

Simulation of de - and remineralization processes in human dental enamel

Monica Păruș, Florin Brânză, Ioan Dănilă, Lucia Bârlean

Iași, Romania

Summary

Hidroxyapatite (HAP) is the main inorganic component in teeth and bone structure and it is structurally similar to calcium hidroxyapatite. The aim of this study was to obtain data regarding HAP crystals architecture and regarding structural changes following de- and remineralization processes in the presence of fluoride ion in different concentrations (226 ppm F vs. 12.300 ppm F).

Material and method. The authors elaborated the tridimensional crystalline model for HAP, fluorapatite (FAP) and carbohidroxyapatite (CHAP), using the Program VrmIPad 2.1™ and VRML View3.0™. The processes of de- and remineralization of dental enamel in the presence and the absence of fluoride ion were simulated based on these initial models. The main conclusion was that the fluoride ion in high concentrations (fluoride gel) tends to accumulate on top of the HAP crystals whilst in low concentration (rinsing fluoride solution) the fluoride ion has the possibility to promote in depth remineralization.

Keywords: simulation, hidroxyapatite, demineralization, remineralization, fluoride.

Aim

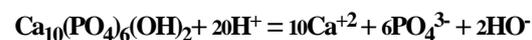
Data regarding hidroxyapatite (HAP), fluorapatite (FAP) and carbonhidroxyapatite (CHAP) crystals architecture were published in previous studies [1,2]. Based on this structures the authors intended to simulate structural changes following de- and remineralization processes in the presence of fluoride ion in different concentrations (226 ppm F vs. 12.300 ppm F).

Material and method

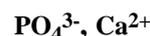
The tridimensional crystalline model was elaborated using the Program VrmIPad 2.1™ and VRML View3.0™ [1,2,3,4,5].

Simulation of de - and remineralization processes

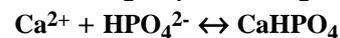
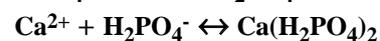
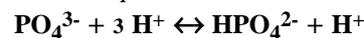
Simulation of demineralization process of enamel structures was performed first, to identify the most vulnerable positions in the crystalline network. Acid attack model was used for demineralization. The functional groups were represented by a single proton (H^+). The following reactions were taken into consideration (to simplify, the reactions referred only to hidroxyapatite) [6,7,8]:



Possible intermediary compounds:



Possible partial reactions:



Initial reaction condition:

- Temperature: 37°C; pH: 4,3;
- Simulation volume: $V=14310\text{\AA}^3$. The volume used for ion counts, functional groups counts and atom counts corresponding to the concentration of any substances involved, was the volume corresponding to 3x3x3 groups of HAP elementary cells ($27 \times 510 \text{\AA}^3$).

The authors considered that chemical reactions took place according to the following steps [9]:

1. reactants diffusion from solution to enamel surface;
2. reactants diffusion into interprismatic spaces;
3. reactants adsorption at dental enamel surface;
4. chemical reaction with the enamel surface atoms;
5. desorption of reaction products from the enamel surface;
6. transfer of reaction products into the interprismatic liquid.

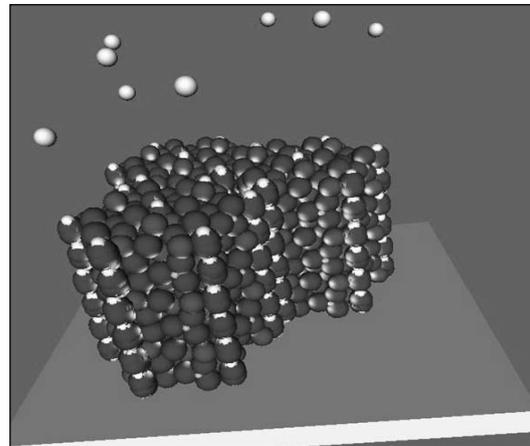
The kinetics of this processes was considered to be identical with HAP demineralization [10].

Results and discussions

1. With the intention to simulate *demineralization in the absence of fluoride ion* the authors estimated the presence of protonic groups as being 4 in the considered volume. 50% of the protons are statistically suitable for an attack. The acid attack can be visualized in *Figure 1* and in *Figure 2*:

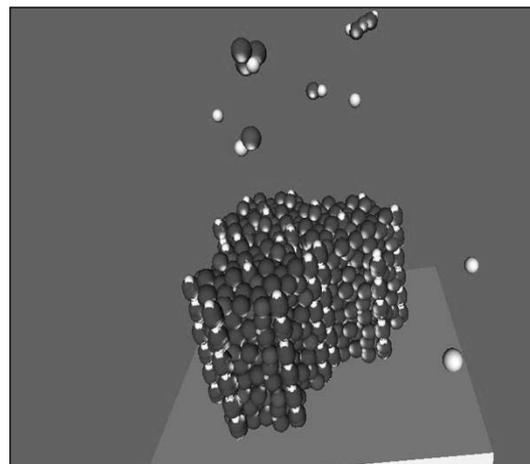
After dissociation, carbonate molecules will leave the prismatic structure and will be released in solution, together with calcium ions. Calcium and phosphate ions will redeposit on the enamel crystal surface but carbonate ions will remain in the solution and will not participate in the reconstruction process.

Figure 1. The moment before acid attack



The prismatic block, after partial dissociation following the acid attack can be visualized in *Figure 2*:

Figure 2. Partial dissociation of the prismatic block

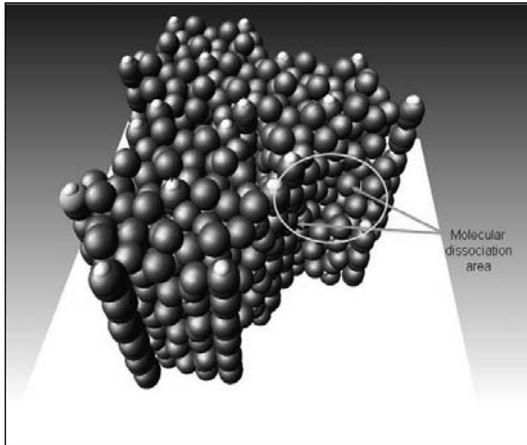


The presence of protons (H^+) (gray color) represents the acidity of the solution, which will produce the molecular dissociation on lateral edges in the demineralization phase. According to previous studies [1,2] the packing density is lower on the edges and promotes preferential dissociation on that level.

The reduced dimensions of the protons will favor its access to superficial and sub-superficial areas of dental enamel and will promote the dissociation reactions mentioned above. The calcium atom, which

leaves from the edge of hexagonal prism, will induce favorable conditions for another calcium atom and a phosphate group to leave the structure. These reactions will result in an area of massive molecular dissociation, which can be visualized in *Figure 3*:

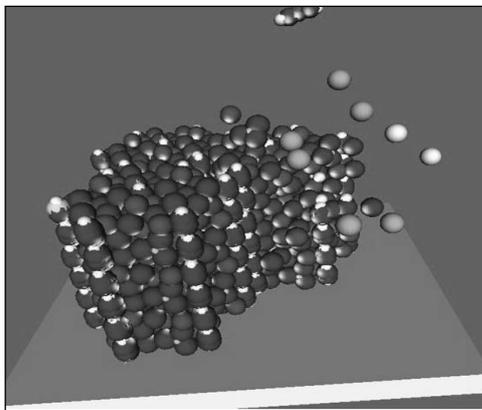
Figure 3. Demineralized HAP prism



These reactions are peculiar to HAP dissolution in acid environment and were studied by Thoman [11] and Zhang and collaborators [12].

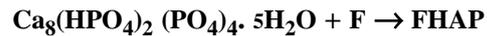
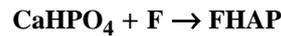
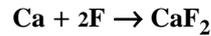
2. *In the presence of fluoride ion*, changes that occur at molecular level in HAP during demineralization process are represented in *Figure 4*. The protons (H^+) from solution will attack the edges of HAP prism inducing molecular dissociation and loss of mineral ions:

Figure 4. Molecular dissociation followed by mobilization of fluoride ions towards vacant positions



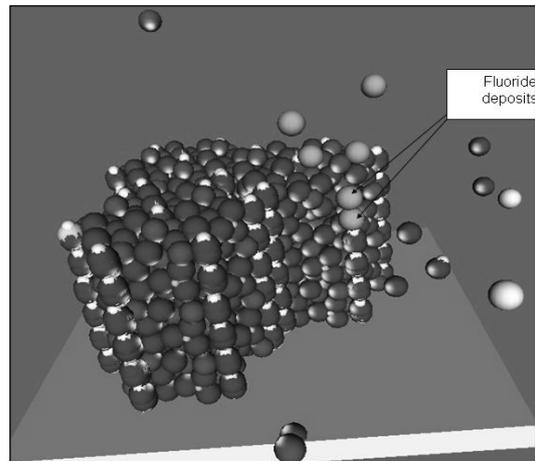
Remineralization in the presence of fluoride ion

At neutral pH and in the presence of fluoride ion, the following reactions can take place [7]:



In *Figures 5* and *6* we represented the changes that occurred at molecular level in the presence of fluoride ion in low concentration (rinsing solution, 226 ppm) comparing to high fluoride concentration (fluoride gel, 12.300 ppm). To simplify, simulation and calculations took into account only the fluoride ion and did not represent the real resulting structures (CaF_2 , FHAP/ FAP).

Figure 5. Positions of fluoride ions from solution (226 ppm F) on the edges of prismatic block

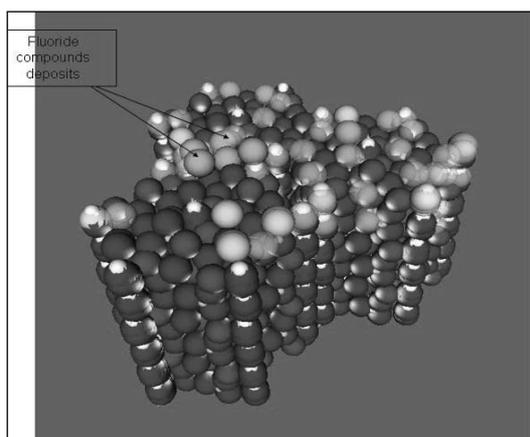


The newly formed structure (FAP, FHAP) will be more resistant to subsequent acid attacks because of their lower solubility. The low concentration fluoride solution allows the access of fluoride ions inside enamel prism and promotes in depth demineralization.

A high concentration compound (fluoride gel) will enable the development of

FAP and FHAP-like deposits, mainly on crystal surface. This reaction can be observed in *Figure 6*:

Figure 6. Fluoride ions deposited on the surface of prismatic block after the use of fluoride gel (12.300 ppm)



The mineral deposits formed on the prism surface will reduce the porosity of superficial layer and will prevent mineral transfer to deep areas, resulting in incomplete remineralization.

Conclusions

1. Dissociation of crystalline structure following demineralization and reconstruction in the presence of fluoride ion (remineralization) was simulated.

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2. It was pointed out that in the presence of fluoride ion in high concentration (fluoride gel), minerals will deposit mainly on the surface of the crystals, while low fluoride concentrations (rinsing solution) could induce a more complete, in-depth remineralization.

3. The incomplete remineralization resulted from surface mineral deposits, blocks the pores and prevents the mineral transfer to deep areas. This action can be followed by a continuation of demineralization in deep areas and the histologically sound layer from the surface could hide a demineralization process below. In the presence of low fluoride ion concentrations, in depth remineralization becomes possible and sub-superficial demineralization is reduced.

4. Based on these findings it can be emphasized that, from a therapeutic point of view, high concentration fluoride products should be used only in high caries risk groups, in conjunction with a frequent use of a low concentration product (such as mouth rinsing solutions and toothpastes).

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Correspondence to: Dr. Monica Păruș, Assist. Prof., PhD, DMD, Discipline of Preventive Dentistry, Faculty of Dental Medicine, „Gr. T. Popa” University of Medicine and Pharmacy. Universității Street, no. 16, Iași. E-mail: mparus@mail.dntis.ro