SUMMARY

This thesis deals with the diffusion of calcium and fluoride ions in bovine enamel. Special attention was given to the mechanism of this diffusion. The experiments were carried out with radioactive labeled ions. The information obtained is relevant with respect to de- and remineralization processes in enamel. Furthermore, information on the transport of fluoride ions is important with respect to caries prevention. Despite the great practical importance very few papers on transport mechanisms in bulk enamel have been published.

In chapter 2 a short atomic description of diffusion processes in solids, liquids and porous materials is given, and experimental methods to determine diffusion coefficients are discussed. Attention is paid to more complex processes also, i.e. diffusion with simultaneous chemical reaction and diffusion in polycrystalline solids. Finally basic principles of tracer kinetics are discussed briefly.

In chapter 3 a short review of the composition and structure of enamel and properties of enamel with relevance to ion transport is given. The experimental methods are described in chapter 4. Extensive attention is paid to the sectioning technique, the detection methods and to the errors involved.

The diffusion of calcium ions in tooth enamel from $^{45}$Ca labeled solutions was measured as a function of the calcium concentration in solution (0.2-5.0 mM) and separately, as a f...
of the temperature (20-45 °C). From the results (chapter 5) it is evident that transport of calcium ions in enamel can be described by two diffusion processes. The fastest process has a diffusion coefficient of $2 \times 10^{-12} \text{ cm}^2/\text{sec}$ at 37 °C. This coefficient is independent of the calcium concentration in solution. The activation energy of this process is 0.7 eV. It is concluded that this process occurs in the relatively wide pores in the interprismatic regions of the enamel. The second slower process has a diffusion coefficient that decreases from $1.5 \times 10^{-12}$ to $5 \times 10^{-14}$ cm$^2$/sec as the calcium concentration in solution increases from 0.2 to 5.0 mM. The activation energy of this process is 1.3 eV. It is concluded that this process is determined by interaction of diffusing calcium ions with hydroxyapatite crystallite surfaces and takes place in the relatively narrow pores in the intraprismatic regions in the enamel. About 2% of the calcium ions in enamel are involved in the diffusion processes. Most likely these ions are located at surface sites of hydroxyapatite crystallites. Consequently, these positions must be accesible in spite of the presence of an organic matrix.

The uptake of fluoride ions in enamel from $^{18}$F-labeled solutions was measured at pH 4, 5 and 7. At pH 4 the influence of phosphate ions on the fluoride uptake was examined also. The $^{18}$F activity of enamel was measured as a function of the immersion time in labeled solutions and penetration profiles of both $^{18}$F and stable F in enamel were determined.

At pH 7 (chapter 6) the $^{18}$F activity of enamel is proportional to the $t^2$-power of the immersion time in the solution. Both the $^{18}$F and the stable F concentration in enamel decrease exponentially with the penetration depth. From models on diffusion in polycrystalline solids a model for the diffusion of fluoride ions in enamel has been developed. The model takes into account diffusion in both pores and hydroxyapatite crystallites as well as a chemical reaction at pore-crystallite interfaces. The diffusion coeffi-
coefficients of fluoride ions in pores and in hydroxyapatite crystallites are \(2 \times 10^{-10}\) and \(2 \times 10^{-17}\) \(\text{cm}^2/\text{sec}\), respectively.

At pH 4 and 5 the uptake of fluoride ions in enamel is more complicated (chapter 7). At high fluoride concentrations (\(\geq 200\ \text{mg/l}\)) a calcium fluoride-rich layer is formed at the enamel surface. The thickness of this layer is proportional to the square root of the immersion time. The diffusion coefficient of fluoride ions in the layer is \(3 \times 10^{-9}\) \(\text{cm}^2/\text{sec}\). From this value it is concluded that the porosity of the calcium fluoride layer is much smaller than the porosity obtained from calculations based on a complete transformation of hydroxyapatite into calcium fluoride.

The uptake of fluoride in enamel decreases markedly on addition of phosphate ions to the solution.

In the last chapter (chapter 8) diffusion of \(^{45}\text{Ca}\) in artificial carious enamel is described. The diffusion process is complicated: initially, the process is determined by the relatively intact surface layer, but the influence of the lesion becomes clearly noticeable after about 24 hours.