Diffusion of fluoride in bovine enamel

G.J. Flim [*]

Z. Kolar [**]

J. Arends [*]

[*] Laboratory for Materia Technica, University of Groningen

[**] Interuniversity Reactor Institute, Delft
The Netherlands

ABSTRACT

The uptake of ^{18}F and the penetration of both F and ^{18}F in bovine enamel was investigated. Sodium fluoride solutions buffered at pH 7 were employed. The uptake of ^{18}F was measured by a method described by Duckworth, R. and Braden, M., Archs.Oral Biol., 12: 217 - 230, 1967. The penetration concentration profiles of fluoride (F, ^{18}F) in the enamel were measured by a sectioning technique. The ^{18}F uptake in enamel was proportional to approximately $t^{\frac{1}{2}}$; t being the uptake time. The ^{18}F concentration as a function of the position in the enamel can be described by: $c^*(x,t) = c_0^*(t)\exp[-\alpha^*(t)x]$. After correction for the initial fluoride concentration in enamel, for unlabeled fluoride the same dependency is obtained. A model based on simultaneous diffusion and chemical reaction in the pores and diffusion in the hydroxyapatite crystallites will be presented. The results show that diffusion coefficients in the pores are $\simeq 10^{-10}$ cm^2/sec and in the apatite crystallites $\simeq 10^{-17}$ cm^2/sec. The limitations and the approximations of the model will be discussed.

INTRODUCTION AND THEORY

Despite the well-established empirical relationship between fluoridation and reduced caries prevalence, the mechanism of fluoride incorporation in tooth enamel is still in doubt. Today we will present a model for diffusion of fluoride ions in enamel at a neutral pH. This pH is important in practice because drinking water fluoridation, the use of fluoride tablets, mouthrinsing and fluor addition to dentifrices are all pertaining to an approximate neutral pH.
Furthermore, we will present experimental results that support the model and diffusion coefficients of fluoride ions in enamel will be deduced from experimentally obtained quantities.

The model takes into account three processes:

i) diffusion of fluoride ions in the pores in the enamel structure

ii) a chemical reaction at the pore boundaries, provided by the surfaces of hydroxyapatite crystallites

iii) diffusion of fluoride ions in the hydroxyapatite crystallites

The reaction is assumed to be fast as compared to the diffusion processes and the fluoride concentration at the pore boundaries is assumed to be proportional to the concentration in the pores.
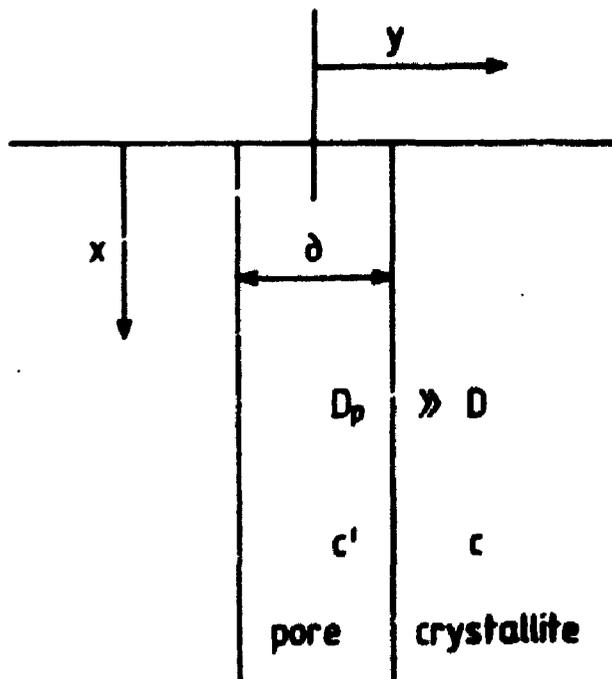

Fig. 1   Coordinate system for the model

Firstly, we consider one single pore with a width δ (Fig. 1). The diffusion coefficient in the pore is D_p and in the crystallites D. D is supposed to be much smaller than D_p. For the concentrations c' in the pore and c in the crystallites diffusion equations can be written down. In the pore:

$$\frac{\delta c'}{\delta t} = D_p \left(\frac{\delta^2 c'}{\delta x^2} + \frac{\delta^2 c'}{\delta y^2} \right) - \frac{\delta s'}{\delta t} \tag{1}$$

where s' is the concentration of ions immobilized from the pores; and in the crystallites:

$$\frac{\delta c}{\delta t} = D \left(\frac{\delta^2 c}{\delta x^2} + \frac{\delta^2 c}{\delta y^2} \right) \tag{2}$$

With the initial condition:

$$c = c' = 0 \qquad x > 0, \ t = 0 \tag{3}$$

and the boundary conditions:

$$c = s' = rc'; \quad D_p \frac{\delta c'}{\delta y} = D \frac{\delta c}{\delta y} \qquad y = \pm \ \delta/2 \tag{4}$$

$$c = c_0 \qquad\qquad\qquad x = 0, \ t > 0 \tag{5}$$

solutions of the diffusion equations can be obtained [1].
In case of enamel with many pores an average pore length per unit area parallel to the exposed enamel surface must be introduced.
An approximate solution of the diffusion equations for large distances x ($x \gg 2 \ (Dt)^{\frac{1}{2}}$) is given by [2]:

$$\bar{c}(x,t) = c_0(t) \ \exp[- \alpha(t)x] \tag{6}$$

where $\qquad c_0(t) = 4c_0 \ (\frac{Dt}{\pi})^{\frac{1}{2}} \ 1 \tag{7}$

$$\alpha(t) = (\frac{2D_r}{\delta D})^{\frac{1}{2}} (\frac{\pi}{Dt})^{\frac{1}{2}} \tag{8}$$

$$D' = D_p/r \tag{9}$$

l in eq. (7) is the average pore length per unit area (Fig. 5).
The diffusion in the pores is governed by an effective diffusion
coefficient D' which is smaller than D_p. This is a result of the
chemical reaction at the pore boundaries [3]; r in eq. (9) is the
ratio of the fluoride concentration at the pore boundaries and in
the pores.

From the quantities $c_0(t)$ and $\alpha(t)$ (eqs. 7 and 8) the diffusion
coefficients D and D' can be otained if the constant surface
concentration c_0, the average pore width δ and the average pore
length per unit area l are known.

An important result is that, according to the model, the uptake
of diffusing ions in enamel M(t) is proportional to the 3/4-th power
of time:

$$M(t) = M_0 t^{\frac{3}{4}} \tag{10}$$

with

$$M_0 = 4c_0 \left(\frac{D'\delta}{2D}\right)^{\frac{1}{2}} \left(\frac{D}{\pi}\right)^{\frac{3}{4}} l \tag{11}$$

EXPERIMENTAL

The ^{18}F activity was measured in bovine enamel as a function of the
immersion time in sodium fluoride solutions, containing 10-100 ppm
fluoride , at pH 7.0 [4].

Furthermore, we measured the fluoride and 18-fluoride concentrations
as a function of the position in enamel after a total immersion time
of 2 or 4 hours [4].

The experiments were carried out on flattened bovine enamel samples [4]
with nearly uniform fluoride distributions and fluoride concentrations
in the range of 100 to 300 ppm. The concentration profiles were measured
by means of a cectioning technique [5]. [18]F activities were determined
with a scintillation detector and fluoride concentrations with a
fluoride electrode [6].

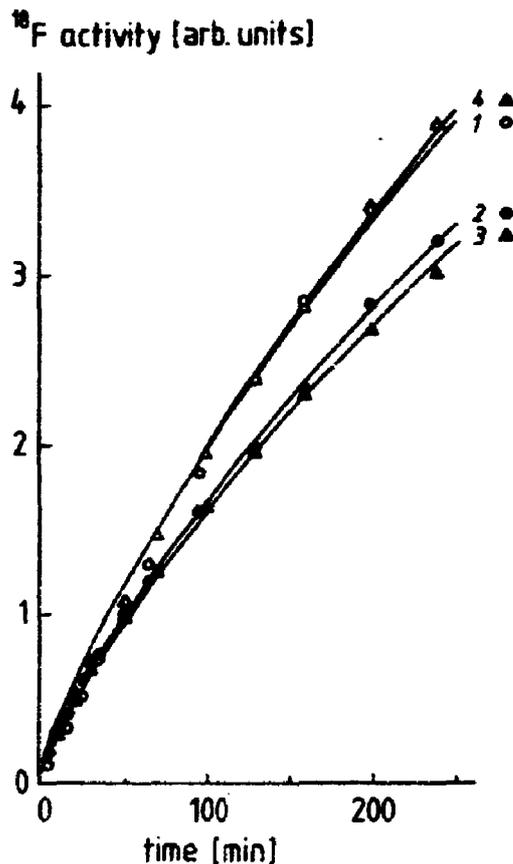Fig. 2 gives the ^{18}F activity as a function of time for four
enamel samples.

Fig. 2 ^{18}F activity of enamel as a function of time

Curves 1 and 2 refer to solutions with 50 ppm fluoride and curves 3 and 4 to solutions with 100 ppm fluoride. The solid lines are values calculated from adaptations of the experimental points to the 3/4-th power of time.

Fig. 3 shows the fluoride concentration as a function of the position x in enamel after a total immersion time of 4 hours. The samples are the same as in Fig. 2. The fluoride concentration decreases exponentially with increasing x down to a constant value at large x. This value represents the initially present fluoride concentration in the samples.
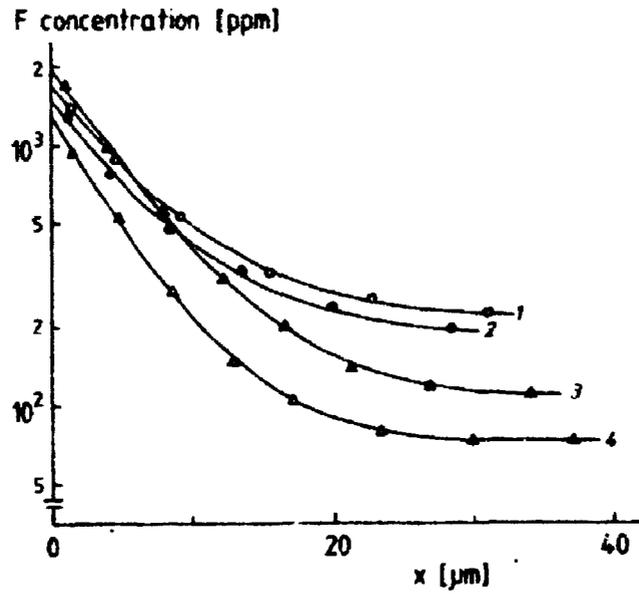
Fig. 3   Fluoride concentration profiles in enamel

In Fig. 4 the ^{18}F concentration in enamel as a function of the position x is shown after total immersion times of 2 and 4 hours.
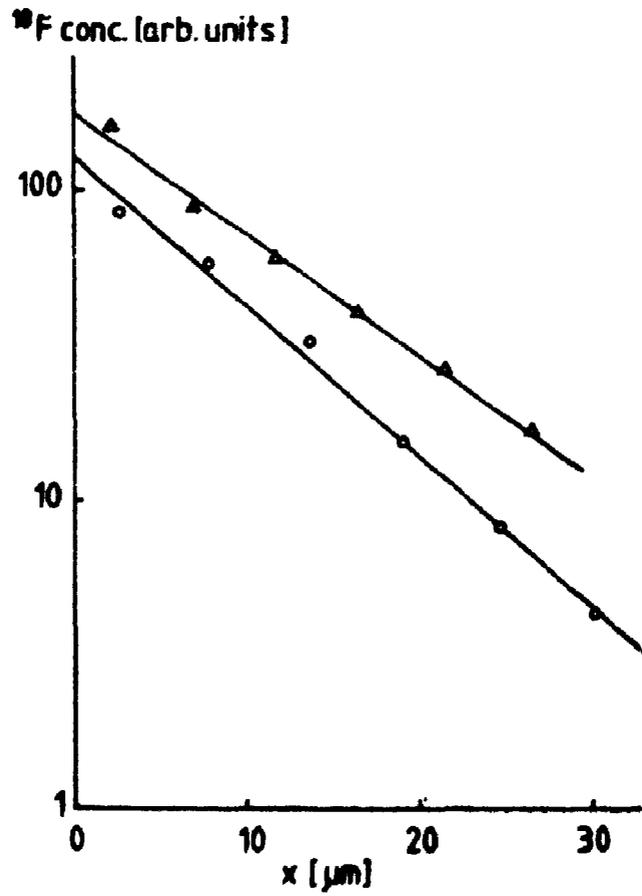

Fig. 4 ^{18}F penetration profiles in enamel

Curve 6 refers to 2 hours. Obviously the ^{18}F concentration decreases exponentially with increasing x.

RESULTS AND DISCUSSION

The ^{18}F activity of enamel was found to be proportional to a power function of time:

$$A(t) = A_0 t^\beta \qquad (12)$$

with an average of $\beta = 0.76 \pm 0.07$. This value is close to the value of 0.75 as predicted by the model.

The ^{18}F concentration could be described by:

$$c^*(x,t) = c_0^* (t) \exp [- \alpha^*(t)x]$$

and the fluoride concentration by:

$$c(x,t) = c_0(t)\exp [-\alpha(t)x] + c_b$$

c_b is the initially present fluoride concentration in enamel (100 - 300 ppm). The average value of $c_0(t)$ was found to be 1510 ± 240 ppm after an immersion time of 4 hours. An important observation is that $\alpha^*(t)/\alpha(t) = 1.0 \pm 0.1$. This means that the average penetration depths (given by $2^{\frac{1}{2}}/\alpha$) for fluoride and 18-fluoride in enamel are identical.

As mentioned before, we may obtain diffusion coefficient from $c(t)$ and $\alpha(t)$ in eqs. (7) and (8) if the values of the surface concentration c_0, the average pore width δ and the average pore length per unit area 1 are known. Since these values are not known for the enamel samples employed, we will make estimations.

For the constant surface concentration c_0, we estimated a value of 3000 ppm. This is about the value of the equilibrium concentration of fluoride in enamel apatite in sodium fluoride solutions containing 50 to 100 ppm fluoride reported by Mc Cann and Bullock [7].

For the average pore length per unit area 1 we estimated a value of $1/21.4$ nm^{-1}. This value is obtained from the assumption of regularly arranged hexagonal apatite crystallites with a width of 37 nm [8] (Fig. 5).
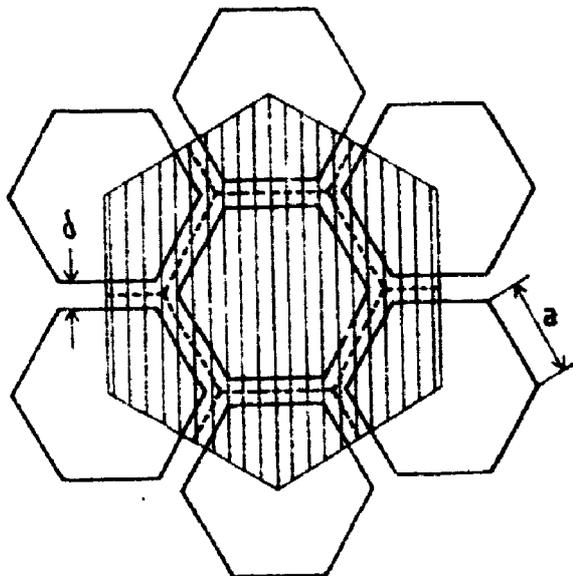
Fig. 5   Schematic model of crystallite arrangement in
enamel. The pore length per unit area 1 is given
by the ratio of total pore length in the shaded
region (9a) and the area of that region
$(6a^2/3^{\frac{1}{2}})$, i.e.: $1 = 3^{\frac{1}{2}}/2a$; $a = 37/2$ nm

For the average pore width we took the value of 2 nm after
Moreno and coworkers [9].

From these values and our experimentally obtained c(t) and
α(t) values we calculated diffusion coefficient of 1.7×10^{-17} cm^2/sec
in the crystallites and 1.9×10^{-10} cm^2/sec in the pores.
From these values average penetration depths after 4 hours can be
calculated. These are 0.005 μm in the crystallites and 16 μm
in the pores. From the experimental α(t) values we calculated an
average penetration depth of 8 μm for the overall diffusion of
fluoride ions in enamel. As a comparison, the average penetration
depth of water in enamel after 4 hours is about 120 μm [10].

SUMMARY

The model presented gives a good description of the experimental
results. The uptake of fluoride ions in enamel is determined by a 3/4-th
power of time relationship and the concentration decreases exponentially
with increasing distance.
The diffusion of fluoride ions in enamel is slowed down with respect to
water diffusion as a result of interactions with enamel apatite.
These interactions are chemical reactions at the apatite surfaces and
diffusion in the apatite crystallites.

REFERENCES

1. This model is similar to Fisher's model for diffusion in poly-crystalline solids. Here a chemical reaction at the pore boundaries is added.
   Fisher, J.C.: J. Appl. Phys., 22, 74(1951).
2. This is essentially Fisher's solution of the Fisher model, adapted to our problem.
3. Crank, J.: The mathematics of diffusion. Clarendon Press, Oxford, 1970, ch. 8.2.
4. Flim, G.J.: Thesis, in preparation.
5. Flim, G.J. and Arends, J.: Calc. Tiss. Res. (accepted).
6. Mc Cann, H.G.: Arch. oral Biol., 13, 475 (1968).
7. Mc Cann, H.G. and Bullock, F.A.: J. Dent. Res., 34, 59 (1955).
8. Jongebloed, W.L. et al.: Calc. Tiss. Res. 19, 109 (1975).
9. Moreno, E.C. and Zahradnik, R.T.: Arch. oral Biol., 18 1063 (1973).
   Zahradnik, R.T. and Moreno, E.C.: Arch. oral Biol., 20 317 (1975).
10. Burke, E.J. and Moreno, E.C.: Arch. oral Biol., 20, 327 (1975).