

A Diffusion Model for Oxygen Reacting with Protein in Ancient Bone

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Abstract

A diffusion model is developed for atmospheric molecular oxygen to react with protein in ancient bones. The model considers protein to be buried beneath rock strata through which gaseous molecular oxygen diffuses and is allowed to react with sites on the protein molecule. Fick's Laws of diffusion and the Arrhenius activation energy/rate equation are used to obtain an equation, dependent on the diffusion constant and activation energy, to compute the rate of reaction. Other applications of the results are also possible.

Key Words

Dinosaur bone, ancient dinosaur protein, ancient protein, protein survival, oxygen diffusion, diffusion.

Introduction

Evidence has been found that soft tissue containing protein exists within ancient dinosaur bones (1-7). Initially this evidence was met with skepticism because good arguments exist that such soft tissue should not survive tens of millions of years but rather should decay on a much shorter time scale (8-9). As a result, the new findings of ancient protein have been controversial (10-14). However the original discoverers of the soft tissue offer explanations, for possible preservation of such soft tissue in fossils, that include rapid mineralization (as distinguished from petrification) of the soft tissue occurring at a rate faster than its decay (15).

The present work does not address the complex questions of the chemistry of early decay of soft tissues nor explanations invoked to explain its preservation. The present work attempts to address only the question of the role of atmospheric oxygen on the possible destruction of initially preserved soft tissue over geologic time, the time since burial, a problem that is not usually addressed. In this work a diffusion model is developed in which atmospheric oxygen diffuses through the rock strata under which the fossil bone is buried and then finally attacks protein sites within the soft tissue.

In the first step oxygen diffuses through the rock overburden before finally colliding with the protein molecules. Diffusion within the bone in this model is not computed separately from that of the rock because it is assumed that the thickness of bone is very small as compared with that of the rock overburden. In fact the diffusion characteristics used for the rock can include that for the bone as in a weighted average. Fick's laws of diffusion are used to compute the frequency with which the oxygen molecule collides with the protein molecule. In the second step the oxygen molecule is allowed to react with sites within the protein molecule. For this step the Arrhenius probability ($\exp(-E_a/RT)$) will be used where E_a is the activation energy. The reaction rate is the product of the collision frequency and the reaction probability. While the results are applied to oxygen diffusing through rock strata toward a buried fossil, the results could be applied to other related problems such as the diffusion and reaction of other chemical species with substrates of paleontological or geological interest.

Method

Fick's second law of diffusion is

$$\frac{\partial C(x, y, z)}{\partial t} = D \nabla^2 C(x, y, z) \quad (1)$$

$C(x, y, z)$ is the concentration of the diffusing oxygen molecules within a medium, in this case the rock overburden above the buried fossil, with diffusion coefficient D . t is time and ∇^2 is the Laplacian, $(\partial^2/\partial x^2 + \partial^2/\partial y^2 +$

$\partial^2/\partial z^2$). In this model, diffusion along only the x coordinate is considered; a one dimensional model. Fick's second law then takes the simpler form:

$$\frac{dC(x)}{dt} = D \frac{d^2C(x)}{dx^2} \quad (2)$$

where x is the distance from the origin and C(x) is the O₂ concentration at x. At steady-state conditions $dC(x)/dt = 0$ and (2) becomes $d^2C(x)/dx^2 = 0$ which after the first integration becomes

$$\frac{dC(x)}{dx} = C_1 \quad (3)$$

where C₁ the first constant of integration. The second integration gives

$$C(x) = C_1x + C_2 \quad (4)$$

where C₂ is the second constant of integration.

Figure 1 shows the boundary conditions to be $C(x=R_d) = CR_d$ and $C(x=R_p) = CR_p$. In Figure 1 the atmosphere is to the left of R_d; the rock through which O₂ diffuses lies between R_d and R_p; and the protein is located to the right of R_p. Substitution of the boundary conditions into (4) gives C₁ and C₂:

$$C_1 = \frac{CR_p - CR_d}{R_p - R_d} \quad \text{and} \quad C_2 = CR_d + R_d \frac{CR_d - CR_p}{R_p - R_d} \quad (5)$$

In the next step only the derivative of C(x) will be used; therefore there is no need to know C₂. C₂ is given in (5) and used in (6) for the sake of completeness. C(x) then becomes

$$C(x) = CR_d + \frac{CR_p - CR_d}{R_p - R_d} (x - R_d) \quad (6)$$

To compute the flux of O₂ through the rock with thickness (R_p - R_d) within the region from R_d to R_p and thereby the collision frequency with the protein, Fick's first law is used. It is

$$J(x) = -D \frac{dC(x)}{dx} \quad (7)$$

After inserting (6) into (7), the result is

$$J = -D \frac{CR_p - CR_d}{R_p - R_d} \quad (8)$$

Using D in units of cm^2s^{-1} , $C(x)$ in units of molecules cm^{-3} , and x in units of cm , J has units of number of O_2 molecules colliding with the surface of the protein per cm^2sec . J is simplified by setting CR_p , the O_2 concentration at R_p to zero, which maximizes the collision frequency. When $R_p - R_d$, the rock thickness, is set equal to B , J becomes

$$J = D \frac{CR_d}{B} \quad (9)$$

A representative protein molecule is considered to have a molecular mass of 50kDaltons comprised of 500 amino acids and to have a volume equal to that of a cube 2 nano meters ($2 \cdot 10^{-7}cm$) on a side, S . Multiplying (9) by the area of the side of the cube located at R_p , the collision frequency (CF) of O_2 with such a molecule is:

$$CF = D \frac{CR_d}{B} S^2 \quad (10)$$

Now the collision frequency is multiplied by the probability that a given collision with a single molecule leads to a reaction, i.e. the Arrhenius probability ($\exp(-E_a/RT)$), the reaction rate (RR) is obtained:

$$RR = D \frac{CR_d}{B} S^2 \exp(-E_a / RT) \quad (11)$$

where E_a is the activation energy in $J/Mole$, $R = 8.3J/MoleK$ and T is temperature in Kelvin.

Finally (11) is multiplied by $3.16 \cdot 10^{15}sec/100$ million years to obtain the number of reactions of O_2 with a single protein molecule over a period of 100 million years:

$$RHMy = 3.16 \cdot 10^{15} D \frac{CR_d}{B} S^2 \exp(-E_a / RT) \quad (12)$$

Results and Conclusions

Equation (12) will now be used to compute combinations of D and E_a for three values of the product of $RHMy$ and B , ($RHMy*B$) namely 10^6 , 10^3 and 1 with B in units of cm . It is suggested here, that a lower limit for $RHMy$ is a value of 1 for a protein molecule to survive with its essential properties intact. The use of equation (12) is shown in Figures 2 and 3. Both figures use $CR_d = 5.4*10^{18}(P)$ molecules of O_2 per cm^3 where P is some fraction of the current oxygen concentration in the atmosphere at earlier times and varies from 0 to 1. The value of P used for both Figures 2 and 3 is 0.86, a value obtained from information given in reference (16), which applies to the last 200 million years. This is 14% less than the present concentration of oxygen in Earth's atmosphere. Figure 2 uses an average Earth global temperature T of 296K, an approximate value obtained by a weighted average over the last 200 million years using data from reference (17). Figure 3 uses $T = 273K$, which will be explained below.

The interpretation of the three lines in Figure 2 is as follows: The top line (line 1) uses the product $RHMy*B$ equal to 10^6 . That is, if $RHMy$ is taken to be equal to 1, B will be $10^6 cm$ or 10^4 meters. If $RHMy$ is taken to be equal to 10, B is $10^5 cm$ or 10^3 meters. Other values of $RHMy$ and B are obtained similarly. For all combinations of $RHMy$ and B whose product is 10^6 , the corresponding values of E_a and D fall on the top line. For all values of E_a and D below that line, the value of the $RHMy*B$ product will be less than 10^6 . The middle line uses the product $RHMy*B$ equal to 10^3 . The bottom line uses the product $RHMy*B$ equal to 1. If the middle line were considered representative of an actual bone-find configuration, and D where taken to be $10^{-10} cm^2sec^{-1}$, not unusual for some minerals, a value of E_a equal to 43.9kJ/Mole would satisfy the criterion. With a B of 10 meters, $RHMy$ is equal to 1.

Because the average temperature under which bones were buried may have been considerably cooler, the results using $T = 273K$ (0 degrees C) are shown in Figure 3. The same comments given above for the 3 curves in

Figure 2 apply with the exception that for the middle curve in Figure 3, at $\log D = -10$, $E_a = 40.5 \text{ kJ/Mole}$ which is about 10% less than 43.9 kJ/Mole when using $T = 296 \text{ K}$ as shown in Figure 2.

The results are relatively insensitive to O_2 concentration: Using $P = 1$ instead of 0.86 the corresponding values of E_a differ by about 1%.

Results using equation (12) can be obtained with other user defined values of the parameters as desired. It is expected that the method and results of this work, illustrated here for oxygen diffusion and its possible effects on buried bone protein, can be used to inquire into the reactivity of other chemical species, transported by diffusion, with buried materials. At a minimum the results presented in this work can provide a framework for discussion when considering the relative importance of the several parameters responsible for destruction of buried material and can provide quantitative answers as measured or computed diffusion constants and activation energies become available.

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Figure 1 Caption

This schematic diagram shows the two boundary conditions used to evaluate constants C_1 and C_2 in equation (4).

Figure 2 Caption

Equation (12) is solved for the diffusion constant D and activation energy E_a using three values for the product of $RHMy$ and B , ($RHMy*B$), namely 10^6 (top line), 10^3 (middle line) and 1(lowest line) with B in units of cm . $CR_d = 5.4*10^{18}(P)$ where $P = 0.86$ and $T = 296K$. See text for more detailed explanation and interpretation.

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Figure 1

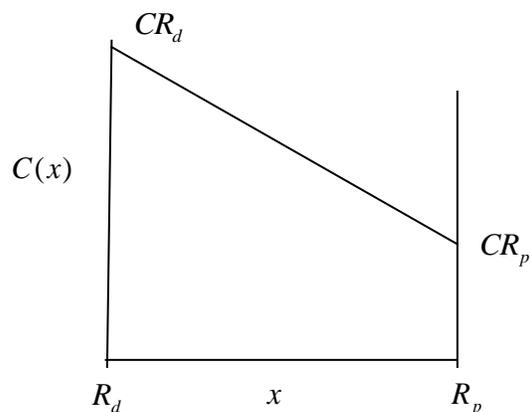


Figure 2

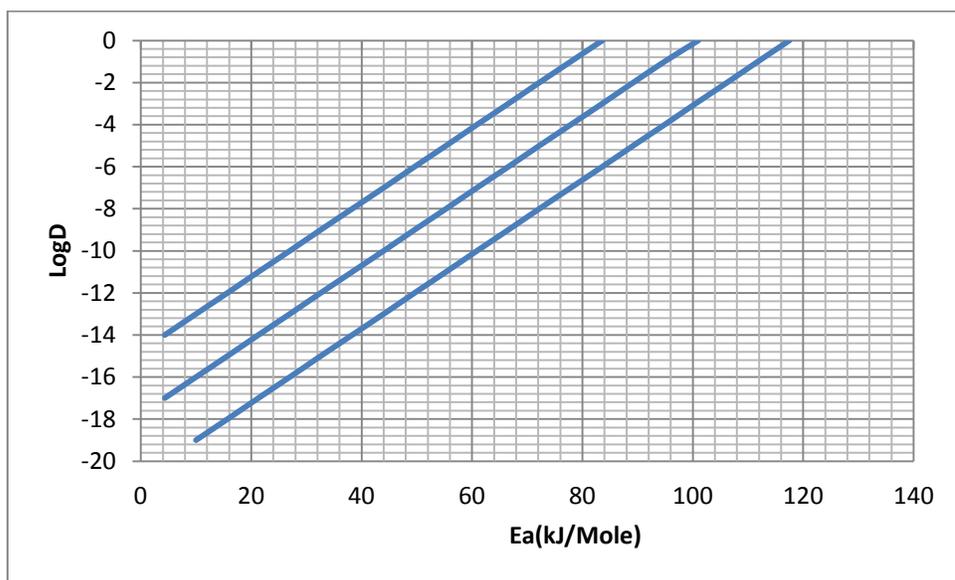


Figure 3

