Effects from pretreatment of stannous fluoride versus sodium fluoride on enamel exposed to 0.1 M or 0.01 M hydrochloric acid

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Preventing enamel erosions caused by acidic soft drinks or from vomiting during eating disorders is a challenge in current dental research. The aim of this study was to examine whether pretreatment of dental enamel with a solution of 0.4% SnF_2 could prevent dissolution of human enamel exposed to solutions of 0.1 M HCl, pH 1.2 or 0.01 M HCl at pH 2.2. Human enamel was pretreated for 18 h with a solution of 0.4% SnF_2 and with control solutions of 2% NaF or distilled water, and then exposed to HCl solutions. Similar experiments were performed with teeth treated for 2 min SnF_2 and then 4 min HCl. The effect was monitored by scanning electron microscopy (SEM) and by chemical analysis. At pH 2.2, NaF and water treatments showed minor inhibition of enamel dissolution, whereas SnF_2 inhibited demineralization significantly also after 2 min pretreatment and 4 min HCl exposure. At pH 1.2, SEM showed severe dissolution of the enamel surfaces regardless of pretreatment. As pH of stomach vomit is usually >1.5, SnF_2 may be an interesting agent for use in the treatment and prevention of dental erosions even in patients with frequent vomiting episodes. □ *Eating disorder; enamel erosions; gastric juice; oral; prophylaxis; sodium fluoride; stannous fluoride*

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Dental erosion is a non-bacterial dissolution of dental enamel caused by extrinsic or intrinsic acids. Erosion caused by extrinsic acids is effected mainly by organic acids from food or beverages such as orange juice or soft drinks. The pH in organic acids is usually from 2.5 to 5. Gastric juice contains HCl, which is a strong acid. During recurrent vomiting or regurgitation, gastric juice of varying strength may reach the oral cavity and act directly on the lingual surfaces of the teeth. The acid may also accumulate between the papillae and in the fissures of the tongue and cause erosion when the tongue comes into contact with the teeth. Pure gastric acid has a pH of 0.9–1.5 (1). However, in patients with vomiting episodes as described above, the gastric juice is buffered in the esophagus (2) and usually diluted with ingredients from food and drinks. The calcium and phosphate contents of saliva will further reduce the acidic challenge in the oral cavity. Milosevic et al. (3) found that the pH of vomit varied from 2.9 to 5.0 with a mean 3.8 in 6 patients with bulimia nervosa. The risk of dental erosion has been found to be 18 times higher in patients with chronic vomiting than in others (4). Peptic ulcer, gastritis, cytostatic drug treatment, alcoholism, migraine headache and eating disorders are all conditions during which long-standing chronic vomiting episodes or regurgitation may occur. Clinical manifestations of dental erosion have been reported not to occur until gastric acid has acted on enamel regularly for 1–2 years (5, 6). Dental erosion from both extrinsic and intrinsic factors is a growing concern in many patients today and little is known about its prevention. Fluoride in the form of sodium fluoride (NaF) appears to have a limited inhibiting effect against severe erosive acid challenges (7, 8). The major cariostatic mechanism of action of NaF is related to the effect on the remineralizing processes in dental plaque. However, when enamel is exposed to very low pH solutions (<4.5), no redeposition of minerals lost occurs and even high fluoride concentrations cannot prevent erosions (7). Consequently, sodium fluoride has minor preventive effects on erosions, particularly erosions caused by gastric acid.

Stannous fluoride has been used in toothpastes, mouth rinses, and topical treatments, and is known to reduce the acid dissolution of enamel by organic acids at pH levels relevant to the dental caries (9, 10).

The aim of the present in vitro study was to examine whether pretreatment of stannous fluoride (SnF_2) in a concentration that may be used in toothpaste or mouth rinses has a protective effect on enamel exposed to relevant concentrations of the strong acid HCl. Treatment with NaF or distilled water was included as controls.

Materials and methods

Teeth

Premolars extracted for orthodontic reasons were used in the present study. After extraction, the teeth were stored in a humid environment at 4°C until use. All the buccal surfaces of the teeth were inspected in a stereomicroscope (magnification $\times 6 - 10$). Teeth showing surface defects such as cracks or demineralized areas were excluded. The teeth were rinsed in distilled water and cleaned with a rotating rubber cup and pumice prior to treatment.

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Scanning electron microscopy (SEM)

Twelve teeth were cut at the enamel-cement junction and the crowns sectioned bucco-palatinally into 2 equal parts, giving 24 crown halves. These were immersed in test-tubes with 10 mL of test solution for 18 h with one of the following aqueous solutions: (i) Distilled water, (ii) neutral 2% sodium fluoride (NaF), or (iii) 0.4% stannous fluoride (SnF_2), pH 3.

The pretreated samples were washed briefly in distilled water and one from each group was subsequently examined by SEM. One group of tooth crowns was exposed to 10 mL of 0.01 M HCl (pH 2.2) and the last to 0.1 M HCl (pH 1.2) in test-tubes for 30 min. Thereafter, they were again washed in distilled water.

All tooth fragments were dried and sputter coated with gold-palladium/carbon (approximately 50 nm thick), and then examined in a Phillips SEM type XL 30 ESEM.

Energy dispersive X-ray analyse (EDXA)

EDXA analyses of the sputter-coated crown halves were carried out to detect the elements tin (Sn) and fluoride (F).

Chemical analysis

The crowns from 62 premolars were cut in the same way as in the SEM experiment, giving 124 test specimens. All crowns were covered with nail varnish except for a window exposing enamel of 3×5 mm^2.

Experiment 1: Thirteen specimens were pretreated with distilled water, 13 with neutral 2% sodium fluoride, and 13 with 0.4% stannous fluoride at pH 3 for 18 h, rinsed and then exposed to 0.01 M (pH 2.2) HCl for 30 min.

Experiment 2: Thirteen specimens were pretreated with distilled water, 13 with neutral 2% sodium fluoride, and 13 with 0.4% stannous fluoride at pH 3 for 18 h, rinsed and then exposed to 0.1 M (pH 1.2) HCl for 30 min.

Experiment 3: Thirteen specimens were pretreated with distilled water, 13 with neutral 2% sodium fluoride, and 13 with 0.4% stannous fluoride at pH 3 for 2 min, rinsed and exposed to 0.01 M (pH 2.2) HCl for 4 min.

Calcium in the solutions after the exposure to hydrochloric acid was measured by atomic absorption spectroscopy (model 3300: Perkin Elmer Analytical Instruments, Shelton, USA).

Statistical analysis

Independent *t* tests and one-way ANOVA were used to test between-group differences. The Bonferroni test was used in post hoc analyses.

Results

Scanning electron microscopy

Enamel surfaces treated with the NaF solution showed normal enamel structures with precipitates of granular materials (Fig. 1A). The SnF_2-treated surfaces showed

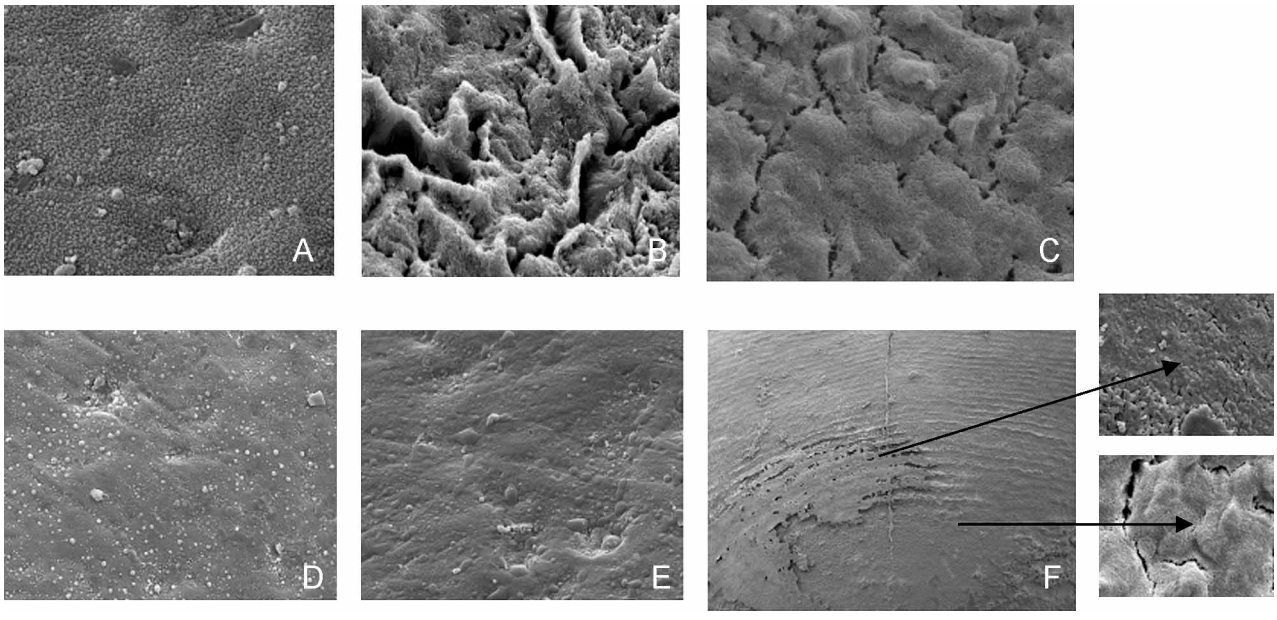

Fig. 1. A. Enamel pretreated with 2% NaF for 18 h (3000×). B. Enamel in the same tooth pretreated with 2% NaF for 18 h, then exposed to 30 min 0.01 M HCl pH 2.2 (3000×). C. Enamel in the same tooth pretreated with 2% NaF for 18 h, then exposed to 30 min 0.1 M HCl pH 1.2 (3000×). D. Enamel pretreated with 0.4% SnF_2 for 18 h (3000×). E. Enamel in the same tooth pretreated with 0.4% SnF_2 for 18 h, then exposed to 30 min 0.01 M HCl pH 2.2 (3000×). F. Enamel in the same tooth pretreated with 0.4% SnF_2 for 18 h, then exposed to 30 min 0.1 M HCl pH 1.2 (3000×). Main picture 60×.

larger deposits in addition to smaller granular structures (Fig. 1D). Enamel surfaces pretreated with NaF or distilled water only and then exposed to 0.01 M HCl showed severely eroded surfaces (Fig. 1B). Enamel surfaces pretreated with SnF_2 and then exposed to the 0.01 M HCl solution showed almost normal enamel surfaces with only scattered areas of dissolution. The small globular precipitates from the SnF_2 treatment were dissolved (Fig. 1E).

Enamel pretreated with NaF or distilled water and then exposed to the 0.1 M HCl solution at pH 1.2 showed a severely eroded surface (Fig. 1C). Enamel treated with SnF_2 and then exposed to the 0.1 M HCl solution is shown in an overview at a magnification of 60×. The enamel surface is partly sound (i), but with large areas that are severely eroded (ii) (Fig. 1F).

EDXA

Tin and fluoride could be detected on the enamel surface after treatment with SnF_2. Fluoride could be detected after NaF pretreatment. These elements were also detectable after HCl exposure.

Chemical analysis

Experiment 1: The calcium losses after 18 h pretreatment and 30 min 0.01 M HCl (pH 2.2) were 6.0 (*s* 1.4) after pretreatment with H_2O, 5.2 (*s* 1.3) after NaF, and 0.5 (*s* 0.5) after SnF_2. One-way ANOVA showed significant differences between the groups $F = 57.51$, $P < 0.001$. Post hoc tests revealed tooth enamel pretreated with SnF_2 to have significantly lower calcium loss than those pretreated with NaF ($P < 0.001$) or distilled water ($P < 0.001$). There was no statistically significant difference between enamel pretreated with NaF and enamel pretreated with distilled water.

Experiment 2: The calcium losses after 18 h pretreatment and 30 min 0.1 M HCl (pH 1.2) were 36.3 (*s* 3.3) after pretreatment with H_2O, 33.7 (*s* 4.9) after NaF, and 24.3 (*s* 3.9) after SnF_2. Even here one-way ANOVA showed significant differences between the groups $F = 32.7$, $P < 0.001$. Post hoc tests revealed tooth enamel pretreated with SnF_2 to have significantly lower calcium loss than enamel pretreated with NaF ($P < 0.001$) or distilled water ($P < 0.001$). There was no statistically significant difference between enamel pretreated with NaF and enamel pretreated with distilled water. The changes in mean calcium loss between pH 2.2 and pH 1.2 were significant under all conditions (water: $t = 5.6$, $P < 0.001$; NaF: $t = 18.6$, $P < 0.001$; SnF_2: $t = 18.3$, $P < 0.001$).

Experiment 3: The calcium losses after 2 min pretreatment and 4 min 0.01 M HCl (pH 2.2) were 1.6 (*s* 0.5) after pretreatment with H_2O, 1.1 (*s* 0.4) after NaF, and 0.3 (*s* 0.3) after SnF_2. Even with this short exposure, ANOVA showed the differences between pretreatments to be statistically significant ($F = 32.32$, $P < 0.001$). Post hoc with Bonferroni tests showed statistically significant differences between SnF_2 and water ($P < 0.001$), between SnF_2 and NaF ($P < 0.001$), and between NaF and water ($P < 0.05$).

Discussion

In the present study, the dissolution of enamel exposed to two concentrations of strong hydrochloric acid solutions after pretreatment with stannous fluoride was investigated in vitro. Since the aim of the study was to test out principles, pretreatment was as long as 18 h in SEM, EDXA, and in the chemical analysis experiments 1 and 2. To approach a more clinically adequate condition, the chemical analysis experiment 3, with pH 2.2, 2 min pretreatment and 4 min of acid exposure, was conducted. The results clearly showed that pretreatment of enamel with SnF_2 reduced the dissolution in 0.01 M HCl at pH 2.2. As expected, NaF pretreatment of the enamel showed significantly less inhibiting effect after exposure to any of the HCl solutions used. This was demonstrated by SEM and by chemical analysis. Furthermore, the inhibition by SnF_2 appeared to be limited to the acids with pH 2.2; when HCl pH was 1.2, the calcium loss and eroded surfaces seen in SEM were substantial even if significantly better than water and NaF. Although pure gastric acid has a pH between 0.9 and 1.5, the pH in the oral cavity after vomiting episodes is seldom or never <1.5. Thus, the inhibitory effect of SnF_2 at pH 2.2 should be of clinical relevance.

The present study does not explain the mechanism of the interaction between enamel and stannous fluoride. Rey et al. (11) found $Sn_3(PO_4)_2$ to be formed upon the interaction of SnF_2 with enamel. Wei (9) and Wei & Forbes (10) showed that tin complexes like $Sn_3F_3PO_4$ and hydrated tin compounds were formed when the exposure period was long. Little is known of the surface chemistry after shorter exposure periods, and reaction products appear to be difficult to identify (9). The EDXA analysis in the present study concluded that tin was present on the enamel surfaces exposed to SnF_2 both before and after acid exposure. However, the chemical nature of the tin compounds was not examined. Substantial amounts of calcium fluoride are also formed when enamel is exposed to SnF_2, and the amount increases with increasing exposure time and at low pH (12). Dissolution of the enamel is greatly reduced by the formation of tin and CaF_2 compounds from SnF_2 exposure (9), although the relative importance of these reaction products is not known.

The interaction between NaF at pH 7 and enamel results in decomposition of surface enamel with the formation of a calcium fluoride such as material contaminated with phosphate (13). Calcium fluoride is known to be less soluble in acid than fluorapatite (14). However, phosphate contaminated CaF_2 is more soluble than pure CaF_2. It is likely that the CaF_2 formed in connection with SnF_2 treatment also contains less internal phosphate and may thus contribute to the inhibition observed in the

present study. $SnCl_2$ did not show any caries-inhibiting effect in a rat model, whereas SnF_2 did (15), which may indicate that CaF_2 is crucial for its preventing effect.

Sodium fluoride is presently widely used in preventive dental care, particularly in caries prevention. However, there is a need for documentation of more acid-resistant compounds. In earlier studies, titanium fluoride has been found to prevent dissolution of enamel exposed to an HCl solution at pH 1.2 for a short time (16) and the interaction of titanium with phosphate-bound oxygen formed a glaze on the enamel (17). The present study indicates that stannous fluoride also prevents dissolution of enamel and may be a promising compound in this context. Further studies should be carried out using a clinically relevant exposure time (e.g. the short variant of exposure used in the present study) to SnF_2 and HCl and the experiments should be conducted in a human oral environment.

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