Diffusion of phosphate and monofluorophosphate ions in bovine enamel
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SUMMARY

The crowns of our teeth are covered with enamel; it varies in thickness from about 1 - 2 mm. Enamel interacts continuously with the oral fluids and can be demineralized by dental plaque.* The demineralization caused by the metabolic products of the plaque - especially lactic acid - may eventually lead to caries and finally to cavitation. The majority of the population in modern society suffers from dental caries and huge costs are involved. Both factors have stimulated considerable efforts in caries prevention. At this moment two important preventive methods are generally accepted: fluoridation and plaque removal by tooth brushing. Fluoride can be applied by various methods, e.g. local fluoride application, dentifrices, mouth rinses, water fluoridation, fluoridating varnishes, fluoride tablets etc.

The fluoridating agents may contain fluoride in various forms e.g. F⁻, monofluorophosphate or organic fluorides. Especially in toothpastes more than one form of fluoride is usually present.

One of the most important aspects of enamel fluoridation is the stimulation of remineralization processes.

In these processes, phosphate is a dominating factor. Phosphate is not only one of the main enamel constituents but it is also present in plaque and in most of the various caries preventive agents mentioned above.

The aim of this study is to investigate phosphate and monofluorophosphate interaction with whole bovine enamel under various circumstances and to develop a model for the experimentally observed behavior. Labelling with radioactive tracers provides a suitable method to determine the amount of phosphate or monofluorophosphate in enamel as a function of depth. The distribution pattern thus found (the so-called diffusion

* a layer of microorganisms and proteins sometimes locally covering the enamel surface
profile) provides information on ion penetration.

Some introductory data on enamel structure and chemical composition are given in chapter 2.

Information on transport phenomena of phosphate and monofluorophosphate in bulk enamel is hardly available. On the other hand, the interaction mechanisms of these ions with synthetic hydroxyapatite as well as powdered enamel have been intensely investigated. A literature survey on the last subject mentioned is given in chapter 3. The results show that qualitatively these data are useful but they cannot be employed to estimate quantitatively diffusion behavior in bulk enamel.

Some principles of diffusion are given in chapter 4. Models are presented for diffusion in homogeneous and polycrystalline materials. Furthermore, some measuring techniques for tracer diffusion are described.

Chapter 5 deals with the diffusion of radioactive labelled phosphate ions in whole bovine enamel at 37 °C and neutral pH. The diffusion profiles found experimentally indicate grain boundary diffusion. If we take the enamel microstructure into account the observed behavior can be interpreted with the aid of two possible models: a prism model or a crystallite model. In both, enamel is assumed to consist of grains in which a slow diffusion takes place and slabs of high diffusivity in between. The difference between the models is, that either the prisms or the crystallites are assumed to represent these grains. The diffusion coefficients can be calculated from the experimental data by using Fisher's grain boundary model. In the prism model this gives diffusion coefficients $D_k = (1.4 \pm 0.8) \times 10^{-12}$ cm$^2$ sec$^{-1}$ for the fast interprismatic diffusion and $D_v = (3.5 \pm 2.1) \times 10^{-17}$ cm$^2$ sec$^{-1}$ for the slow diffusion in the prisms. In the crystallite model $D_k = (2.4 \pm 1.5) \times 10^{-12}$ cm$^2$ sec$^{-1}$ and $D_v = (4.5 \pm 2.7) \times 10^{-21}$ cm$^2$ sec$^{-1}$ for the diffusion between and in the crystallites, respectively. On the basis of these results only, no definite choice for one of the models could be made. Whether the value for $D_v$ in the crystallite model is a realistic value for lattice diffusion is questionable: no values for diffusion in hydroxyapatite single crystals are known and extrapolation from high temperature data is highly unrealistic.

In chapter 6 the temperature dependency of phosphate diffusion in the range 5 - 50 °C gives activation energies for the fast and slow diffu-
sion process of $0.5 \pm 0.1$ and $0.7 \pm 0.1$ eV, respectively. These values indicate that the diffusion most likely takes place in the medium between prisms and crystallites. The value of 0.7 eV for the activation energy is too low for lattice diffusion and therefore the prism model gives the most realistic description of the diffusion. The time dependency of the diffusion behaves as predicted by the theoretical grain boundary model. No dependency of the phosphate concentration could be found in the range $(0.5 - 5) \times 10^{-3}$ mol $l^{-1}$.

In chapter 7 the influence of pH on phosphate diffusion from pH 5 to 9 is investigated. Both $D_k$ and $D_v$ values show an increase with decreasing pH; this is most pronounced for $D_v$. At acidic pH the diffusing phosphate ion will be mainly $H_2PO_4^-$, whereas at alkaline pH the $HPO_4^{2-}$ ion will be dominating. The experiments indicate strongly that the charge of the diffusing ion and its interaction with the enamel have an important influence on the diffusion coefficients. This influence is more important in the intercrystallite than in the interprismatic areas.

Monofluorophosphate (MFP) diffusion has been investigated at various diffusion periods and MFP concentrations in solution at neutral pH (chapter 8). The prism model for grain boundary diffusion is also applicable for MFP diffusion. Values for the fast and slow MFP diffusion coefficients are $D_k = (1.7 \pm 0.4) \times 10^{-13}$ cm$^2$sec$^{-1}$ and $D_v = (1.8 \pm 0.6) \times 10^{-18}$ cm$^2$sec$^{-1}$, respectively.

These values are 2 - 3 times smaller than the values for phosphate diffusion. Most likely this is due to the fact that the monofluorophosphate ion can occur as divalent ion only.

The shape of the MFP diffusion profiles indicates, that no hydrolysis of monofluorophosphate took place. An important practical conclusion is that at neutral pH values monofluorophosphate in enamel is transported as $FP0_3^{2-}$ ions.