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Diffusion Controlled Dissolution and Precipitation*

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Dissolution and precipitation reactions that occur in biological systems and in non-stirred in vitro systems generally are diffusion-controlled. Sub-surface demineralization of tooth enamel in dental caries, which has been the subject of considerable interest, is an example of such processes. In the caries process ions from solubilized tooth mineral, i.e., Ca, PO₄, and OH, need to be transported from the lesion below the tooth surface to the plaque and eventually into the saliva. Concomitantly, plaque acid ions must diffuse into the caries lesion to affect demineralization. Several mathematical models have been proposed to describe the diffusion process during caries lesion progression¹⁻⁴. An important factor which until recently had not been taken into consideration in caries models is the effect of the difference in rates of diffusion of the various ions that participate in the demineralization process⁵⁻⁷. We report here the results of a study in which a diffusion cell (Figures 1. and 2.) comprising two compartments separated by a membrane of known ion permselectivity was used as an experimental model to study how the dynamics of diffusion affect dissolution and precipitation of hydroxyapatite and other sparingly soluble calcium phosphates.

Effect of membrane permselectivity on the composition of »lesion« solution: In this bench-scale simulation of the caries process one compartment (the »lesion«) contained an excess of hydroxyapatite, and the solution was kept saturated by stirring. An undersaturated acidic calcium phosphate solution flowed continuously through the other compartment (the »plaque-saliva«), thus providing the driving force for dissolution of the crystals as modified by the permselectivity of the membrane. It was found that the passage of ions through the permselective barrier has profound effects on

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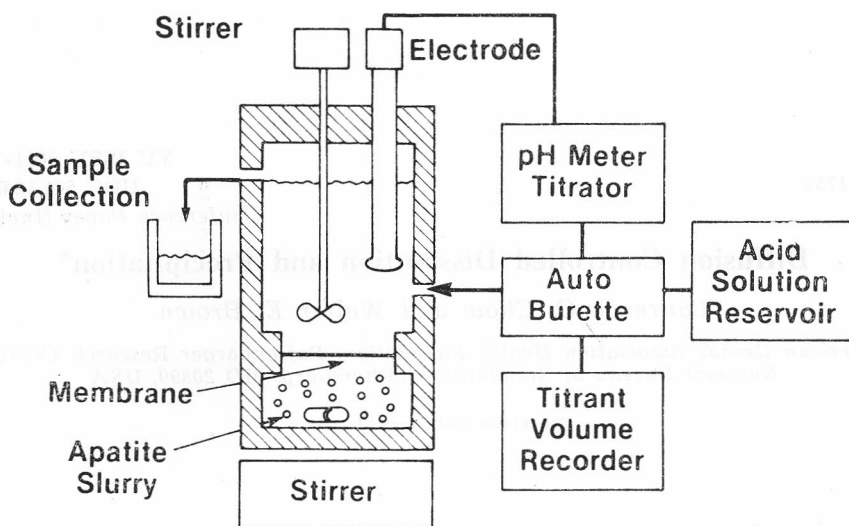


Figure 1.

the composition of the solution within the »lesion«. These changes are produced by unequal rates of diffusion of Ca and PO_4 ions prior to reaching the steady state. Although a neutral salt, such as NaCl, does not directly participate in the dissolution process, it disproportionates under the influence of the membrane potential developed by the unequal rates of diffusion of the »consumed« ions. As a result, even if the Na and Cl concentrations were about equal in the »plaque-saliva« compartment, they become unequal in the »lesion« solution. This in turn caused huge changes in the Ca and P concentrations in the »lesion« solution. With the highly permselective commercial membranes used in these experiments, the Ca/P ratio in the »lesion« solution changed from an initial value of 1.6 to a value as high as 53 or as low as 0.01 at steady state. These large changes in concentration within the »lesion« compartment were found to affect significantly the overall rate of demineralization as described next.

Effects of membrane permselectivity on rates of demineralization: A modified two-compartment diffusion cell (Figure 2) was used in this study. The rates of loss of mineral from the »lesion« compartment were measured by the rates of addition of the solvent acid using a constant composition technique. The results are as follows: (1) the rate of mineral loss decreased with increasing pH of the demineralizing solution. And (2) for a given »plaque« solution the rate of demineralization was the highest with the cation permselective membrane and was the lowest with the anion permselective membrane; the ratio of the two rates was as high as 80 at pH 3.2. It appears that the permselectivity of the membrane strongly affects the rate of demineralization through the following two mechanisms: (1) the unequal diffusion rates through the membrane cause the »lesion« solution composition to change by one or more orders of magnitude from that of the initial state; the new composition in turn affects the diffusion rates of ions. And (2) the permselectivity of the membrane can modify the dominant

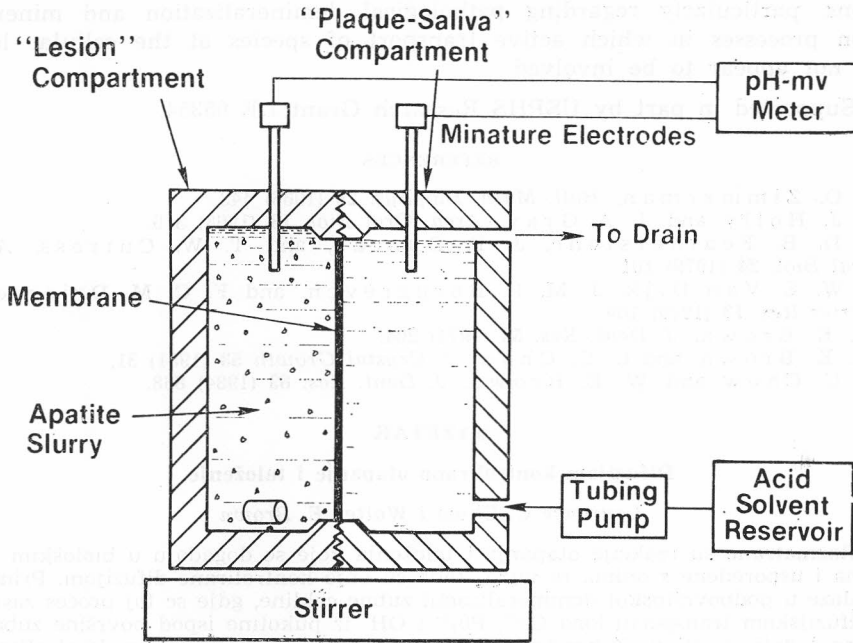


Figure 2.

driving forces for demineralization such that for a given »plaque« acid solution the effective driving force for demineralization can vary greatly with the membrane.

A mechanism for simultaneous dissolution and precipitation of hydroxyapatite: A thermodynamic mechanism is proposed to explain how mineral precipitation is induced by interdiffusion of ions from two solutions. It can be shown that two solutions, both saturated with respect to hydroxyapatite, can have greatly different chemical potentials for the component Ca(OH)_2 or H_3PO_4 . When two such solutions are brought into contact through a membrane, the flow of ions would cause the solution with the lower Ca(OH)_2 potential to become supersaturated, and thus capable of precipitating the mineral. It appears that the major role of the membrane, which can be permselective or neutral, is to prevent free mixing of the solutions. In biological systems the membrane could be the surface of the tissue in which the deposits form. Alternatively, when a solution is in contact with two surfaces of significantly different charges, the above situation may prevail without the presence of a membrane. The model, which is supported by both experimental and theoretical evidence, provides a plausible mechanism for formation/dissolution of mineral deposits, including the formation of a mineral-dense layer over the subsurface caries lesion.

The analysis given above for diffusion-controlled dissolution and precipitation of calcium phosphates can readily be applied to other systems containing salts of weak acids. The results given here have important impli-

cations, particularly regarding pathological demineralization and mineralization processes in which active transport of species at the cellular level does not appear to be involved.

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SAŽETAK

Difuzijom kontrolirano otapanje i taloženje

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Razmatrane su reakcije otapanja i taloženja koje se događaju u biološkim sustavima i uspoređene s onima *in vitro*, kada su obje kontrolirane difuzijom. Primjeri se nalaze u podpovršinskoj demineralizaciji zubne cakline, gdje se taj proces zasniva na difuzijskom transportu iona Ca^{2+} , PO_4^{3-} i OH^- iz pukotine ispod površine zuba do cakline i dalje u slinu. Zakonitosti tog procesa opisuju se difuzijom kontroliranim otapanjem i taloženjem hidroksiapatita, ali se zakonitosti mogu primijeniti i na druge sustave soli i slabih kiselina.