]. The highest amounts of aluminium are released during the first day after setting [15]. During the maturation of the glass ionomer cement, the release of aluminium decreases because the aluminium ions close to the surface are washed out of the cement, and the rest of them are trapped deep within the matrix [16].

Other restorative materials are also capable of releasing fluoride. These include polyacid-modified composite resins (“compomers”), which share some of the chemistry of glass ionomers [11–13], and also conventional composite resins. The latter can be modified by inclusion of fluoride compounds, and thus become capable of releasing clinically useful amounts of fluoride [10]. These materials have been considered in the present study.

It is not only the presence of fluoride that influences the progression of caries within a tooth. Other factors include the chemical composition of the enamel and dentin, morphological and structural differences between the deciduous and the permanent teeth and the fact that the thickness of primary hard tissues is lower than the permanent one [17, 18]. In fact, there are substantial microstructural differences between permanent and primary teeth including, significantly, that the latter have a lower degree of mineralization [19].

Young immature permanent teeth have their own differences compared to the permanent teeth, with complete apex closure. In particular, they have voluminous pulp chambers, with high pulpal horns. The dentine channels are extremely wide, with a thin layer of peritubular dentine and without any intratubular dentine. When the teeth appear in the mouth, the enamel acts as a semi-permeable membrane and the teeth become susceptible to caries. Also, the immature enamel and dentine can permit the transport of certain molecules towards the pulp [17, 18].

In the current study, the aim was two-fold: First, to study how the release of aluminium and fluoride varied between various restoratives placed in different types of tooth, and second to determine how the type of tooth influenced the overall pattern of ion release. Conditions were designed to simulate as closely as possible those that exist in a patient’s mouth, and used artificial saliva as the storage medium throughout.

2 Materials and methods

A total of 80 teeth, 40 deciduous and 40 permanent were used in this investigation. Indication for extraction was the exfoliation of the deciduous teeth and orthodontic reasons for the young permanent teeth. After the extraction, the surfaces of the teeth were cleaned, the radices cut with a diamond bur with water cooling to the level of the cemento-enamel junction, and the remnants of the pulpal tissue were discarded. Class V cavities were prepared on every tooth using diamond bur and turbine with water cooling, according to conventional dental techniques. Cavities were of dimensions 2.5 × 1.5 mm.

After the preparation, the teeth were divided into four groups at random, and filled with one of four different materials, given in Table 1. After cure, excess material was removed using appropriate hand instruments. The light-cured materials were polished immediately, whereas the conventional glass-ionomers were protected with varnish, placed in artificial saliva, then polished after 24 h. Each of the groups, consisting of 10 deciduous and 10 young permanent teeth, was divided in two subgroups; the first was conditioned, and the other one left unconditioned. The group filled with the composites (5 deciduous and 5 young permanent immature teeth), were all conditioned. No unconditioned teeth were prepared, because this is not done in clinical practice, and therefore any findings would lack clinical relevance. The conditioning and the filling was performed according to the manufacturers’ instruction, as listed in Table 1.

The teeth were stored at room temperature in British Standard artificial saliva [20], the composition of which is given in Table 2. After a time interval of 1 month, the artificial saliva solutions were analysed for aluminium and fluoride concentrations.

Aluminium was determined directly by flame atomic absorption spectrophotometry, and the procedure involved initially preparing a calibration curve. For this, a series of standards in the range of 0.00–5.00 mg/l were prepared by dissolution of the standard compound ($AlCl_3$) in water.

Table 1 Materials used

Material	Type	Manufacturer	Conditioning option
Fuji IX	Conventional GIC	GC, Japan	Cavity conditioner (GC, Japan)
Fuji II LC	Resin-modified GIC	GC, Japan	Cavity conditioner (GC, Japan)
Dyract AP	Polyacid-modified composite resin	Dentsply De Trey, Germany	H_3PO_4 (37%) then Prime& Bond NT (Dentsply, Germany)
Unifil flow	Fluoride-releasing composite resin	GC, Japan	Unifil Bond (GC, Japan)

Table 2 Components of the artificial saliva [20]

Component	Concentration (g l^{-1})
NaCl	0.50
$NaHCO_3$	4.20
$NaNO_3$	0.03
KCl	0.20

Subsequently, 1.0 ml NaCl in 10 ml standard solution was added, the absorbance measured and calibration curve constructed. Determination was then a carried out as follows: In 100 ml from the sample, 0.5 ml HNO_3 and 5.0 ml HCl were added, heated to reduce the volume to 10 ml without boiling. After cooling 1.0 ml NaCl was added and the absorbance and concentrations measured. The amount of aluminium was then calculated according to the equation: Al mg/l = 100a, where a = concentration of aluminium in 10 ml on the calibration curve.

Fluoride in artificial saliva was determined by spectrophotometry after isolation of the fluorides with distillation. These techniques are based on observation of colour change by chemical reaction between fluoride ion and an indicator (in this case SPADNS). The procedure required initial creation of a calibration curve. This used a series of standards with concentrations from 0.00 to 1.40 mg/l prepared with a dilution of 50 ml using standard potassium fluoride solution (1 ml = 0.01 mg F^-). Determination involved distillation, as follows: 400 ml water was put in a flask for distillation and 200 ml of concentrated sulphuric acid was added, this solution was boiled to 180°C and afterwards cooled to 100°C. The specimen was diluted in distilled water and 300 ml of this solution was added to the distillate. The solution was boiled to 180°C again. Finally, 50 ml of the distillate were put into Nessler pipe and mixed with 10 ml of SPADNS (with addition of acidic cyrconil), after which the absorbance was determined. If the concentration of aluminium was above 3 mg/l, then the reading of the results was delayed for 3 h, as has been suggested previously [21]. This is because of possible interaction of fluoride with aluminium in solution, an effect that diminishes with time, and allows true fluoride levels to be determined. The fluoride level was calculated by substituting into the following equation:

$$\text{Fluoride mg/l} = 50A/V,$$

where A = amount of fluoride (mg) measured by spectrophotometry, V = volume of the specimen (ml).

3 Results

Table 3 shows the results for the aluminium and fluoride release from each restorative material. Statistically significant differences ($p < 0.05$) were found between the deciduous and the young permanent immature teeth for both ions, with the disparity being especially large for aluminium release. Differences between the conditioned and unconditioned samples were generally not significant, except for Dyract AP, where there was a significant difference in aluminium release between the conditioned and the unconditioned teeth.

The aluminium/fluoride release ratio (Table 4) was highest in the glass ionomer cements, and lowest with the composite resin. However, for each material, this ratio was highest for the deciduous teeth and decreased for the young immature permanent teeth. Notable observations were the high levels of aluminium release from Fuji IX and Fuji II LC when placed in deciduous teeth. Fluoride did not demonstrate such large differences as aluminium in release levels between the tested groups, though results were nonetheless significant (to $p < 0.05$).

4 Discussion

Previous studies have shown that fluoride release is different in glass ionomer cements and other restorative materials. In glass ionomers, there is a large initial burst of fluoride release for the first day or say, after which there is a much smaller but steady release that can last for several years [22, 23]. The initial burst is assumed to occur from the surface, whereas the second one is a steady diffusion-based process that involves fluoride from deeper within the cement. It is the latter that is released continuously into the surrounding medium, and continues for long periods of time [12].

Composite resins and compomers are also capable of releasing fluoride, but with a different mechanism, which does involve the initial burst of high levels of fluoride. The steady state rate of release is generally found to be lower than from glass ionomers [24, 25]. Our results confirm this release for up to 1 month. Compomers have to absorb water to initiate the acid-base reaction which will enable steady fluoride release from their matrix. Their short-term release is a result of release of additional fluoride, in the form of a fluoride compound such as ytterbium fluoride [26].

The composite resins do not have the acid-base reaction, so the only source of fluoride is from a fluoride compound, which may or may not be incorporated into the filler. Movement of such fluoride ions through a predominantly organic matrix is a slow diffusive process [27], though some short-term elution is able occur because some of the fluoride is located close to the surface. Unifil Flow is formulated from fluoroaluminosilicate glass, and this has been shown to provide an acceptable level of fluoride release.

For glass ionomers, fluoride release is accompanies by release of other ions, which may include aluminium. It has

Table 3 Release of aluminium and fluoride from restorative/tooth combination (standard deviations in parentheses)

	Element	Tooth type	Element levels in solution/ppm
Fuji IX	Aluminium	Deciduous	22.96^{a} (2.62)
		Deciduous (conditioned)	26.30^{a} (1.68)
		Young permanent	12.06^{b} (1.69)
		Young permanent (conditioned)	10.60^{b} (1.76)
	Fluoride	Deciduous	8.57^{d} (0.15)
		Deciduous (conditioned)	9.58^{b} (0.17)
		Young permanent	11.08^{b} (1.16)
		Young permanent (conditioned)	10.99^{b} (0.87)
Fuji II LC	Aluminium	Deciduous	20.14^{a} (1.96)
		Deciduous (conditioned)	19.50^{a} (2.73)
		Young permanent	11.04^{b} (0.99)
		Young permanent (conditioned)	10.88^{b} (1.41)
	Fluoride	Deciduous	9.95^{c} (0.69)
		Deciduous (conditioned)	9.43^{c} (0.32)
		Young permanent	11.58^{b} (1.16)
		Young permanent (conditioned)	10.83^{b} (0.81)
Dyract AP	Aluminium	Deciduous	13.58^{b} (2.25)
		Deciduous (conditioned)	16.80^{d} (0.91)
		Young permanent	15.18^{d} (1.81)
		Young permanent (conditioned)	14.78^{d} (1.43)
	Fluoride	Deciduous	10.22^{b} (0.80)
		Deciduous (conditioned)	11.28^{b} (1.14)
		Young permanent	13.13^{e} (0.78)
		Young permanent (conditioned)	13.36^{e} (0.69)
Unifil Flow	Aluminium	Deciduous	11.00^{b} (2.23)
		Young permanent	11.46^{b} (2.33)
	Fluoride	Deciduous	5.16^{f} (0.34)
		Young permanent	10.48^{b} (0.53)

Superscripts indicate groups which do not differ significantly

Table 4 Ratio of aluminium to fluoride from different materials

Material	Tooth type	Al:F ratio (by mass)
Fuji IX	Deciduous	2.68
	Deciduous (conditioned)	2.75
	Young permanent	1.09
	Young permanent (conditioned)	0.96
Fuji II LC	Deciduous	2.02
	Deciduous (conditioned)	2.07
	Young permanent	0.95
	Young permanent (conditioned)	1.00
Dyract AP	Deciduous	1.33
	Deciduous (conditioned)	1.49
	Young permanent	1.16
	Young permanent (conditioned)	1.11
Unifil Flow	Deciduous	2.13
	Young permanent	1.09

been suggested that this aluminium forms complexes with the fluoride resulting in reduced levels of the free fluoride. Whether or not these complexes interfere with the anti-cariogenic effect of fluoride at the tooth surface is not clear [28, 29]. Our results show that lower levels of aluminium occurred in the artificial saliva where young immature teeth were stored, which suggests that the hard dental tissues of the young immature permanent teeth have a higher affinity for aluminium than deciduous teeth. This is probably because of the fact that the incompletely matured teeth are porous, the enamel prisms are not so compact and the interprismatic spaces are wider than in matured teeth. So, this might be a factor which promotes the transport of certain substances into the enamel. It is not clear, though, why there is higher absorption of aluminium than fluoride.

For all materials except the release of aluminium from Dyract AP, ion release into artificial saliva was not significantly different between conditioned and unconditioned teeth. These teeth would have some differences, since they were treated with acidic conditioners (polyacrylic acid or phosphoric acid), so they would have been partly demineralized. This suggests that the loss of mineral phase by conditioning does not reduce the available surface for adsorbing ions to any significant extent, hence makes no difference to the ion concentration in solution.

5 Conclusions

The study has shown that aluminium and fluoride are both released from various restorative materials placed in teeth (deciduous or young permanent) but at levels that vary with type of tooth. Young permanent teeth were associated with lower level of ions released into artificial saliva than deciduous teeth, and this was attributed to the absorption of the ions by the enamel. This absorption is assumed to occur because the incompletely matured teeth are porous, have less compact enamel prisms and wider interprismatic spaces than mature teeth. On the other hand, conditioned samples were found to be associated with similar levels of ions released to unconditioned ones, suggesting that the removal of some mineral phase on conditioning does not lead to a significant reduction in the amount of surface available for uptake of ions.

Deciduous teeth were found to give higher Al:F ratios in artificial saliva than young immature teeth, showing that they absorbed proportionately less aluminium than young permanent teeth. This demonstrates that type of tooth also influences the selectivity for fluoride ions over aluminium.

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