Model for the Dissolution of Calcium Hydroxyapatite Powder

S. Mafé,1,6 J. A. Manzanares,1,6 H. Reiss,*1 J. M. Thomann,1 and P. Gramain1

Department of Chemistry, University of California, Los Angeles, California 90024, and Institut Charles Sadron, CNRS, 67083 Strasbourg Cedex, France (Received: July 31, 1991; In Final Form: September 11, 1991)

A physical model for the dissolution of calcium hydroxyapatite (HAP) is proposed. The experimentally observed self-inhibiting dissolution mechanism is modeled by using the scaled particle theory of hard disks. A Langmuir adsorption isotherm is proposed for the formation of a calcium-rich layer on the surface that constitutes a charged interface inhibiting dissolution. The model provides a quantitative explanation of a number of experimental facts. HAP is the main constituent of bone and dental inorganic tissues, and the proposed theory may constitute a new approach for studying related important phenomena like carious processes.

I. Introduction

Calcium hydroxyapatite (HAP) is the main constituent of biological hard tissues such as the bone and dental inorganic tissues, and its chemical behavior forms a model for the study of important biological phenomena such as carious processes. Therefore, the dissolution mechanism of synthetic or natural HAP in acid media has been extensively analyzed (see refs 1-8 and references therein). A series of experimental studies on the kinetics of dissolution of calcium HAP powder1,2 has been presented by Gramain and co-workers. In particular, the systematic analysis of calcium HAP powder dissolution reported in refs 7 and 8 has been conducted very carefully from the experimental viewpoint, but the proposed theoretical model is based on a rather phenomenological approach. This approach gives a simple first-order law having a rate-reduction factor for the flux of the hydrogen ions causing the dissolution of the HAP. The aim of this paper is to provide a new, simple physical model for the formation of a calcium-rich layer of low apparent permeability to protons on the HAP surface. The model leads to a self-inhibiting mechanism that explains the observed rate-reduction factor, allowing the layer that forms to protect the surface of HAP from continuous dissolution caused by acid attack. The proposed model is based on a Langmuir isotherm for the calcium ions adsorbed onto the HAP surface, a hard disk theory that automatically provides a decrease in the HAP surface area available for attack by hydrogen ions as calcium adsorption is increased, and a simplified form of the Nernst–Planck equation for the calcium transport through the boundary layer between the HAP surface and the bulk solution.

The structure of the paper is as follows. First, we introduce the dissolution reaction, present the physical model, and carefully discuss the simplifying assumptions. Later, we evaluate the Langmuir adsorption isotherm parameters and compare the model with experiment. Finally, we give some plausibility arguments for the order of magnitude of our results. The study of the dissolution of HAP involves many concepts from physics and chemistry and poses a really multidisciplinary problem. It is hoped that by giving a particular physical picture for the HAP dissolution, future experiments aimed to understand the complex interface behavior can be designed and, ultimately, new ideas for the dissolution of HAP may be formulated. The reason for this, of course, is the large size of the molecule. Sixty atoms are involved in forming a molecular vacancy.

VII. Summary and Conclusion

The pairwise central force model was applied to certain molecular properties of C60. Starting with a potential whose constants were determined from the energy of sublimation and the lattice parameter of solid C60, it was used to compute the second virial coefficient of the gas phase, the compressibility, the lattice vibrational specific heat, the surface energy, and the vacancy formation energy of the solid. Not many experimental data are available for comparison, but the results are consistent with existing data.

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References

(2) Fox, J. L.; Doshiya, M. G.; Higuchi, W. I.; Fawzi, M. B.; Wu, M. J. Colloid Interface Sci. 1978, 67, 312.
the study of carious processes will be suggested.

II. Formulation of the Problem

1. Dissolution Reaction of HAP. The dissolution reaction of HAP can be written in the form

\[
(n_c = 1)\text{H}_2\text{O} + \text{Ca}_5(\text{PO}_4)_3\text{OH} \leftrightarrow 5\text{Ca}^{2+} + \\
3[x_1\text{PO}_4^{3-} + x_2\text{HPO}_4^{2-} + x_3\text{H}_2\text{PO}_4^- + x_4\text{H}_3\text{PO}_4] + n_0\text{OH}^{-} \tag{1}
\]

where \( n_c \) is the number of protons consumed when 1 equiv of HAP is dissolved, and \( x_i \) (\( i = 1-4 \)) define the mole fractions of the different phosphate forms present in the solution. Clearly \( n_c \) and the \( x_i \)'s are related by the demands of stoichiometry. The phosphate ion equilibria are

\[
\text{H}_3\text{PO}_4 \leftrightarrow \text{H}_2\text{PO}_4^- + \text{H}^{+}, \quad \text{pK}_1 = 2.19 \tag{2a}
\]

\[
\text{H}_2\text{PO}_4^- \leftrightarrow \text{HPO}_4^{2-} + \text{H}^{+}, \quad \text{pK}_2 = 7.18 \tag{2b}
\]

\[
\text{HPO}_4^{2-} \leftrightarrow \text{PO}_4^{3-} + \text{H}^{+}, \quad \text{pK}_3 = 12.3 \tag{2c}
\]

If a congruent dissolution is assumed,\(^8\) the hydrogen ion flux \( J_H \) and the calcium ion flux \( J_{Ca} \) are related through eq 3, where \( -J_H = R_c J_{Ca} \)

\[
R_c = n_c/s \quad \text{gives the number of protons consumed when one calcium ion is released. According to eqs 2, we have that} \\
R_c = [1 + 3(x_1 + x_2 + x_3 + x_4)]/s \tag{4}
\]

It is clear that \( R_c \) depends on the pH of the solution through the phosphate equilibria defined by eqs 2. For instance, \( R_c = 1.43 \) for pH = 3.5, but \( R_c = 1.30 \) for pH = 6.5.

2. Reactive HAP Surface Area: Scaled Particle Theory for Hard Disks and Langmuir Adsorption Isotherms. As stated in the Introduction, the formation of a calcium-rich layer prevents the solid surface of HAP from continuous dissolution by acid attack.\(^7\)\(^8\)

Here we will simulate this layer by replacing the adsorbed calcium ions on the HAP surface to the bulk solution. Therefore, \( c_c \) in eq 8, as a function of the solution pH, are those characteristic of saturated HAP solutions (see Figure 4 in ref 8).

3. Transport Equation. The transport of calcium ions from the HAP surface to the bulk solution is assumed to occur through a boundary layer of thickness \( d \) (see Figure 3). [It seems necessary to include this layer in the model since experiments\(^7\)\(^8\) show that the dissolution kinetics are stirring-dependent. Figure 3 assumes a quasi-steady state for the calcium transport. This is a reasonable first approximation, since typical experimental times\(^7\)\(^8\) are of the...
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order of 1 min, while the diffusional relaxation time for calcium ions is $t_d = d^2 / D_{Ca} \approx 1$ s for $d = 5 \times 10^{-3}$ cm, and a diffusion coefficient $D_{Ca} \approx 10^{-5}$ cm$^2$/s. Eliciting to look at the system on this temporal scale means that our treatment ignores (1) the initial time needed for the establishment of an equilibrium layer of adsorbed calcium ions and (2) the transient, i.e., the time evolution of the calcium concentration profile in the boundary layer toward the final linear profile. Moreover, it should also be emphasized that exceedingly long times cannot be allowed in our model if we wish to ignore the change in surface area due to the dissolution of HAP. (A study on the variation of particle size with time under the dissolution conditions of ref 6 can be found in ref 13.) However, according to refs 7 and 8, the surface area corresponding to the "sides" of the HAP platelets is negligible compared to the potential in the boundary layer. In our case, it is clear that the adsorbed calcium ions are activated by the absence of information on the change of the dissolution conditions of ref 6 can be found in ref 13.)

The transport equation describing the calcium ion flux is the (simplified) Nernst–Planck equation

$$J_{Ca} = -D_{Ca} \left( \frac{dc}{dx} + 2c \frac{dp}{dx} \right)$$

where $c$ is the calcium concentration, $x$ the spatial coordinate, and $p$ the electric potential in units of $RT/F$. Note that the transport is assumed to occur only in the direction normal to the surface (see Appendices B and C for details). The activity coefficient $\gamma_{Ca}$ is taken to be constant through the boundary layer. This assumption considerably simplifies the problem and is motivated by the absence of information on the change of $\gamma_{Ca}$ with concentration for the complex multicomponent system analyzed in refs 7 and 8. Moreover, the use of a supporting electrolyte in the experimental studies (0.08 M potassium chloride in refs 7 and 8) allows us to neglect the term involving the gradient of electric potential in the boundary layer (see ref 11 for a detailed analysis of the validity of this assumption throughout the volume of a boundary layer). In our case, it is clear that the adsorbed calcium ions create an electric field at $x = 0$. However, the concentrated potassium chloride solution employed as supporting electrolyte causes this field to be screened within a few Debye lengths from $x = 0$. Bearing in mind that $d \approx 5 \times 10^{-3}$ cm $\gg L_D \approx 10^{-2}$ cm, it is reasonable to neglect the second term in the right-hand side of eq 9. Thus

$$J_{Ca} \approx -D_{Ca} \frac{dc}{dx} \approx D_{Ca} \frac{c_i - c_b}{d}$$

![Figure 3. Schematic picture of the concentration profile of calcium ions through a boundary layer of thickness d.](image)

Figure 3. Schematic picture of the concentration profile of calcium ions through a boundary layer of thickness $d$. We denote by $c_i$, $c_b$, and $c_a$ the surface concentration, the volume concentration just outside the adsorption layer, and the bulk concentration of calcium, respectively. A quasi-steady state with a linear concentration profile gradient is assumed.

$\gamma_{Ca}$ is the calcium concentration, $x$ the spatial coordinate, the volume concentration just outside the adsorption layer, and the bulk concentration of calcium, respectively. A quasi-steady state with a linear concentration profile gradient is assumed.

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where the quasi-steady state assumption assumed in Figure 3 has been employed. Note that the effects of stirring observed in refs 7 and 8 can be incorporated into the model through a stirring-dependent value of $d$. From eqs 3 and 10, it is clear that

$$J_{H} = J_{H0} S_0 \approx -R_{Ca} D_{Ca} \frac{c_i - c_b}{d} = -\frac{S_0}{S} \left( \frac{D_{Ca} S}{d} \right) \left( c_i - c_b \right)$$

where we introduce the total specific surface area $S$, and refer $J_{H0}$ to mol g$^{-1}$ s$^{-1}$ and $J_{H}$ to mol cm$^{-2}$ s$^{-1}$. Equation 11 can be readily compared to the final eq 4 of ref 8. If we define $P_{Ca} = D_{Ca} S/d$ and introduce activities instead of concentrations $c$, then eq 11 is identical to eq 4 in ref 8, except for the fact that we now have a particular interpretation for the phenomenological coefficient $1/(1 + k)$ introduced in ref 8 to reconcile theory and experiment (this coefficient is $(S_0/S)$ in our model). We will show in the next section that this interpretation of the adherent surface layer can explain the observed dependence$^b$ of $1/(1 + k)$ on experimental conditions.

### III. Results

1. Evaluating Parameters $\kappa$ and $n_i$ of the Adsorption Isotherm.

Parameters $\kappa$ and $n_i$ can be readily evaluated by comparing our theoretical expression for $S_0/S$ (see eqs 5, 8, and 11) to the experimental results for $1/(1 + k)$ in Figure 3 (full line) of ref 8. This latter figure is a plot of $1/(1 + k)$ vs pH obtained from the experimental slopes of the proton uptake fluxes $J_{H0}$ vs mean calcium activities (see Figure 2 of ref 8). The fitting procedure is as follows. First, we choose different values for the pH and read the corresponding $c_i$ values from the theoretical curve. Then, we substitute the values for $c_i$, and the latter into eq 5, so that five different theoretical points ($S_0/S$, pH) are obtained as functions of the two parameters $\kappa$ and $n_i$. On the other hand, from what has been said above the experimental $S_0/S$ values can be read as $1/(1 + k)$ from Figure 3 in ref 9. Finally, a nonlinear least-squares fitting procedure is applied to the set of five points ($S_0/S$, pH), and the values of the adsorption isotherm parameters are found to be

$$n_i = 2.60 \times 10^{-11} \text{ mol/cm}^2 = 1.56 \times 10^{13} \text{ sites/cm}^2 = 1 \text{ site/640 A}^2$$

$$\kappa = 1.76 \times 10^3 \text{ M}^{-1}$$

The experimental value$^a$ $S_0 = 45 \text{ m}^2 \text{ g}^{-1}$ has been used in the above computations.

2. Variation of $S_0/S$ with pH. Given the $n_i$ and $\kappa$ values of eqs 12, it is possible to plot $S_0/S$ vs pH and compare our theory with experiment. This is done in Figure 4, where the experimental points have been read from Figure 3 of ref 8 and are represented by full squares. It seems clear that the agreement between the two parameter theory and experiment is quite good and provides a physical interpretation of the phenomenological "rate-reduction factor" $1/(1 + k)$ introduced previously$^a$ in order to reconcile theory and experiment. It should be emphasized that such a good agreement cannot be obtained with any other trivial fitting (e.g.,

![Figure 4. $S_0/S$ vs pH. The full squares represent the experimental points in ref 8. The continuous line corresponds to eq 5 in the text with the adsorption parameters of eq 12.](image)
conclusion that the adsorbed calcium ions are relatively immobile by the constant dissolution of the surface itself. Press: Boca Raton, FL, c, be sufficiently smeared out, proportional to the exclusion effect introduced in our model via the hard disk mobile, one might expect that the boundary concentration would have to be the case. For example, if the calcium ions were very on a site, it protects a minimum area of some lo3 site per 9, theory might constitute a first approximation for the study of related important phenomena, e.g., carious processes. Such studies can be motivated by consideration of the orders of magnitude of n, and So/S derived from a comparison of our theory with experiment. To this end, consider the crystallographic data for HAP. The surface of crystalline HAP can be viewed as composed of rhombi of side = 9.4 Å and area s = 75 Å². If we draw a circle of radius r centered at one common vertex (see Figure 5), we see that nine rhombi are approximately totally or partially included within it. Suppose now that only one calcium ion can adsorb onto one of these rhombi. Then, we have one adsorption site per 9 x 75 Å² = 675 Å². This figure can now be compared to the previous result of n = 1 site/640 Å² obtained from our theory. That is, according to our model, if a calcium ion is placed on a site, it protects a minimum area of some 0.1 Å² of HAP against dissolution. In fact, this area is much greater because of the exclusion effect introduced in our model via the hard disk theory. Besides this quantitative agreement, there is the fact that the theory reproduces the experimental requirement that the rate be proportional to c, - c. It is not immediately evident that this would have to be the case. For example, if the calcium ions were very mobile, one might expect that the boundary concentration would be sufficiently smeared out, so that it was more like (S0/S)c, than c, itself. Appendices B and C address this point and lead to the conclusion that the adsorbed calcium ions are relatively immobile and that the equilibrium configuration of the disks is established by the constant dissolution of the surface itself.

**IV. Discussion**

A model for the dissolution of HAP has been presented. The proposed self-inhibiting mechanisms (Langmuir adsorption plus hard disks approximation) is very simple and introduces only two free parameters, κ and νₙ, that characterize the adsorption isotherm. It provides a physical picture by means of which the charged interface, invoked in previous work⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-
probability that a circular region of at least radius \( r \), free of particle centers, will be found. The empty circular region of radius \( r \) is bounded by a circular shell of area \( 2\pi r \). Let \( \rho(\rho_0) \) be the conditional density of centers in this shell. The basic technique is to define a function \( G(r, \rho_0) \) so that

\[
\rho(r, \rho_0) = \rho_0 G(r, \rho_0)
\]  

(A.1)

Thus, \( 2\pi r \rho_0 G(r) \, dr \) has the meaning of the probability of finding a particle center in the shell of a cavity of radius \( r \) (we have omitted the explicit dependence of \( G \) on \( \rho_0 \) for the sake of simplicity). The chance that the shell is empty is given by \([1 - 2\pi r \rho_0 G(r)] \, dr\), and therefore we have that

\[
P_0(r + dr) = P_0(r) \left[ 1 - 2\pi r \rho_0 G(r) \, dr \right]
\]  

(A.2)

Upon expansion of the left-hand side of eq A.2 and subsequent integration between \( r = 0 \) and \( r = 1 \), using \( P(0) = 1 \), we obtain

\[
P_0(r) = \exp \left[ - \int_0^r 2\pi r \rho_0 G(r) \, dr \right]
\]  

(A.3)

\( P_0(r) \) may be given another interpretation. If we denote by \( S_0(r) \) the shaded area in Figure 1, then \( P_0(r) = \frac{S_0(r)}{S} \) and represents the probability that a point chosen randomly in the surface \( S \) will be located in the shaded region.

Let \( L_D \) be the radius of the hard disks. Then the centers of the two particles can never be closer than \( 2L_D \). It can be shown\(^{10} \) that function \( G(r) \) takes the form

\[
G(r) = \begin{cases} 
1, & r < L_D \\
\frac{1}{1 - \pi^2 \rho_0}, & r > L_D 
\end{cases}
\]  

(A.4)

where the first equation in eq A.4 is exact and the second is known to be an excellent approximation.\(^{10} \) Furthermore the following exact\(^{10} \) conditions must be satisfied:

\[
G(L_D) = G(L_D^+) \quad G(\infty) = 1 + 2\pi L_D^3 \rho_0 G(2L_D)
\]  

(A.5)

By applying conditions A.5 to eq A.4, it may be easily shown that

\[
B_0 = \frac{1}{(1 - f)^2} \quad B_1 = -L_D \frac{f}{(1 - f)^2}
\]  

(A.6)

where \( f \) has already been defined in eq 5. Equations A.6 are now substituted into eq A.4 and the resulting function \( G(r) \) into the integral in eq A.3, with the result

\[
\frac{S_0}{S} = \frac{S_0(2L_D)}{S} = P_0(2L_D) = (1 - f) \exp \left\{ - \frac{(3 - 2f) f}{(1 - f)^2} \right\}
\]  

(A.7)

which is the relation appearing in eq 5.

### Appendix B. Dependence of Flux on Boundary Concentrations

It should be noted that in the case under consideration the surface is not homogeneous, so that the diffusive flux of calcium ions diverges from certain surface areas where acid attack takes place. The boundary concentration just out of the reactive domain may be taken equal to \( c_b \). However, with a divergent flux, will the total flux diverge from certain surface areas where acid attack takes place?

To examine this question, we look at the general case proposed in Figure 6. The steady-state continuity equation reduces to Laplace’s equation

\[
\nabla^2 c = 0 \quad \text{over } V
\]  

(B.1)

subject to the boundary conditions

\[
c = c_i \quad \text{over } \Omega_a
\]  

(B.2)

\[
c = c_b \quad \text{over } \Omega_b
\]  

(B.3)

\[
\mathbf{n} \cdot \nabla c = 0 \quad \text{over } \Omega_c
\]  

(B.4)

where \( \mathbf{n} \) represents the outer unit normal vector of the surface \( \Omega_c \) (at every point).

The transformation

\[
C = \frac{c - c_b}{c_i - c_b}
\]  

(B.5)

changes the above equations to

\[
\nabla^2 C = 0 \quad \text{over } V
\]  

(B.6)

\[
C = 1 \quad \text{over } \Omega_a
\]  

(B.7)

\[
C = 0 \quad \text{over } \Omega_b
\]  

(B.8)

\[
\mathbf{n} \cdot \nabla C = 0 \quad \text{over } \Omega_c
\]  

(B.9)

Then, Stokes’ theorem requires

\[
0 = \int \int \int \nabla C dV = \int \int \int \nabla \cdot \mathbf{D} dV = \int \int \int_{\Omega_b} \mathbf{n} \cdot \nabla C dA + \int \int \int_{\Omega_a} \mathbf{n} \cdot \nabla C dA + \int \int \int_{\Omega_c} \mathbf{n} \cdot \nabla C dA
\]  

(B.10)

Note that the last integral in the right-hand side of eq B.10 is equal to zero because of boundary condition B.9. Finally, the total flux can be easily written in the form

\[
J = -D \int \int \int_{\Omega_a} \mathbf{n} \cdot \nabla C dA = (c_i - c_b) \int \int \int_{\Omega_a} \mathbf{n} \cdot \nabla D dA
\]  

(B.11)

If the surface \( \Omega_b \) is of relatively infinite extent compared to \( \Omega_a \) (a configuration that is approximately the case), the \( \Omega_c \) can be chosen to coincide with some of the outermost flow lines of the diffusion pattern, and eq B.9 will be precisely correct. Furthermore, the bulk of the total flux will have been encompassed since very little will exist beyond these outermost flow lines. Thus it can be seen that eq B.11 is asymptotically exact.

Equation B.11 then implies that in the case of diverging diffusion, the total flux is always proportional to the concentration difference \( c_i - c_b \), with a proportionality constant dependent on the particular geometry of the system.

### Appendix C. Effects Due to the Redistribution of Calcium Ions on the Surface

In Appendix B a divergent flux from a single source was studied. However, the HAP surface contains multiple sources distributed according to the equilibrium configuration of hard disks. Such multiple sources must give rise to a “coupled” flux, and it is necessary to inquire into whether the conclusions of Appendix B can be retained under such coupling. To investigate this question, we examine a two-dimensional situation since the associated flux distribution is easier to diagram in two dimensions. However, the reader will quickly see that no essential change in the results would be occasioned by the treatment of the actual three-dimensional case.

Although the multiple sources are statistically (even if not randomly) distributed, we will compromise the reality of our model by assuming that they are positioned on the sites of a regular lattice. For example, in a two-dimensional case, the picture will resemble Figure 7. Here the heavy lines at the bottom of the figure indicate exposed (reactive) source lengths (areas in the three-dimensional case) while the upper dashed line indicates the limit of the Nernst layer of thickness \( d \). The lattice parameter governing the source locations is \( \lambda \). The sources themselves are of length \( \xi \) so that the spaces between them are of length \( \lambda - \xi \). Symmetry allows us to focus on a unit cell of the system like the one shaded in Figure 7.

We introduce an \((x,y)\) coordinate system \((y\) in the vertical direction). The center of the source lies at \((0,0)\) and the boundaries of the unit cell are at \((\pm \lambda/2,0)\). The limit of the Nernst layer lies at \( y = d \). The boundary conditions

\[
\frac{dc}{dy} = 0 \quad y = 0 \quad -\xi/2 < x < -\xi/2
\]

\[
\frac{dc}{dy} = 0 \quad y = 0 \quad -\xi/2 < x < \xi/2
\]

\[
\frac{dc}{dy} = 0 \quad y = d \quad c = c_b \quad y = 0
\]

\[
\frac{dc}{dy} = 0 \quad y = d \quad c = c_i \quad y = 0
\]

\[
\frac{dc}{dy} = 0 \quad y = d \quad c = c_b \quad y = 0
\]

\[
\frac{dc}{dy} = 0 \quad y = d \quad c = c_i \quad y = 0
\]

\[
\frac{dc}{dy} = 0 \quad y = d \quad c = c_b \quad y = 0
\]

\[
\frac{dc}{dy} = 0 \quad y = d \quad c = c_i \quad y = 0
\]

\[
\frac{dc}{dy} = 0 \quad y = d \quad c = c_b \quad y = 0
\]

\[
\frac{dc}{dy} = 0 \quad y = d \quad c = c_i \quad y = 0
\]
are obvious. The first of eqs C.1 derives from the fact that outside the source and the sink (limit of the Nernst layer) there can be no normal flux. The boundary conditions on the sides of the cell
\[
\frac{\partial c}{\partial x} = 0 \quad x = \pm \lambda/2 \quad 0 < y < d \quad (C.2)
\]
stem from considerations of symmetry (a result of the lattice model). Using eqs C.1 and C.2, it requires very little thought to construct an approximate but essentially correct map of the diffusional flux lines. We exhibit this map in Figure 8.

Because of the boundary conditions, an equivalent of the surface in Figure 6 can be found consisting of the horizontal boundaries represented by the dotted lines at the bottom of the cell together with the vertical boundaries of the cell. Thus, the result of Appendix B applies to this cell and the total flux must be proportional to \( c - c_b \).

This would complete our argument if it were not for the fact that the reactive areas were determined by the locations of the calcium ions (the disks) that are constantly changing their positions (although maintaining the equilibrium configuration) as the surface dissolves. If this change of configuration is rapid enough the boundary at \( y = 0 \) would be a "smeared out" uniform entity where the concentration might be something like
\[
c(x,0) = \frac{S_0}{S} c_i \quad (C.3)
\]
Furthermore the flux lines in Figure 8 would be parallel and vertical throughout the length \( d \) so that the flux would be
\[
J = \frac{D}{d} \left( \frac{S_0}{S} c_i - c_b \right) \quad (C.4)
\]
(where \( D \) is the diffusion coefficient) and no longer proportional to \( c - c_b \). We therefore need to estimate the smallest relaxation time of the source distribution that can be tolerated if eq (C.4) is not to be in force. This is rather easy to do. Note that in Figure 8 the flux does become uniform, even with an absolutely immobile distribution of sources, above \( y = h \). Thus, the flux at \( y \geq h \) is essentially ignorant of any reconfiguration of the sources. Also simple scaling ideas indicate that \( h \) must have a length of the order of the cell parameter \( \lambda \). Thus we can set \( h = \lambda \) without damaging the validity of our order of magnitude considerations.

Then, in order to avoid having to use eq C.4, it is necessary only for a diffusing particle to traverse the distance \( h = \lambda \) in a time less than the relaxation time of the source configuration. Thus, if \( \tau \) is this relaxation time, we require
\[
\lambda^2 / D \leq \tau \quad (C.5)
\]
On the real two-dimensional surface there will be \( N_c \) reactive areas of average area \( (s) \) such that \( S_0 = N_c(s) \). Molecular dynamics studies for disks of diameter \( 2L_D \) have been performed (last entry of ref 10) to yield both \( N_c \) and \( (s) \) as a function of the packing fraction \( f \). The unit cell in Figure 7 should be assigned (in the three-dimensional case), the area \( S / N_c \) and the characteristic length \( \lambda \) of the order of \((S/N_c)^{1/2}\). At a value of \( f = 0.5 \), the molecular dynamics result gives
\[
\lambda \approx 50L_D \quad (C.6)
\]
while \( D \) can be estimated as
\[
D \approx 10^{-5} \text{ cm}^2 / \text{s} \quad (C.7)
\]
Substitution of these numbers into eq C.5 gives \( \tau > 7 \times 10^4 \text{ s} \). Thus, this is the shortest relaxation time that can be tolerated. The longest possible relaxation time \( \tau \) should be of the order of the rate of dissolution of a single crystalline plane in HAP; it corresponds to a velocity of dissolution of
\[
v = a / \tau \quad (C.8)
\]
where \( a \) is the lattice parameter normal to the direction of dissolution. If we use the estimate \( a = 10^{-4} \text{ cm} \), then eq (C.7) gives \( v = 10^{-2} \text{ cm/s} \). Clearly, the crystal does not dissolve at this enormous velocity, so that \( \tau \gg 10^4 \text{ s} \). As a result, eq C.4 would be inapplicable. On the other hand, \( \tau \) might be shorter than the time required for the dissolution of a lattice plane. However, the agreement between theory and experiment, in the sense that the rate is proportional to \( c - c_b \), suggest that \( \tau \) is comparable to the time of dissolution of a lattice plane. A simple mechanism for this would involve having the calcium ions so strongly bound to the surface as to be relatively immobile.

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