Abstract
Dental erosion develops through chronic exposure to extrinsic/intrinsic acids with a low pH. Enamel erosion is characterized by a centripetal dissolution leaving a small demineralized zone behind. In contrast, erosive demineralization in dentine is more complex as the acid-induced mineral dissolution leads to the exposure of collagenous organic matrix, which hampers ion diffusion and, thus, reduces further progression of the lesion. Topical fluoride induction the formation of a protective layer on dental hard tissue, which is composed of CaF\textsubscript{2} (in case of conventional fluorides like amine fluoride or sodium fluoride) or of metal-rich surface precipitates (in case of titanium tetrafluoride or tin-containing fluoride products), appears to be most effective on enamel. In dentine, the preventive effect of fluorides is highly dependent on the presence of the organic matrix. In situ studies have shown a higher protective potential of fluoride in enamel compared to dentine, probably as the organic matrix is affected by enzymatical and chemical degradation as well as by abrasive influences in the clinical situation. There is convincing evidence that fluoride, in general, can strengthen teeth against erosive acid damage, and high-concentration fluoride agents and/or frequent applications are considered potentially effective approaches in preventing dental erosion. The use of tin-containing fluoride products might provide the best approach for effective prevention of dental erosion. Further properly designed in situ or clinical studies are recommended in order to better understand the relative differences in performance of the various fluoride agents and formulations.

Dental erosion is defined as substance loss by exogenous or endogenous acids without bacterial involvement. The most important sources are dietary acids [1] and those originated from the stomach, like gastric acids from regurgitation and reflux disorders [2].

In contrast to initial caries, enamel erosion is predominantly a surface phenomenon with a centripetal bulk substance loss combined with a small partly demineralized surface layer with decreased microhardness (fig. 1). In dentine, the erosive demineralization is mostly diffusion controlled, as the increasing exposure of organic matrix hampers ion diffusion, and thus reduces further progression of dentine erosion (fig. 2) [3, 4].

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Fig. 1. Scanning electron microscopy (a) and clinical picture (b) of enamel erosion. Pictures are not from the same tooth.

Fig. 2. a Scanning electron microscopy of dentine erosion showing opened dentinal tubules; however, the tubules also can be partially or totally closed in the clinical situation. Reprinted from Kato et al. [59], with permission. b Clinical picture of dentine erosion. Pictures are not from the same tooth.
There is evidence that the prevalence of erosion is steadily increasing [5]. Preventive strategies in the management of dental erosion consider dietary counseling, stimulation of salivary flow, modification of erosive beverages, adequate oral hygiene measures and fluoride treatment as the most relevant [6].

This chapter will give an overview of the current knowledge on the use of fluorides, including conventional and metal fluorides, for the prevention of erosive and combined erosive-abrasive dental loss. Due to the fact that the histology of enamel and dentine erosion is considerably different, this chapter will be divided into two parts: (1) fluorides and enamel erosion; (2) fluorides and dentine erosion.

**Fluorides and Enamel Erosion**

Extrinsic and/or intrinsic acids with low pH (pH 1.0–3.5) initially cause either the dissolution of the prism cores or interprismatic areas, showing a honeycomb structure in prismatic enamel. In aprismatic enamel, the demineralization is irregular, without a clear structural pattern. If the erosive challenge is ongoing, the dissolution process results in surface loss accompanied by a progressive softening of the surface. As the demineralized layer of eroded enamel is considerably small when compared to the enamel loss, fluoride application predominately aims to prevent erosive tissue loss rather than to remineralize softened enamel.

Conventional fluorides, whose beneficial effect against caries is well known [7], have been tested for prevention or control of dental erosion [8]. The potential of conventional fluorides, such as sodium fluoride (NaF) and amine fluoride (AmF), to prevent erosive demineralization is mainly related to the formation of a calcium fluoride (CaF$_2$) layer [9, 10] (fig. 3). This layer is assumed to behave as a physical barrier that hampers the contact of the acid with the underlying enamel or to act as a mineral reservoir which is attacked by the erosive challenge. Thereafter, released calcium and fluoride might increase the saturation level with respect
to dental hard tissue in the liquid adjacent to the surface, thus promoting remineralization (fig. 4, 5).

The formation of the CaF$_2$-like layer and its protective effect against demineralization is highly dependent on the pH, the concentration of fluoride and the frequency of application. The deposition of CaF$_2$ on the surface increases with increasing concentration and frequency of application and decreasing pH of the agent. Fluoride agents with a pH below 5 seem to induce a higher CaF$_2$ deposition on dental surface than neutral ones [9].

Ganss et al. [10] evaluated the retention of CaF$_2$ on human enamel under neutral and acidic conditions in vitro and in situ. Fluoride
(10,000 ppm, AmF) was applied once for 5 min, and the enamel specimens were exposed to erosive demineralization (3 × 30 s/day, 4 days in vitro; 3 × 2 min/day, 7 days in situ) or neutral conditions (artificial saliva in vitro; human saliva in situ). It was shown that more CaF$_2$ was lost under erosive compared to neutral conditions in vitro, while the intraoral environment was considerably protective for CaF$_2$-like precipitates, especially on enamel.

Although toothbrushing might affect the progression of eroded dental hard tissues adversely by removing the softened layer of enamel [11, 12], it was shown that the use of fluoridated (NaF) toothpastes might diminish the abrasive effect to some extent [11]. However, as the overall protective effect of toothpastes with 1,100–5,000 μg/g fluoride is limited [14, 15], the use of highly concentrated fluoride varnishes (22,600 μg/g) was anticipated to be more effective due to their capacity

Fig. 5. Illustration of enamel treated with conventional fluoride. a CaF$_2$ layer final dissolution. b Simultaneous calcium and fluoride saturation provoking remineralization. c Subsequent erosive challenge. d Bulk substance loss combined with a small partly demineralized surface layer.
Fluorides and Erosion

Fig. 6. Scanning electron microscopy of enamel treated with 4% titanium tetrafluoride varnish (6 h). Reprinted from Magalhães et al. [19] with permission.

to adhere to the tooth surface and create a CaF$_2$ reservoir [16, 17]. Indeed, the application of NaF varnish (22,600 μg/g) was effective in reducing enamel erosion for 30 min of acid exposure, but the protective effect declined thereafter [18, 19]. However, as placebo varnishes also showed some protection against enamel erosion and combined erosion/abrasion, it is believed that the protective effect of fluoride varnishes is mainly related to the mechanical rather than to the chemical protection [20, 21].

As the anti-erosive effect of conventional fluorides requires a very intensive fluoridation regime [22], recent studies have focused on fluoride compounds which might deliver a higher level of efficacy. In this context, compounds containing polyvalent metal ions such as stannous fluoride or titanium tetrafluoride were tested.

Several in vitro studies have shown an inhibitory effect of 0.4–10% TiF$_4$ solution on dental erosion [23–27], which is attributed not only to the effect of fluoride, but mainly to the action of titanium [23, 28]. Its protective effect is related to the formation of an acid-resistant surface coating, the increased fluoride uptake and the titanium incorporation in the hydroxyapatite lattice. The glaze-like surface layer observed after the application of TiF$_4$ is assumed to be due to the formation of a new compound (hydrated hydrogen titanium phosphate) that might primarily act as a diffusion barrier [23, 29–32] (fig. 6, 7). The increased fluoride uptake found after application of TiF$_4$ can be explained by the ability of the polyvalent metal ion to form strong fluoride complexes firmly bound to the apatite crystals [30, 32].

Information regarding the efficacy of TiF$_4$ under clinical conditions is scarce and contradictory, as only two in situ studies showed 1.6% TiF$_4$ (0.5 m fluoride) to be as effective as SnF$_2$ or AmF in the prevention of erosion or combined erosion/abrasion [33, 34], while other did not show any protective effect of 4% TiF$_4$ [20, 21, 35]. The efficacy of TiF$_4$ is highly dependent on the pH of the agent, since it was shown that enamel erosion can be significantly reduced by TiF$_4$ (0.5 m fluoride) at native pH (pH 1.2) but not at a pH buffered to 3.5 [36]. One study indicated that TiF$_4$ applied in the form of a varnish might be of higher efficacy than as a solution [19]. However, it should be consider
Fig. 7. Illustration of the formation of (CaF₂) layer and an acid-resistant surface coating composed of hydrated hydrogen titanium phosphate after the application of TiF₄, or composed of metal-rich precipitates [Ca(SnF₃)₂, SnOHPO₄, Sn₃F₆PO₄] after the application of tin-containing fluoride mouth rinses [40].

a) CaF₂ layer and the metal-rich precipitates (in orange).
b) Erosive challenge.
c) CaF₂ layer dissolution.
d) CaF₂ layer final dissolution and the preservation of the metal-rich precipitate.
e) Progressive erosive challenges.
f) Final dissolution of the metal-rich layer and consequent enamel loss.
that the low pH of TiF$_4$ products does not allow self-application by the patient.

Tin-containing fluoride products have shown promising results in several studies [37–41]. The mode of action of tin-containing fluoride solutions is probably attributed to the formation of metal-rich surface precipitates [Ca(SnF$_3$)$_2$, SnOHPO$_4$, Sn$_3$F$_4$PO$_4$], which were shown to be of high acid resistance [42] (fig. 7–9). Further, tin may penetrate and become incorporated into the demineralized layer when high concentrated tin containing fluoride mouth rinses are used [38, 43].

**Fig. 8.** Scanning electron microscopy of enamel treated with SnF$_2$ solution (0.48 m, pH 2.7, 3 min) before erosion. Reprinted from Yu et al. [60] with permission.

**Fig. 9.** Scanning electron microscopy of enamel treated with SnF$_2$ solution after erosion (6 × 1 min/day, 5 days), showing no alteration. Reprinted from Yu et al. [60] with permission.
Ganss et al. [44] evaluated the relevance of cations in different fluoride compounds for their effectiveness as anti-erosive agents and showed that SnCl₂ (800 ppm tin), NaF (250 ppm fluoride), AmF/SnF₂ (250 ppm fluoride/390 ppm tin) and SnF₂ (250 ppm fluoride/809 ppm tin) solutions could reduce enamel erosion. Treatment with solutions containing SnF₂ was most effective. The combination of AmF/NaF/SnCl₂ with high (2,800 ppm tin/1,500 ppm fluoride) and low (700 ppm Sn/1,500 ppm fluoride) tin concentrations reduced erosion by 90 and 70%, respectively [38, 39].

Some possible side effects of high-concentration tin-containing mouth rinses may include a dull feeling on the tooth surface, astringent sensation and tooth discoloration (1,900 ppm tin) [45]. Therefore, tin-containing solutions of lower concentration (800 ppm tin/500 ppm fluoride) were tested in vitro and in situ [46, 47]. Under severe erosive conditions, the SnCl₂/NaF/AmF exhibited a high potential to reduce enamel erosion (67% reduction), and showed no adverse side effects [47]. Besides mouth rinses, tin-containing fluoride toothpastes were tested using in vitro protocols, and shown to perform significantly better under erosive challenges when compared with NaF- and MFP-containing toothpastes [41]. Further research should test specially formulated tin-containing fluoride products to minimize aesthetic negatives seen with high-concentration tin-containing products, which may provide a highly effective means to help prevent dental erosion using a consumer-friendly approach.

**Fluorides and Dentine Erosion**

The preventive effect of fluorides on dentine erosion is highly dependent on the presence of the organic matrix [48]. Initial studies showed that a very intensive fluoridation regimen combining toothpaste (0.15% fluoride, NaF), mouth rinse (0.025% fluoride, AmF/NaF) and gel (1.25% fluoride, AmF/NaF) was most effective in the prevention of dentine erosion [22, 49]. However, after enzymatic removal of the organic matrix, fluoride was ineffective [3, 50]. It was assumed that the demineralized organic dentine matrix has a buffering capacity sufficient to prevent further dentine demineralization, especially in the presence of high amounts of fluoride [3]. Moreover, the exposed organic matrix of etched dentine involves an increased surface area and increased diffusion pathways – enhancing the amount of structurally bound and KOH-soluble fluoride compared to sound dentine [51]. However, it remains unclear to what extent the organic material is retained under clinical conditions, when the collagen layer might be affected by enzymatical and chemical degradation as well as by abrasive influences [50, 52]. From the clinical appearance of dentine-erosive lesions, it seems likely that the collagenous layer is at least partly removed. This hypothesis might also explain why fluorides such as NaF were less effective in dentine than in enamel under in situ conditions [10, 22, 38] but not in laboratory experiments [27, 53].

The application of slightly acidic fluoride formulations such as NaF or AmF results in the formation of CaF₂ precipitates on both enamel and dentine (fig. 10), but the precipitates are less stable on dentine than on enamel under erosive conditions [10]. Although the preventive potential of NaF and AmF solution and dentifrice on dentine erosion and combined erosion/abrasion was shown in different in situ studies [22, 34, 54], information about the ideal fluoride concentration and frequency of application is scarce. Also, the resistance of dentinal CaF₂ precipitates against abrasion has not so far been assessed directly; only an in situ study indicated that the protective potential of AmF against erosion is not affected by additional brushing treatment [34].

Considering the severe and chronic acid exposure in patients suffering from dental erosion, the effect of CaF₂ precipitates is probably limited.
over time [10], and fluoride compounds with a distinct potential to resist an erosive challenge are required.

Titanium tetrafluoride was shown to induce some coating on dentine surfaces, which partly covered dentinal tubules [55] (fig. 11). However, its protective potential did not exceed the efficacy of NaF or AmF [27, 34, 56], and the low pH required for the efficacy of the agents has not so far allowed for a clinical application [57].

Tin-containing fluoride solutions have been demonstrated to exhibit promising anti-erosive
effects not only on enamel but also on dentine [38, 44, 46]. The suggested mechanism of action is related to the incorporation of tin in mineralized dentine when the organic matrix is allowed to develop and to surface precipitation when the organic matrix is enzymatically removed [58]. In cases where the organic matrix is preserved, phosphorus, phosphorylated phosphoprotein or phosphophoryn might attract the tin ion, which is then retained in the organic matrix to some extent, but also accumulates in the underlying mineralized tissue. In cases where the organic matrix is removed, tin reacts with the mineral by forming different salts, e.g. Sn(OH)2, Sn2(PO4)OH, Ca(SnF3), Sn3F5PO4, Sn2(OH)PO4, Sn3F5PO4 or SnHPO4 [58]. Recent in situ studies demonstrated that mouth rinses containing AmF/NaF/SnCl2 (500 ppm F, 800 ppm Sn) reduced dentine erosion by 50% and were significantly more effective than an NaF-containing mouth rinse (500 ppm F) [38, 47].

Comparing the protective effect of different fluoride compounds on dentine erosion, Ganss et al. [48] showed that solutions containing AmF and/or SnF2 performed only slightly better than solutions containing NaF and/or AmF in the presence of the organic matrix. However, continuous removal of the organic matrix influenced the efficacy of the fluoride compounds distinctly and demonstrated a significantly better preventive effect of the SnF2- and AmF/SnF2-containing solutions compared to all other solutions.

Conclusion

Conventional fluorides with a known anti-cariogenic potential offer some, but limited, protection against erosion as the CaF2 precipitates formed on the surface are readily soluble in acids. Metal-containing fluoride compounds showed promising results in prevention of erosion, but might involve some adverse side effects due to the very low pH (in case of titanium tetrafluoride) and the potential to cause slight discoloration, a dull feeling on the tooth surface and an astringent sensation (in case of highly concentrated tin-containing fluoride solutions).

There is convincing evidence that fluoride, in general, can strengthen enamel against erosive acid damage; high-concentration fluoride agents and/or frequent applications are considered potentially effective approaches to prevent dental erosion. However, fluorides might be more effective in enamel than in dentine, as the organic matrix influencing the efficacy of fluorides might to some extent be affected by enzymatical and chemical degradation as well as by mechanical abrasion. The use of tin-containing fluoride products might provide the best approach for effective prevention of dental erosion.

References

Fluorides and Erosion


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