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A mathematical model for the distribution of dissolved silicon in interstitial waters—an analytical approach

by George T. F. Wong¹ and Chester E. Grosch¹

ABSTRACT

A mathematical model for the distribution of dissolved silicon in interstitial waters is studied. This model includes the input flux of particulate silicon, bioturbation, the dissolution of silicon particles, and the diffusion of dissolved silicon in the interstitial water. It is shown that the model reduces to a nonlinear eigenvalue problem. This problem is shown to have only one eigenvalue which is determined by the solution of a simple algebraic equation. The eigenfunction is shown to be expressible in closed form in terms of elementary functions. The solution falls into one of three classes: 1) all the particles dissolve and the interstitial water at depth is not saturated; 2) all the particles dissolve and the interstitial water at depth is saturated; and 3) the interstitial water at depth is saturated but not all the particles are dissolved. The equations and solutions are analyzed and the dependence of concentration profiles on the parameters of the model is discussed. An exact predictor equation for the particulate flux in terms of the model parameters is also derived. The results of a number of sample calculations and simulations of the concentration profile for two actual cores are also given.

1. Introduction

Marine geochemists have devoted a considerable amount of effort to study of the composition of sediments and interstitial waters (Riley and Chester, 1976a, 1976b). One objective of these investigations is to improve the understanding of the history of the earth because marine sediments may contain the most complete record available. Moreover, these studies may allow the investigators to assess the fluxes of chemical species into and out of the sediments. These fluxes could have a profound effect on the geochemical mass balance of the oceans (Gieskes, 1975). In order to reach these goals, mathematical models have often been used to quantify the various processes that may affect the distribution of an element in the sediments and interstitial waters and to identify their relative importance. (Anikouchine, 1967; Berger and Heath, 1968; Tzur, 1971; Guinasso and Schink, 1975; Imboden, 1975; Lerman and Lietzke, 1977; Goreau, 1977; Schink and Guinasso, 1977).

Silicon is one of the elements in sediments and interstitial waters that has been intensively studied (Siever *et al.*, 1965; Anikouchine, 1967; Fanning and Schink,

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1969; Fanning and Pilson, 1971; Bischoff and Sayles, 1972; Hurd, 1973; Schink *et al.*, 1974, 1975) because it may play a central role in buffering the pH of seawater and in controlling the concentrations of major cations in seawater (Sillen, 1961; Garrels, 1965; Mackenzie and Garrels, 1965).

The earlier models of Anikouchine (1967) and Hurd (1973) were based on the assumption that the distribution of dissolved silicon in interstitial waters is controlled by physical processes, such as diffusion and advection, and the dissolution of silicon containing solid phases. Advection was found to be unimportant when the sedimentation rate is low as in the deep ocean. Anikouchine proposed clays as a possible silicon source and Hurd suggested biogenic particulate silicon, such as opal, as the solid phase. In both models, it was assumed that saturation is reached with respect to a certain solid phase at depth and that an equilibrium concentration is reached. Schink *et al.* (1975) realized that large variations in concentrations in interstitial waters have been observed in both the Atlantic (Schink *et al.*, 1974) and the Pacific (Hurd, 1973), and that these variations are not related to the mineral distributions. Moreover, it has been long recognized that stirring by benthic organisms, or, bioturbation, may have a significant effect on the concentration profile of an element in the sediments (Berger and Heath, 1968). Thus, they proposed a modified model in which both the input flux of particulate silicon and bioturbation have been incorporated together with diffusion and the dissolution of particles.

The mathematical form of the model is a pair of coupled nonlinear partial differential equations in time and one space dimension together with boundary conditions. Schink *et al.* (1975) first assumed that the concentrations are in steady state thereby reducing the equations to ordinary differential equations. Then they replaced the spatial derivatives by finite difference approximations and solved the coupled difference equations by an iterative procedure. This model has certainly offered substantial improvements over the earlier models and has approximated the natural conditions more closely.

The results of these calculations are quite interesting but the solution procedure presents a number of problems. Fundamentally, these problems arise from the fact that the structure of the equations and solutions are not analyzed but are only inferred from a large number of numerical calculations. The equations and boundary conditions, as used by Schink *et al.* (1975), contain seven independent dimensional parameters, thus requiring a large number of calculations to explore the solution space. The use of numerical calculations in place of analysis obscures the basic structure of the problem and leads to an erroneous statement; namely that there are no steady state solutions if the pore water saturates (siliceous ooze). Finally the two predictor equations derived from the results of these numerical calculations are only approximate.

In this paper, we shall use the same mathematical equations as Schink *et al.* (1975) for dissolved silicon in interstitial waters. However, instead of using a numeri-

cal procedure for solving the equations, we shall obtain a solution analytically. We shall show that this model reduces to a single second order, nonlinear eigenvalue problem which contains only two independent, dimensionless parameters. For any pair of values of these parameters, there is only one eigenvalue and the corresponding eigenfunction can be expressed in closed form in terms of elementary functions. The numerical solutions of Schink *et al.* (1975) are special cases of the general solutions presented here. Moreover, in contrast to the statement of Schink, *et al.* (1975) there are steady state solutions to the model for the case of siliceous ooze. In addition we will derive exact predictor equations for the interstitial water concentration at depth and the flux of dissolved silica from the sediments in terms of the parameters of the model. Finally, we will present a number of sample calculations to illustrate the analytical solution procedure. Our results suggest that, aside from being mathematically elegant, the analytical approach can yield substantially more information and provide a better tool for understanding and quantifying the processes governing the distribution of dissolved silicon in interstitial waters.

2. The diffusion-dissolution model

Schink *et al.* (1975) proposed that the concentration of silicon in interstitial waters may be described by the following equations:

$$(\phi + K^*_D) \frac{\partial C}{\partial t} = \phi D_c \frac{\partial^2 C}{\partial z^2} + K_B \frac{(C_f - C)}{C_f} B, \quad (1)$$

$$\frac{\partial B}{\partial t} = D_B \frac{\partial^2 B}{\partial z^2} - K_B \frac{(C_f - C)}{C_f} B, \quad (2)$$

where: z is the distance below the water-sediment interface, and $z = 0$ at the interface,

t is time,

C_f is the saturation concentration of silicon in solution (g/cm^3),

B is the concentration of dissolvable particulate silicon in the sediments (g/cm^3),

ϕ is the porosity of the sediment and is equal to the ratio of the partial volume of the liquid phase to the total volume of the liquid and solid phases,

D_c is the 'effective' molecular aqueous diffusion coefficient (cm^2/sec). That is $D_c = D_m/\theta^2$, with D_m the molecular aqueous diffusion coefficient and $\theta = dl/dz$ with l the path length in the aqueous phase.

K^*_D is the mean distribution coefficient for adsorption of the dissolved silicon onto the sediments,

K_B is the first-order reaction rate constant for the dissolution of the particulate silicon ($1/\text{sec}$),

D_B is the 'effective' particulate diffusion coefficient due to sediment mixing by benthic organisms (cm^2/sec).

C is the concentration of dissolved silicon in interstitial waters at z .

Schink *et al.* (1975) assumed that ϕ , K^*_D , D_C , K_B , C_f , and D_B are constants and looked for steady state solutions to equations (1) and (2). Their steady state model is then

$$\phi D_c \frac{d^2 C}{dz^2} + K_B \frac{(C_f - C)}{C_f} B = 0, \quad (3)$$

$$D_b \frac{d^2 B}{dz^2} - K_B \frac{(C_f - C)}{C_f} B = 0. \quad (4)$$

The imposed boundary conditions are:

$$C = C_o \text{ at } z = 0 \quad (5)$$

$$\frac{dC}{dz} \rightarrow 0 \text{ as } z \rightarrow \infty, \quad (6)$$

$$D_B \frac{dB}{dz} = F_B \text{ at } z = 0, \quad (7)$$

$$\frac{dB}{dz} \rightarrow 0 \text{ as } z \rightarrow \infty. \quad (8)$$

F_B is the flux of particulate silicon through the water-sediment interface.

3. Scaling of the equation and boundary conditions

Equations (3)-(8) contain seven constants. The analysis and solution of this problem are facilitated by scaling the equations and boundary conditions. Let

$$x = z / \sqrt{\phi D_B / K_B}, \quad (9)$$

$$r = \phi (C_f - C) / C_f, \quad (10)$$

$$b = (D_B / D_C) (B / C_f). \quad (11)$$

Then equations (3)-(8) are, in nondimensional form,

$$\frac{d^2 r}{dx^2} - br = 0, \quad (12)$$

$$\frac{d^2 b}{dx^2} - rb = 0, \quad (13)$$

$$r(0) \equiv r_o = \phi (C_f - C_o) / C_f \quad (14)$$

$$\frac{dr}{dx} \rightarrow 0 \text{ as } x \rightarrow \infty, \quad (15)$$

$$\left(\frac{db}{dx} \right)_{x=0} \equiv F_o = (\sqrt{\phi D_B / K_B}) (F_B / C_f D_C), \quad (16)$$

$$\frac{db}{dx} \rightarrow 0 \text{ as } x \rightarrow \infty . \quad (17)$$

The differential equations are, in this form, parameter-free. The only parameters of the problem appear in the boundary conditions and they are r_0 , the dimensionless concentration defect at the water-sediment interface and F_0 , the dimensionless particulate flux at the water-sediment interface.

4. Solution of the boundary-value problem

Equations (12) and (13) are a pair of coupled nonlinear ordinary differential equations and the general properties of the solution to this boundary-value problem can be easily found. The general solution can be expressed in terms of familiar, known functions: Elliptic or Pseudo-Elliptic integrals, or equivalently, Jacobian Elliptic functions.

First, subtract equation (12) from (13) giving

$$\frac{d^2b}{dx^2} - \frac{d^2r}{dx^2} = 0 . \quad (18)$$

Integrating once

$$\frac{db}{dx} - \frac{dr}{dx} = A , \quad (19)$$

where A is a constant. Because $\frac{db}{dx}$ and $\frac{dr}{dx}$ approach zero as $x \rightarrow \infty$, we must have $A \equiv 0$. Reverting to dimensional variables, equation (19) is equivalent to

$$D_B \frac{dB}{dz} = -\phi D_c \frac{dC}{dz} \quad (19a)$$

This equation states that the downward flux of particulate silica is equal to the upward flux of dissolved silica at all depths; in particular $z = 0$, the water-sediment interface.

Setting $A = 0$ and integrating (19), we have

$$b - r = \lambda \quad (20)$$

with λ a constant. Thus the difference between the dimensionless particulate silicon concentration and the dimensionless dissolved silicon defect is a constant at all x . In dimensional form, equation (20) implies that

$$D_B B + \phi D_c C = (\lambda + \phi) D_c C_f \quad (20a)$$

Since the diffusion coefficients, porosity and λ are constants, the weighted sum of the concentration of particulate silicon and dissolved silica is constant at all depths. In other words, the total mass of silica per unit volume is a constant, independent

of depth. This is the result of the assumptions that a steady state exists and that silica is conserved. As will be shown below, λ is not an arbitrary parameter but is a function of the concentration of dissolved silica and the flux of particulate silica at the water-sediment interface.

Now

$$b = r + \lambda \quad (20b)$$

and substituting into equation (12)

$$\frac{d^2r}{dx^2} - \lambda r - r^2 = 0. \quad (21)$$

The boundary conditions for equation (21) are, equation (14),

$$r(0) = r_0, \quad (22)$$

and, using equations (16) and (19), with $A = 0$,

$$\left(\frac{dr}{dx} \right)_{x=0} = F_0, \quad (23)$$

as well as equation (15)

$$\frac{dr}{dx} \rightarrow 0 \text{ as } x \rightarrow \infty. \quad (23a)$$

Equation (21) is nonlinear but is of a form that can be made exact by multiplying by an integrating factor. Multiply equation (21) by $2 \frac{dr}{dx}$ and integrate, thus

$$\begin{aligned} \int_0^x \left[2 \frac{dr}{dx} \frac{d^2r}{dx^2} \right] dx &= 2 \int_0^x \left[\lambda r \frac{dr}{dx} + r^2 \frac{dr}{dx} \right] dx, \\ \left(\frac{dr}{dx} \right)^2 - F_0^2 &= \lambda (r^2 - r_0^2) + (2/3) (r^3 - r_0^3), \\ F^2 &\equiv \left(\frac{dr}{dx} \right)^2 = F_0^2 + \lambda (r^2 - r_0^2) + (2/3) (r^3 - r_0^3). \end{aligned} \quad (24)$$

The boundary conditions at $x = 0$, equations (22) and (23), have been used. Integrating once more, assuming that $F < 0$ (It is assumed that C increases with depth, so $(dC/dz) > 0$ and this implies that $F = (dr/dx) < 0$.)

$$\int_r^{r_0} \frac{d\xi}{\sqrt{P(\xi)}} = \sqrt{2/3} x, \quad (25)$$

where

$$P(r) \equiv r^3 + \frac{3}{2} \lambda r^2 + \frac{3}{2} \left[F_0^2 - \lambda r_0^2 - \frac{2}{3} r_0^3 \right]. \quad (26)$$

The integral on the left-hand side of equation (25) can be expressed in terms of Elliptic or Pseudo-Elliptic integrals, or alternatively we can write r in terms of Jacobian Elliptic Functions of x . Note that this solution satisfied the boundary conditions at $x = 0$ for any value of λ , ie, $r = r_0$ and $F = \frac{dr}{dx} = F_0$ at $x = 0$.

5. Determination of λ and the solutions

Although it has not been stated explicitly, there is one further condition which the solutions to equations (12)-(17) must satisfy in order to be acceptable: r , b , and their derivatives through second order must be continuous functions of x . There are three classes of solutions which are acceptable.

The first class consists of those solutions for which all the particles dissolve and the interstitial water is *not* saturated. If all the particles dissolve at some depth x_1 , say, then $b(x_1) \equiv b_1 = 0$. In order for the solution to be continuous, $F(x_1) \equiv F_1 = 0$; therefore $r(x_1) \equiv r_1$ must be the largest real root of (24) or alternatively (26). Now from (20b)

$$0 = b_1 = r_1 + \lambda, \quad (27)$$

or $-\lambda$ must be the largest real root of equation (26). Substituting $-\lambda$ for r in (26), we see that

$$\lambda^3 - 3r_0^2\lambda + 3F_0^2 - 2r_0^2 = 0, \quad (28)$$

and that $0 < -\lambda < r_0$. Assuming that a root of equation (28) lies in this range, the solution in $0 < x < x_1$ is given by equation (25).

If λ is a root of (28) such that $0 < -\lambda < r_0$, then it can be shown that

$$P(r) = (r + \lambda)^2(r - \lambda/2), \quad (29)$$

and that the integral in equation (25) is a Pseudo-Elliptic integral and can be expressed in terms of elementary functions. The solution, which is the eigenfunction of the problem, is

$$r = \left(\frac{-\lambda}{2} \right) \left\{ 3 \left[\frac{1 + \Gamma_1 \exp(-\sqrt{-\lambda} x)}{1 - \Gamma_1 \exp(-\sqrt{-\lambda} x)} \right]^2 - 1 \right\} \quad (30)$$

where

$$\Gamma_1 = (\sqrt{r_0 - (1/2)\lambda} - \sqrt{-(3/2)\lambda}) / (\sqrt{r_0 - (1/2)\lambda} + \sqrt{-(3/2)\lambda}). \quad (31)$$

and $x_1 = \infty$, that is $r \rightarrow -\lambda$, $F \rightarrow 0$ and $b \rightarrow 0$ as $x \rightarrow \infty$.

The second class of solutions consists of those solutions for which all the particles have dissolved at the same depth at which the interstitial water saturates. In order to have a solution in this class

$$\lambda = 0, \quad (32)$$

$$F_0^2 = -\frac{2}{3} r_0^3. \quad (33)$$

For this class of solutions,

$$P(r) = r^3, \quad (34)$$

and the solution, which is the eigenfunction, is

$$r = r_0 / (1 + \sqrt{r_0/6} x)^2. \quad (35)$$

As $x \rightarrow \infty$, $r \rightarrow 0$, $F \rightarrow 0$, and $b \rightarrow 0$.

The third class of solutions consists of those solutions for which the interstitial water is saturated before all the particles dissolve. If the interstitial water is saturated at some depth x_1 , say, then $r(x_1) \equiv r_1 = 0$. In order for the solution to be continuous $F(x_1) \equiv F_1 = 0$; therefore $r_1 = 0$ must be the largest real root of equation (26). If $r_1 = 0$ is a root of equation (26) then

$$\lambda = (F_0/r_0)^2 - \frac{2}{3} r_0, \quad (36)$$

and from equation (20b), $\lambda > 0$.

If such a value of λ exists, then the solution is given by equation (25) for $0 < x < x_1$.

For this class of solutions,

$$P(r) = r^2 \left(r + \frac{3}{2} \lambda \right), \quad (37)$$

and the integral in equation (25) is again a Pseudo-Elliptic Integral. The integration is performed and the solution, which is the eigenfunction, is

$$r = \left(\frac{3}{2} \lambda \right) \left\{ \left[\frac{1 + \Gamma_2 \exp(-\sqrt{\lambda} x)}{1 - \Gamma_2 \exp(-\sqrt{\lambda} x)} \right]^2 - 1 \right\} \quad (38)$$

where

$$\Gamma_2 = (\sqrt{2r_0 + 3\lambda} - \sqrt{3\lambda}) / (\sqrt{2r_0 + 3\lambda} + \sqrt{3\lambda}). \quad (39)$$

and $r \rightarrow 0$, $b \rightarrow \lambda$, and $F \rightarrow 0$ as $x \rightarrow \infty$, ie $x_1 = \infty$.

In summary, physically acceptable solutions of class one exist if, and only if

$$F_0^2 < -\frac{2}{3} r_0^3, \quad (40)$$

of class two, if and only if

$$F_0^2 = -\frac{2}{3} r_0^3, \quad (41)$$

and of class three, if and only if,

$$F_0^2 > \frac{2}{3} r_0^3. \quad (42)$$

This discussion shows that λ is an *eigenvalue*. The differential equation (21) and boundary condition (22) through (23a) constitute a nonlinear eigenvalue problem, although Schink *et al.* (1975) who first proposed the problem in the form of equations (3) through (8), apparently might not have realized this. This problem can be solved in closed form in terms of elementary functions [equations (30), (34), and (39)] and the eigenvalue equation is an algebraic equation.

In addition to the closed form solutions, this analysis has yielded several important results. First, and perhaps most important, we have found a simple, explicit criterion to determine from the flux and interstitial water concentration at the water-sediment interface whether the silicon particles will completely dissolve, leaving the interstitial water unsaturated or whether the interstitial water will saturate before all the silicon particles are dissolved. If

$$F_0^2 > \frac{2}{3} r_0^3,$$

the interstitial water saturates before all particles are dissolved. If

$$F_0^2 < \frac{2}{3} r_0^3,$$

all particles dissolved before the interstitial water is saturated. Finally, if

$$F_0^2 = \frac{2}{3} r_0^3$$

the last of the particles dissolve at the same depth as the interstitial water saturates. Putting equation (41) back into dimensional quantities gives a critical value of the particle flux at the water-sediment interface.

$$(F_B)_{\text{crit}} = \frac{2}{3} \phi^2 (K_B D_c^2 / C_I D_B) (C_I - C_0)^3. \quad (43)$$

If $F_B < (F_B)_{\text{crit}}$, all the silicon particles dissolve before the interstitial water saturates. If $F_B > (F_B)_{\text{crit}}$, the interstitial water saturates before all particles are dissolved.

Schink *et al.* (1975) have stated (see caption to Figure 9 of their paper) that the model does not have steady state solutions if the interstitial water saturates. This is not correct. Steady state solutions of the third class (the interstitial water is saturated and not all the particles are dissolved) exist if $F_0^2 > (2/3)r_0^3$ and these solutions satisfy the differential equations, the boundary conditions and are continuous and have continuous derivatives through second order, in fact of all orders, for all $x < 0$. We will give an example of this class of solutions below.

Once the eigenvalue, λ , has been found by solving the algebraic equation (28), (32), or (36), the surface concentration of particles can be determined immediately

as well as the concentration of dissolved silicon and the equilibrium concentration of silicon particles at great depths. Letting the subscript ' ∞ ' refer to values as $x \rightarrow \infty$, we have: For a solution of the first class,

$$F_0^2 < \frac{2}{3} r_0^3,$$

$$b_\infty = \left(\frac{db}{dx} \right)_\infty = \left(\frac{d^2b}{dx^2} \right)_\infty = 0,$$

A solution of the second class is found if ($\lambda=0$), $F_0^2 = 2/3 r_0^3$.

Then

$$r_\infty = \left(\frac{dr}{dx} \right)_\infty = \left(\frac{d^2r}{dx^2} \right)_\infty = 0,$$

$$b_\infty = \left(\frac{db}{dx} \right)_\infty = \left(\frac{d^2b}{dx^2} \right)_\infty = 0.$$

Finally, a solution of the third class has

$$F_0^2 > 2/3 r_0^3,$$

$$r_\infty = \left(\frac{dr}{dx} \right)_\infty = \left(\frac{d^2r}{dx^2} \right)_\infty = 0$$

$$b_\infty = \lambda, \left(\frac{db}{dx} \right)_\infty = \left(\frac{d^2b}{dx^2} \right)_\infty = 0.$$

6. The flux of silica through the water-sediment interface

One quantity of great interest to geochemists is the flux of dissolved silicon through the water-sediment interface. From equation (19a) we see that

$$-\left(\frac{dC}{dz} \right)_{z=0} = \phi \left(\frac{D_B}{D_c} \right) \left(\frac{dB}{dz} \right)_{z=0}$$

but, in general, the particulate flux, $\frac{dB}{dz}$, is not easily measurable. Therefore, we must derive an equation for $\frac{dC}{dz}$ at $z=0$ in terms of the other parameters of the model. Apart from the diffusion coefficients, dissolution rate, and porosity, two parameters which are measurable are C_0 and C_∞ , the concentrations of dissolved silicon at the water-sediment interface and the equilibrium concentration at great depth in the sediment. We have derived expressions for the flux of dissolved silicon in terms of C_0 , C_∞ , or in the case of siliceous ooze of B_∞ , and the other model parameters.

For the Class I solutions, from equation (27)

$$r_\infty = -\lambda.$$

Substituting for λ in equation (28), expressing the variables in dimensional terms and using equations (7), (16) and (19a)

$$\begin{aligned} \text{Flux} &= \phi D_c \left(\frac{dC}{dz} \right)_{z=0} \\ &= \phi D_c C_f \left\{ \left(\frac{2}{\phi} \right) \left(1 - \frac{C_0}{C_f} \right)^2 + \left(1 - \frac{C_\infty}{C_f} \right) \left[\left(1 - \frac{C_\infty}{C_f} \right)^2 - 3 \left(1 - \frac{C_0}{C_f} \right)^2 \right] \right\}^{1/2} / \sqrt{3D_B/K_B} \end{aligned} \quad (44)$$

An analogous expression can be obtained for the Class II solutions. In this case

$$\text{Flux} = \phi D_c \left(\frac{dC}{dz} \right)_{z=0} = \phi D_c C_f \left(1 - \frac{C_0}{C_f} \right)^{3/2} / \sqrt{3D_B/2K_B}. \quad (45)$$

A Class II solution may never exist in nature because the existence of this type of solution requires an exact balance between the flux and the surface concentration. Nevertheless, this case is extremely important because it provides a lower limit of the flux for siliceous oozes to exist. If the interstitial water is saturated at depth, then

$$\text{Flux} = \phi D_c \left(\frac{dc}{dz} \right)_{z=0} \geq \phi DC C_f \left(1 - \frac{C_0}{C_f} \right)^{3/2} / \sqrt{3D_B/2K_B}. \quad (46)$$

Thus, if no residual dissolvable particulate silicon is present at depth, aside from the approximately known constants D_c , C_f , D_B , and K_B (Schink *et al.*, 1975), the flux of silicon into the water column will depend on the variables C_0 , C_∞ and ϕ , and these values can be easily measured.

Finally, for the Class III solution, in siliceous oozes, we find, in a similar way, that

$$\begin{aligned} \text{Flux} &= \phi D_c \left(\frac{dC}{dz} \right)_{z=0} \\ &= \phi D_c C_f \left(1 - \frac{C_0}{C_f} \right) \left[\left(\frac{D_B}{\phi D_c} \right) \left(\frac{B_\infty}{C_f} \right) + \frac{2}{3} \left(1 - \frac{C_0}{C_f} \right) \right]^{1/2} / \sqrt{D_B/K_B} \end{aligned} \quad (47)$$

In this case, the interstitial water is saturated so that $C_\infty = C_f$, and, the residual concentration of particulate silicon, B , and the ratio of bioturbation to diffusion rate (D_B/D_c) may also become important in determining the flux of dissolved silicon into the water column.

7. Some sample problems

In order to illustrate the behavior of the solutions, we have calculated the con-

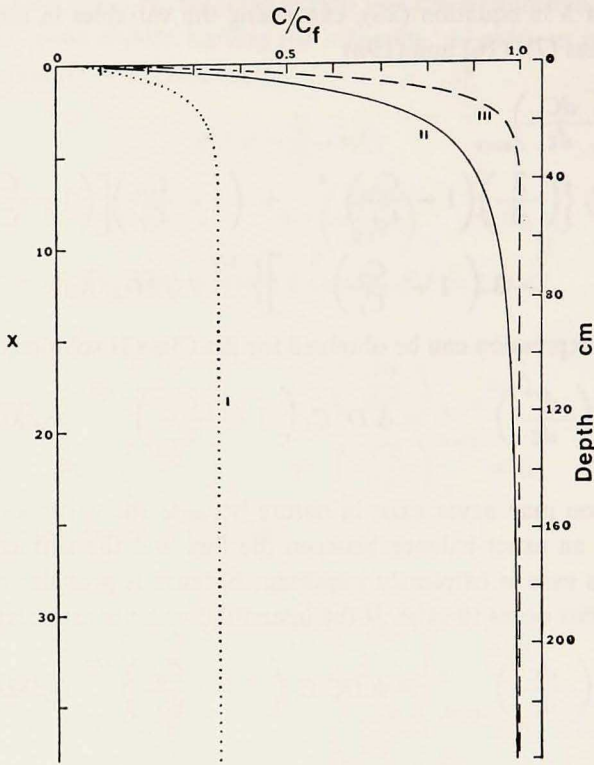


Figure 1. Simulated profiles of dissolved silicon in interstitial waters with increasing particulate flux. C and C_f are the concentration at any depth z and concentration at saturation respectively. x is the nondimensional depth as shown in equation 9 of the text. z is the corresponding real depth if porosity (ϕ) is 0.8. The rate of dissolution (K_B) and the bioturbation diffusion coefficient (D_B) are 10^{-9} sec^{-1} and $5 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ respectively. The three cases represent the situations where saturation is not reached at depth (I), where saturation is reached at depth but all dissolvable particulate silicon has been exhausted (II), and where saturation is reached at depth and excess particulate silicon is present (III), respectively.

centration-depth profiles for a few sample cases. Schink *et al.* (1975) gave ranges of values of the parameters and we have chosen median values from these ranges. These values are:

$$\begin{aligned}\phi &= 0.8 \\ D_c &= 4 \times 10^{-6} \text{ cm}^2/\text{sec} \\ K_B &= 10^{-9} \text{ sec}^{-1} \\ D_B &= 5 \times 10^{-8} \text{ cm}^2/\text{sec} \\ C_f &= 1.0 \mu \text{ mol}/\text{cm}^3 \\ C_0 &= 0.05 \mu \text{ mol}/\text{cm}^3\end{aligned}$$

and three values of F_B ; 1.000×10^{-7} , 2.705×10^{-7} , and 4.500×10^{-7} μ mol/cm²-sec. With this choice of values $r_0 = 0.760$ for all cases and $F_0 = 0.200$, 0.541, and 0.900.

The first example, $r_0 = 0.760$, $F_0 = 0.200$, gives a solution of the first class; the second, $r_0 = 0.760$, $F_0 = 0.541$, gives a solution of the second class; while the third example yields a solution of the third class. These examples show the effect of increasing particle flux, while holding all the other parameters constant.

Figure 1 is a plot of C/C_f versus the dimensionless depth, x . The scale on the right-hand side is the depth in centimeters. In all cases the surface concentration is the same, $C_0/C_f = 0.05$. In the first case (I), the particles dissolve and the equilibrium concentration is reached at $x \cong 6$ (e.c. $\cong 30$ cm). The other two cases have the pore water saturated at depth. For the second case (II), $C \rightarrow C_f$ quite slowly with increasing x because of the algebraic dependence (equation 35) of r on x . Finally, in the third case (III), the interstitial water is effectively saturated at a depth of about 40 cm.

These sample calculations show that by using values presently considered reasonable for the various parameters in the model, most of the concentration changes occur in the top 10 to 20 cm of the core. Thus, the common practice of sampling interstitial waters by squeezing 10 cm slabs of the cores will hardly be adequate for a realistic description of the distribution of dissolved silicon with depth. Sampling at 1 cm intervals would seem to be more appropriate for this purpose.

The dimensionless depth (x) is related to the real depth (z) by the equation

$$z = \sqrt{\phi D_B / K_B} x$$

which is a rearrangement of equation (9). Thus, the simulated distribution in terms of real depth will vary with D_B/K_B . This is particularly important in the reactive zone before an equilibrium concentration is reached. In other words, the shape of the profile in this zone may be significantly altered by changing the rates of bioturbation and/or dissolution of particulate silicon.

The calculations also show that the equilibrium concentration of dissolved silicon at depth may acquire any value up to the saturation concentration. The particular concentration reached in each case will be determined by the flux of dissolvable particulate silicon supplied to the sediment in that area if all other parameters are held constant.

We have also simulated the distribution of dissolved silicon in the interstitial waters of two cores (Fig. 2), which were used by Schink *et al.* (1975) for illustrating their model. We used the same input parameters as theirs; these parameters are given in Table 1. The model can reproduce the measured data reasonably well except in the surface sample. The measured concentration does not show the steep increase in concentration with depth in the top 10 cm because the entire 10 cm length of the core is represented by only one sample.

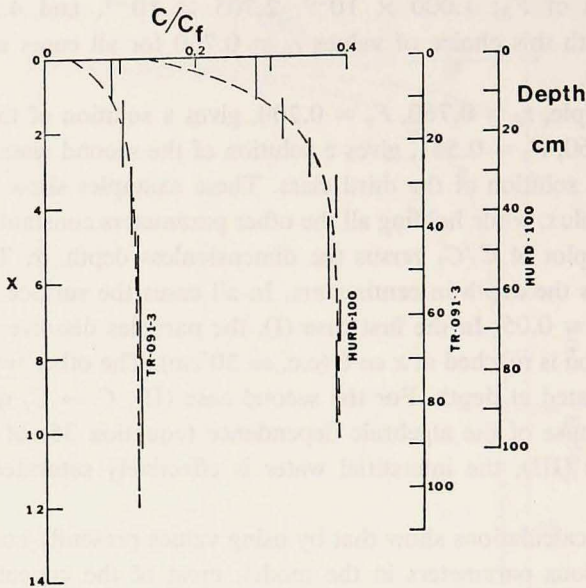


Figure 2. Simulated profiles of dissolved silicon in the interstitial waters of two cores: TR-091-3 (Fanning and Pilson, 1971) and Hurd 100 (Hurd, 1973). (Schink *et al.* (1975) have mislabeled the second core as Hurd 101.) The ratios of the observed concentrations to the saturation concentration (assumed to be $1000 \mu \text{mol l}^{-1}$) instead of just the observed concentrations are given in the figure. The depth scales are given in both the nondimensional form and the corresponding real depths for each core. The vertical bars represent the observed concentrations. The simulated profiles are represented by the smooth curves.

8. Summary

The major findings of our study may be summarized as follows:

1. The mathematical model, proposed by Schink *et al.* (1975) for describing dissolved silicon in interstitial water which includes diffusion, bioturbation and dissolution of particles can be solved analytically in closed form instead of numerically.
2. Actual profiles can be adequately simulated by this model. This suggests that physical and chemical as well as biological processes may be important in determining the distribution of silicon in interstitial waters.

Table 1. Input parameters for two cores in Figure 2.

	C_0 $\mu \text{mol l}^{-1}$	ϕ	F_B $\mu \text{mol cm}^{-2} \text{s}^{-1}$	D_B/K_B cm^2	D_c $\text{cm}^2 \text{s}^{-1}$
TR-091-3	35	0.75	2.5×10^{-8}	100	4×10^{-6}
HURD 100	125	0.90	8.4×10^{-8}	100	4×10^{-6}

3. Contrary to the finding of Schink *et al.* (1975), the model does not break down when saturation is reached at depth. Thus, the model may be applied to areas where siliceous oozes are found.

4. The concentration of dissolved silicon at depth is controlled primarily by the flux of dissolvable particles.

5. The shape of the profile in the reactive zone, where large concentration gradients may be observed, depends primarily on D_B/K_B .

6. In areas where all dissolvable particles dissolve at depth, the flux of silicon out of the sediment-water interface is controlled by the variables C_0 , C_∞ and ϕ . If excess dissolvable particulate silicon is present, the flux will also be dependent on B_∞ .

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