THE MATHEMATICS OF EARLY DIAGENESIS: FROM WORMS TO WAVES

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Abstract. The changes that sediments undergo after deposition are collectively known as diagenesis. Diagenesis is not widely recognized as a source for mathematical ideas; however, the myriad processes responsible for these changes lead to a wide variety of mathematical models. In fact, most of the classical models and methods of applied mathematics emerge naturally from quantification of diagenesis. For example, small-scale sediment mixing by bottom-dwelling animals can be described by the diffusion equation; the dissolution of biogenic opal in sediments leads to sets of coupled, nonlinear, ordinary differential equations; and modeling organisms that eat at depth in the sediment and defecate at the surface suggests the one-dimensional wave equation, while the effect of waves on pore waters is governed by the two- or three-dimensional wave equation. Diagenetic modeling, however, is not restricted to classical methods. Diagenetic problems of concern to modern mathematics exist in abundance; these include free-boundary problems that predict the depth of biological mixing or the penetration of O2 into sediments, algebraic-differential equations that result from the fast-reversible reactions that regulate pH in pore waters, inverse calculations of input functions (histories), and the determination of the optimum choice in a hierarchy of possible diagenetic models. This review highlights and explores these topics with the hope of encouraging further modeling and analysis of diagenetic phenomena.

1. INTRODUCTION

Have you ever dug for clams on a mudflat on a warm summer’s day? When your spade breaks the sediment and exposes it to the air, a complex chemical, biological, and geological structure is revealed (Plate 1). Tubes and burrows (tunnels) created by clams, worms, and other creatures become obvious, often coated or outlined by different-colored sediment. A whiff of the odor of rotten eggs (H2S) can assail you, and you may notice areas or layers of black material. Shell debris may also be evident, and digging deeper will prove to be harder and harder, as the sediment gains consistency through compaction. As happenstance will dictate, you may or may not locate the desired mollusk, but you have come into intimate contact with the world of early diagenesis.

Diagenesis is the term given to all the changes that occur to sediments after their deposition; these include alterations due to chemical reactions, like the precipitation of minerals; biological transformations as a result of the activities of microbes and the manipulations of larger fauna living in the sediments; and geophysical effects, such as compaction from self-weight and resuspension by currents and turbulence. The adjective “early” indicates those modifications that occur near the sediment-water interface, say, within a few to a few tens of meters.

Diagenetic changes can be profound and contribute significantly to the chemical balances of ecosystems and the geochemistry of the Earth’s surface [Berner, 1980; Chester, 1990; Libes, 1992]. For example, (1) organic matter is oxidized and nutrients are returned to the water column, a process that can lend important support to biological production in shallow water; (2) new minerals are created, such as ferromanganese nodules and pyrite; (3) oil formation depends in part on favorable conditions in the upper sediment column; (4) CO2 is “neutralized” by reaction with accumulated CaCO3; and (5) a remarkable benthic biological community is supported that man has successfully exploited since prehistoric times. In fact, the chemical changes occurring in the top 10 cm of sediment can be greater than those observed in the entire overlying water column, certainly so in shallow waters.

Given the consequential role of early diagenesis, quantification of its processes and results ranks among the central aims of aquatic geochemistry. The variety and complexity of diagenetic phenomena, as suggested in Plate 1, speak of the difficulty of this task for the modeler; nevertheless, substantial progress has been...
made, as summarized in specialist monographs by Lerman [1979], Berner [1980], Thibodeaux [1996], Boudreau [1997], and Giles [1997] and in previous reviews by Berner [1974], Domenico [1977], Lerman [1977, 1978], Aller [1982, 1988], Reible et al. [1991], van der Weijden [1992], Van Cappellen et al. [1993], Matisoff [1995], and Van Cappellen and Gaillard [1996]. Yet knowledge of these advances remains modest outside the diagenetic community itself. My goal with this review is therefore to give a broader readership a taste for the progress in diagenetic modeling while noting parallel problems that have arisen in other fields.

In reading what follows, it should be kept in mind that a short paper by Berner [1964] contains the first explicit diagenetic model. Consequently, this field has been in development for only about 35 years prior to the writing of the current paper, a very short time indeed. By comparison, modeling in physics arguably dates from the golden age of the Greeks (2000 years), and certainly calculus-based modeling has been widely available to the physics community since the publication of Newton’s *Principia*, in 1687. If at any point the reader feels that diagenetic models are simplistic or primitive, we practitioners in this field have the universal defense of youth on our side.

### 2. MATHEMATICAL REPRESENTATION OF SEDIMENTS

What do sedimentary geochemists hope to achieve with their models? As a group, we are primarily interested in spatial and temporal distributions of dissolved and solid chemical components of sediments, for example, solutes like Ca$^{2+}$, O$_2$, or $^{222}$Rn in pore waters and solids like CaCO$_3$, organic matter or MnO$_2$, and the fluxes (i.e., areal exchange rates) of these same species with the overlying waters. Our contention is that the observed concentrations, their variations, and the resultant fluxes can be explained, even predicted, with mathematical models that account for the processes affecting these components within sediments.

Sediments are heterogeneous in their composition, made of discrete sediment particles in a background pore water matrix when examined at a fine scale (Figure 1). Accounting for such complexity is essentially impossible and, from a practical point of view, unnecessary. One approach to circumventing this problem is to idealize the sediment as a collection of superimposed (geochemical) continua [Truesdell and Toupin, 1960], one each for the components of interest that occupy each and every point of the sediment and are infinitely divis-

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**Plate 1.** Photograph of a slice through a mudflat sediment from the northwestern coast of the United States, exposed with a spade (courtesy of S. Woodin). The bulk sediment is gray as a result of sulfate reduction, while the sediment-water interface and the linings of burrows and tubes are brownish, indicating the presence of oxide minerals. Both linear and U-shaped burrow and tubes are visible, which are dwellings for large worms (polychaetes).
Isaac Newton (1642–1727) and Gottfried Leibnitz (1646–1716) have provided the natural theoretical tool for modeling changes in continua with their joint discoveries of the calculus. The calculus is well suited to the description of many diagenetic phenomena. The first aim in using this methodology is to derive the general equation that specifies the change in concentration of a component at each point and time; this is accomplished by stating symbolically the principle of (mass) conservation. Conservation, in this context, does not denote that a component cannot be removed or added or accumulated in the model; it simply means that all such actions have causes and determined effects.

To accomplish this goal, consider any arbitrary volume $V$ within a sediment. The increase or decrease of a component’s amount (mass or moles) in $V$ in a time interval $\Delta t$ is given by the time and volume integration of the temporal rate of change at each point in the volume, i.e.,

$$\text{net accumulation} = \int_{t}^{t+\Delta t} \int_{V} \frac{\partial C}{\partial t} dV dt,$$

where $C$ is the generic concentration for a volume of bulk sediment (i.e., total solids + pore water), $t$ is time, $V$ is volume, and $dV$ is a differential element of volume. Any such changes can be ascribed to the difference between the fluxes through the surface of the volume and/or sinks and sources within the volume. The net effect of the fluxes is given by their integration over the area $S$ of the volume $V$ for the period of time in question:

$$\text{net flux} = -\int_{S} \int_{V} \mathbf{F} \cdot \mathbf{n} dA dt,$$

where $\mathbf{F}$ is the flux vector across the surface $S$ that bounds the volume $V$, $\mathbf{n}$ is the unit normal vector, and $dA$ is a differential element of area. The negative is needed to assure that a flux into the volume causes an increase in concentration.

Finally, sources and sinks are created both by geochemical reactions and by certain types of transport processes taking place within $V$, as will be discussed later. The net effect of these sources and sinks is represented by summing their individual rates $R$, at each point and integrating over the volume and time interval, i.e.,

$$\text{net source/sink} = \int_{t}^{t+\Delta t} \int_{V} \sum R_i dV dt.$$

The overall balance is then obtained by equating these three terms:

$$\int_{t}^{t+\Delta t} \int_{V} \frac{\partial C}{\partial t} dV dt = -\int_{S} \int_{V} \mathbf{F} \cdot \mathbf{n} dA dt + \int_{t}^{t+\Delta t} \int_{V} \sum R_i dV dt.$$

\[4\]
Equation (4) can be simplified by first applying Gauss’s theorem, which states that
\[
\int_S \mathbf{F} \cdot \mathbf{n} \, dA = \int_V \nabla \cdot \mathbf{F} \, dV, \tag{5}
\]
where \( \nabla \cdot \) is the divergence operator. (The form of the divergence operator depends on the coordinate system, but in Cartesian coordinates,
\[
\nabla = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z},
\]
where \( i, j, \) and \( k \) are the unit vectors in the three perpendicular directions [see Schey, 1973].) This allows conversion of the effects of the surface flux from an integral over the bounding surface to one in the volume; thus, with this theorem, (4) reduces to
\[
\int_{t=0}^{t+\Delta t} \int_V \left( \frac{\partial \hat{C}}{\partial t} + \nabla \cdot \mathbf{F} - \sum R_i \right) \, dV \, dt = 0. \tag{6}
\]

Now the volume \( V \) in (6) has been arbitrarily chosen (i.e., it has no specific size, area, or location), but it must be large enough to treat both solids and pore water as continua [see Boudreau, 1997]. In addition, the time interval is also stated in a discretionary way. Consequently, the only way the left-hand side of (4) can be zero for all volumes and time intervals is if the integrand, the quantity in the parentheses being integrated, is itself always zero, i.e.,
\[
\frac{\partial \hat{C}}{\partial t} + \nabla \cdot \mathbf{F} - \sum R_i = 0. \tag{7}
\]

This is the (mass) conservation equation for a sediment component in the form of a differential equation, entirely equivalent to conservation equations used in other branches of science and engineering [e.g., Bird et al., 1960; Truesdell and Toupin, 1960; Bear, 1972; Okubo, 1980; Slattery, 1981; Clark, 1996].

The form of the flux \( \mathbf{F} \) must be specified before specific cases of diagenetic modeling can be explored. The flux of a solute normally includes advection, due to burial and compaction, and diffusion,
\[
\mathbf{F} = \left( \mathbf{u} \varphi_w \mathbf{c} - \varphi_w \mathbf{D} \nabla \mathbf{c} \right)_{\text{advective flux}} \left( \mathbf{w} \varphi_s \mathbf{B} - \varphi_s \mathbf{D} \nabla \mathbf{c} \right)_{\text{diffusive flux}}, \tag{8}
\]
while that of a solid will include burial and perhaps diffusive mixing that is induced by either resuspension/ fluidization or the activities of infauna (i.e., creatures living in the sediment),
\[
\mathbf{F} = \left( \mathbf{w} \varphi_s \mathbf{B} - \varphi_s \mathbf{D} \nabla \mathbf{c} \right)_{\text{advective flux}} \left( \mathbf{w} \varphi_s \mathbf{B} - \varphi_s \mathbf{D} \nabla \mathbf{c} \right)_{\text{diffusive flux}}. \tag{9}
\]

where \( C \) is the concentration of a solute (i.e., \( \hat{C} = \varphi_w C \)), \( B \) is the concentration of a component solid (i.e., \( \hat{C} = \varphi_s B \)), \( D \) is a generic diffusion coefficient (ionic or molecular diffusion, biodiffusion, dispersion, etc., as defined explicitly in the subsequent examples), \( D_B \) is the mixing coefficient, \( \mathbf{u} \) is velocity of the pore water phase, \( \mathbf{w} \) is velocity of the solid phase, \( \varphi_w \) is the volume fraction of water, and \( \varphi_s \) is the volume fraction of solids (note that \( \varphi_s = 1 - \varphi_w \)). The validity of treating biological mixing as a diffusion or gradient-type law, as in (9), is explored by Boudreau [1986a, b] and Boudreau and Imboden [1987].

Diagenetic changes are often largely confined to the vertical direction [Berner, 1980], chosen to be the z direction in a Cartesian coordinate system. Equation (7) then takes on a simpler form:
\[
\frac{\partial \hat{C}}{\partial t} + \frac{\partial F_z}{\partial z} - \sum R_i = 0. \tag{10}
\]

where \( F_z \) is the flux component in the vertical direction and \( z \) is positive into the sediment, so that \( F_z \) is positive in that direction.

The remainder of this review examines the variety of applications and solutions of (7) and (10) that have emerged from diagenetic studies. In order to help organize this presentation, my examples are divided into two sections: those problems that can be considered as classical, that is, that someone working at the turn of the twentieth century would have readily recognized, and those more akin to the modern problems of applied mathematics.

3. DIAGENETIC PROCESSES THAT LEAD TO CLASSIC MODELS

3.1. Steady State, One-Dimensional Models: Simple ODEs

This section illustrates some diagenetic models that result from the assumption of steady state, \( \partial C/\partial t = 0 \), and unidimensionality. Steady state constitutes one of the most useful approximations available in geochemical modeling. The particular form employed in diagenetic studies is illustrated in Figure 2; it holds that the measure of a property, such as concentration, always has the same value at a set depth relative to the sediment-water interface. Anchoring the depth axis \( z \) to this moving interface and invoking steady state then reduces (10) for a solute, for example, to
\[
\frac{d}{dz} \left( \frac{\varphi_w D}{\varphi_s D} \frac{dC}{dz} \right) - \frac{\partial \varphi_w}{\partial s} \frac{\mathbf{D}}{\varphi_w} - \sum R_i = 0, \tag{11}
\]
which is an ordinary differential equation (ODE). Let us look at some specific examples.

3.1.1. Example 1: Sediment mixing as a diffusion process. As Plate 1 illustrates, sediments constitute a prime habitat for numerous species of infauna. These
organisms manipulate and displace the sediment grains in order to locate food, build and maintain dwellings (tubes and burrows), hide from predators, etc. These activities result in mixing of the sediment and any components they contain, known as bioturbation. This type of mixing is popularly assumed to be diffusive [Goldberg and Koide, 1962; Guinasso and Schink, 1975; Nozaki et al., 1977; Aller, 1982; Matisoff, 1995], which is justifiable if the mixing is rapid, small-scale, and random [Boudreau, 1986a, 1997; Wheatcroft et al., 1990]. The mixing coefficient associated with this diffusion, $D_B$, can be determined by modeling the depth distribution of radioisotopes, for example, $^{210}$Pb, that are continuously supplied to the sediment-water interface by production in the water column and subsequent settling by attachment to particles.

At steady state the depth distribution of a solid isotopic tracer in a bioturbated sediment will, at constant porosity, obey the equation

$$\frac{d}{dz} \left[ D_B(z) \frac{dB}{dz} + wB \right] = -\lambda B + 0, \quad (12)$$

where $B$ is activity of the isotope, $D_B(z)$ is the bioturbation coefficient, $w$ is the velocity of solid sediment relative to the sediment-water interface, and $\lambda$ is a first-order decay constant (a traditional choice). If $D_B$ is assumed to be a constant, the solution to (12) is in terms of exponentials that can be easily applied to data, as shown in Figure 3.

Despite the common assumption of constant $D_B$, data on infaunal distributions (Figure 4) strongly suggest that this coefficient is some decreasing function of depth. An analytical solution to the resulting model is possible in terms of modified Bessel or Gauss functions for simple quadratic functionalities and Tricomi-Kummer functions for an exponential depth-dependence [Nozaki, 1977; Officer and Lynch, 1982; Boudreau, 1986a; Swaney, 1999]. Christensen [1982] also provides an illustrative example of a simple approximate solution with a Gaussian depth-dependence:

$$D(z) = D_0 \exp \left( -\frac{z^2}{2\sigma^2} \right), \quad (13)$$

Christensen [1982] develops a truncated series solution for this model that is valid to a finite depth $z = L$, where the effects of mixing become effectively negligible (see below for further discussion of this depth). After expanding (13) in a four-term power series, substitution of another truncated power series into (12) produces

$$B(z) = a_0 + a_1 z + a_2 z^2 + a_3 z^3 + a_4 z^4 + \cdots + a_N z^N \quad (N \text{ finite}), \quad (14)$$

where $a_0$ is activity at $z = 0$ (i.e., $B(0)$), $a_1 = k/w$, and the other constants in the series are obtained from a recursion formula given in the original paper [Chris-
tensen, 1982]. Figure 5 displays some model-generated activity profiles used to fit data from two sites in Green Bay, Wisconsin, with $L = 4$ cm. The model clearly supplies a smooth transition between the mixed zone and the underlying historical layer with no mixing and provides quantitative estimates for the mixing parameter and the sediment accumulation rate. The continuity of the profile is not always possible with a constant $D_B$ model.

Nonsteady state versions of (12) have been considered by Guinasso and Schink [1975], Santschi et al. [1980], Olsen et al. [1981], Cochran [1985], Li et al. [1985], Boudreau [1986a], Christensen and Bhunia [1986], LaPicque et al. [1987], Anderson et al. [1988], Thomson et al. [1988], Robbins et al. [1990], Walling and Qingping [1992], and Sugai et al. [1994], among others, for the description of transient inputs of solid tracers. Nevertheless, steady state tracers and their related models remain the preferred choice for mixing studies because when valid, they are simpler to interpret.

Finally, below the zone of bioturbation or in sediments overlain by anoxic water, the absence of infauna requires that $D_B = 0$, and (12) degenerates into a first-order ordinary differential equation. In this case, the coefficients of the equation remain, in general, spatially dependent because of the effects of compaction [Berner, 1980; Fukumori et al., 1992; Boudreau, 1999], as illustrated by Christensen [1982].

### 3.1.2. Example 2: The dissolution of opal: Nonlinearly coupled ODEs

Some species of phytoplankton and zooplankton form their exoskeletons by precipitating opal, $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Opal is undersaturated in most aquatic environments, so that it dissolves after the organisms die, sink, and are incorporated into sediments. Diagenetic models can explain the distribution of dissolved silica in pore waters and the preservation of solid biogenic opal in a sediments [e.g., Hurd, 1973; Berner, 1974; Schink et al., 1975; Schink and Guinasso, 1977, 1978; Wong and Grosch, 1978; Schink and Guinasso, 1980; Boudreau, 1990a, b; Archer et al., 1993; McManus et al., 1995; Van Cappellen and Qiu, 1997]. Specifically, a steady state balance can be established between the transport, primarily bioturbation, and dissolution of the opal in the sediment and the upward diffusion of dissolved $\text{H}_4\text{SiO}_4$; in this case, and assuming constant porosity, the dissolved silica and opal are governed by two coupled, nonlinear, ordinary differential equations:

$$D_i \frac{d^2C}{dz^2} + \frac{k_i}{\rho} (C_s - C) B = 0$$  \hspace{1cm} (15)

$$\text{H}_4\text{SiO}_4 \text{diffusion} \hspace{1cm} \text{production by opal dissolution}$$

Figure 4. Example of the burrowing frequency observed with depth in a sediment (lacustrine in this case). The falloff in the burrowing activity with depth suggests that the mixing coefficient $D_B$ should also decrease with depth, although the functional relationship between the two has not been definitely established. Adapted from McCall and Tevesz [1982] with kind permission from Plenum Publishing.

Figure 5. Depth profile of $^{210}\text{Pb}$ in a core taken in Green Bay, Wisconsin, and the fit of equation (14) to the data which are based on a Gaussian decrease in $D_p(z)$ (equation (13)) in the upper 4 cm of the sediment. Below 4 cm the sediment is assumed to be undisturbed by mixing and the $^{210}\text{Pb}$ is governed by a balance between burial and decay. Reprinted from Christensen [1982].
The concentration of dissolved silica, $B$, is the concentration of opal, $D'_s$ is the tortuosity-corrected diffusion coefficient, $\rho_B$ is the pure-phase density of opal, $k_s$ is the rate constant, and $C_s$ is the concentration at saturation/thermodynamic equilibrium. (Diffusing solutes cannot penetrate the solid phase of sediments and must travel a longer path around the solid grains. As a consequence, the effective diffusion coefficient for a solute in a porous medium, $D'_s$, must be decreased by a factor that reflects the effect of the actual tortuous path, i.e., $D'_s = D/\theta^2$, where $D$ is the free-solution value and $\theta$ is tortuosity. See Boudreau [1996a] for a more extensive discussion of $\theta$.) The solute advection term, due to burial and compaction, has been neglected in (15), as it is usually small relative to molecular diffusion. Rabouille and Gaillard [1990] have debated the plausibility of such a balance in the face of discrete mixing events, but when mixing is sufficiently fast to make $B$ essentially constant [e.g., Hurd, 1973] or when little opal accumulates [e.g., Wong and Grosch, 1978], then analytical solutions are possible and numerical solutions are needed [e.g., Schink and Guinasso, 1980; Archer et al., 1993]. Figure 6 displays the fits to dissolved silica data provided by the Wong and Grosch [1978] analytical solution.

A first integral of these equations is also possible when $D_B = 0$, i.e., when there is no mixing, as in an anoxic basin [Boudreau, 1990b]. The resulting first-order ODE is much easier to integrate numerically than the original pair. This “no-mixing” model provides excellent agreement with data collected in San Pedro Basin sediments (Figure 7) by Berelson et al. [1987].

### 3.2. Transient and Multidimensional Diagenesis

Many processes in diagenesis require the presence of transient terms, for example, seasonal forcings or time-varying input, or more than one spatial dimension. In either case, partial differential equations (PDEs) must be solved.

#### 3.2.1. Example 3: Pore water irrigation and Aller’s tube model

Many tube-dwelling worms exchange their tube water with overlying water so as to prevent the buildup of metabolic toxins. In a brilliant stroke of insight, Aller [1980a, b, c] advanced that a sediment inhabited by a population of such irrigators could be idealized as a regular packing of tube-sediment annuli (Figure 8). The tube contains overlying water, while solute concentration in the sediment portion of an annulus is governed by the equation

\[
\frac{D}{d^2 B} - \frac{d B}{d z} + \frac{\varphi k_s}{(1 - \varphi) \rho_B} (C_s - C) B = 0,
\]

where $C$ is the concentration of dissolved silica, $B$ is the concentration of opal, $D'_s$ is the tortuosity-corrected diffusion coefficient, $\rho_B$ is the pure-phase density of opal, $k_s$ is the rate constant, and $C_s$ is the concentration at saturation/thermodynamic equilibrium. (Diffusing solutes cannot penetrate the solid phase of sediments and must travel a longer path around the solid grains. As a consequence, the effective diffusion coefficient for a solute in a porous medium, $D'_s$, must be decreased by a factor that reflects the effect of the actual tortuous path, i.e., $D'_s = D/\theta^2$, where $D$ is the free-solution value and $\theta$ is tortuosity. See Boudreau [1996a] for a more extensive discussion of $\theta$.) The solute advection term, due to burial and compaction, has been neglected in (15), as it is usually small relative to molecular diffusion. Rabouille and Gaillard [1990] have debated the plausibility of such a balance in the face of discrete mixing events, but when mixing is sufficiently fast to make $B$ essentially constant [e.g., Hurd, 1973] or when little opal accumulates [e.g., Wong and Grosch, 1978], then analytical solutions are possible and numerical solutions are needed [e.g., Schink and Guinasso, 1980; Archer et al., 1993]. Figure 6 displays the fits to dissolved silica data provided by the Wong and Grosch [1978] analytical solution.

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\[
D \frac{d^2 B}{dz^2} - \frac{dB}{dz} + \frac{\varphi k_s}{(1 - \varphi) \rho_B} (C_s - C) B = 0
\]

where $C$, $B$, $D_s'$, $\rho_B$, $k_s$, and $C_s$ are as defined above.

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\[
D \frac{d^2 B}{dz^2} - \frac{dB}{dz} + \frac{\varphi k_s}{(1 - \varphi) \rho_B} (C_s - C) B = 0
\]
where \( z = L \) is the depth of penetration of the annuli, \( C_0(t) \) is the known concentration of the overlying water, and \( F_L \) is a known flux from the underlying sediment.

Equation (18b) is the crucial element of the model. It assures that the concentration in the tube is that of the overlying waters; the effect is to invaginate the sediment-water interface to a depth of as much as 20–25 cm into the sediment. Deeper sediment need not exchange pore water solutes via the long and slow vertical route, but much more rapidly in the horizontal direction.

Solution methods for this type of PDE were considered by many of the greats of applied mathematics, including Joseph Fourier (1786–1830) in the context of heat conduction and P. S. de Laplace (1749–1827) with respect to gravitational attraction, and later by C. Sturm (1803–1855), J. Liouville (1809–1882), P. G. L. Dirichlet (1805–1859), K. G. Neumann (1825–1925), H. S. Carslaw (1870–1954), and J. C. Jaeger (1907–1979). For a steady state the specific solution for the given boundary conditions is [Aller, 1980a]

\[
C(z, r) = C_0 + \frac{2}{D \cdot L} \sum_{n=0}^{\infty} \frac{G_n}{\mu_n} \left[ \frac{U_0(\mu_n \rho)}{U_0(\mu_n \rho_1)} - 1 \right] \sin(\lambda_n z),
\]

where

\[
\sin(\lambda_n z),
\]

\[
\lambda_n = \frac{n \pi}{L},
\]

\[
\mu_n = \frac{n \pi}{L},
\]

\[
G_n = \frac{n \lambda_n^2}{\mu_n^2},
\]

\[
J_n(\mu_n \rho),
\]

\[
J_n(\mu_n \rho_1),
\]

\[
\Delta C = C_s - C_w.
\]

Figure 7. (a) Dissolved silica data from nonmixed sediments of the San Pedro Basin of the California borderlands, United States, as reported by Berelson et al. [1987], and the model curves generated with equations (15) and (16) with no mixing term, i.e., \( D \mu = 0 \). The labels correspond to different values of \( \nu_s \) in units of per year. (b) The model-predicted flux of dissolved silica out of the sediment-water interface as a function of the value of \( \nu_s \) and the difference between the silica at great depth in the sediment, \( C_s \), and that at the interface, \( C_w \), i.e., \( \Delta C = C_s - C_w \). The dashed line is the observed value of the flux and \( \Delta C \) of about 0.4 for the San Pedro site; thus a \( \nu_s \) of 200 yr\(^{-1}\) is indicated, which is consistent with the curves in Figure 7a. Reproduced from Boudreau [1990b] with kind permission from Pergamon Press.
\[ g_n = \frac{k(C_0 - C_i) - R_1}{\lambda_n} + \frac{R_0\left(-1 \alpha e^{-\alpha L} - \lambda_n\right)}{\alpha^2 + \lambda_n^2} \]  
\[ (20c) \]

\[ U_0(\mu, \nu) = K_0(\mu r_2)I_0(\mu r) + I_1(\mu r_2)K_1(\mu r) \]
\[ (20d) \]

and \( I_0(\mu, \nu) \), \( K_0(\mu, \nu) \), \( I_1(\mu, \nu) \) and \( K_1(\mu, \nu) \) are modified Bessel functions of indicated order. (Solutions to linear PDEs in various coordinate systems are well known and are cataloged, for example, by Carslaw and Jaeger [1959], Crank [1975], and Özisik [1980], and to some extent by Rikitake et al. [1987] and Boudreau [1997].) Equivalent one-dimensional (1-D) profiles, consistent with the type of pore water data usually collected by geochemists, can be obtained by radially averaging this solution.

Aller [1980a, b, c] illustrates the power of this model by examining the data in Figure 9, taken from an irrigated sediment. Dissolved silica is produced with depth by dissolution of opal, as explained above, while ammonia is a product of organic matter decomposition; consequently, both \( \text{NH}_3 \) and Si should increase with depth like \( 1 - e^{-\alpha x} \) in the absence of irrigation. Conversely, sulfate is consumed by organic decay and should disappear with depth in a roughly exponential manner. The data in Figure 9 exhibit large deviations from this expected behavior that can be explained easily by \( (19) \), a true triumph! Work on irrigation models has continued with papers by Aller [1983, 1984, 1988], Aller and Aller [1998], Emerson et al. [1984], Christensen et al. [1984], Boudreau [1984], Martin and Banta [1992], Boudreau and Marinelli [1994], Marinelli and Boudreau [1996], Wang and Matisoff [1997], Matisoff and Wang [1998], and Meile [1999], among others.

3.2.2. Example 4: Head-down deposit feeding.

The wave equation, in its various incarnations, is arguably the most studied equation in mathematical physics. It not only describes wave-like motions, but it is also at

Figure 8. (a) Sketch of the upper region of a burrowed sediment, idealized as a collection of close-packed annuli. (b) Vertical cross section of the sediment with the idealized diffusion geometry in Figure 8a. Adapted from Aller [1980a] with kind permission from Pergamon Press.

\[ \lambda_n = \left( n + \frac{1}{2} \right) \frac{\pi}{L} \]  
\[ (20a) \]

\[ \mu_n = \left( \frac{k}{D} + \lambda_n^2 \right)^{1/2} \]  
\[ (20b) \]

Figure 9. Dissolved (a) sulfate, (b) ammonia, and (c) silica concentration profiles in pore water from Mud Bay, South Carolina, plotted as vertical bars. The dashed bars are the radially averaged predictions from Aller’s tube model, i.e., equations (17) and (18), whereas the solid line is a one-dimensional (1-D) diffusion-reaction model for comparison. Note that the tube model captures the critical trends in the data, i.e., weak depletion in sulfate and the minimum in the ammonia, while the 1-D model does not. Adapted from Aller [1980a] with kind permission from Pergamon Press.
the heart of stability analyses. The wave equation surfaces in diagenetic modeling when considering at least two phenomena: head-down deposit feeding, the subject of this example, and true pore water waves, the next example.

Most infauna acquire food by consuming bulk sediment, processing out the useful organic matter through digestion and excreting the rejected materials as feces. A particular group of sediment processors does so by adopting a vertical posture in sediments with their mouths downward and their posteriors located near the sediment-water interface (Figure 10). Their consumption is thus at depth, and excretion is at the surface. The void created by their feeding is infilled by self-weight compaction of the sediment. Consequently, sediment in the vicinity of such head-down deposit feeders is caught in a conveyor-belt-like motion.

Organisms do not normally appear explicitly in diagenetic models; as a result, the removal of material at depth takes on the form of a sink, while there is a source of material at the sediment that supplements normal sedimentation and equals the integrated rate of material removal from depth. Fisher et al. [1980] were the first to develop a mathematical model for this process. Specifically, assuming the feeding is constant with time and that porosity is constant with depth, total sediment conservation is governed by

$$\frac{dw}{dz} = -Af(z),$$

where $A$ is the maximum magnitude of the feeding rate and $f(z)$ is the normalized feeding distribution with depth, that is, the depth integral of $f(z)$ is equal to 1. Thus the apparent velocity of burial changes with depth in proportion to the local feeding rate.

A solid tracer caught in the conveyor will obey the conservation equation

$$\frac{\partial C}{\partial t} + \frac{\partial wC}{\partial z} = -\lambda C - Af(z)C,$$

where $\lambda$ is the decay constant, if needed. Equation (22) is a first-order wave equation. The solution to (22) for a spike of $^{137}$Cs into an experimental microcosm (aquarium) of sediment is illustrated as the dashed line in Figure 11, from Robbins et al. [1979]. The model accurately hindcasts the position of the pulse of the tracer, including its downward advection and the reappearance of the tracer once the spike enters the main feeding zone. The scatter in the data is best explained if a little biodiffusion (see example 1) is added to the model, but it is not necessary in order to capture the main features.

Continued research on modeling the mixing from head-down deposit feeding and other nonlocal processes is reported by Krezoski et al. [1984], Krezoski and Robbins [1985], Robbins [1986], Boudreau [1986b], Rice [1986], Smith et al. [1986, 1987], Boudreau and Imboden [1987], Gardner et al. [1987], Pope et al. [1996], and Fornes et al. [1999]. These authors consider models in the form of integrodifferential equations.

3.2.3. Example 5: Wave-induced transport in sediments. While waves are generally created in overlying waters by wind or density instabilities or tidal action, etc., these phenomena will penetrate into sediments that possess sufficient permeability where they propagate to cause pore water motions and are dampened by frictional or viscous interactions with the sediment grain surfaces [see Huettel and Webster, 2000]. (Only sediments coarser than fine silts have the required permeabilities to respond on a timescale relevant to waves.) The so-called damping of waves within the underlying sediment is a problem of long concern to physical oceanographers [e.g., Putnam, 1949; Reid and Kajiura, 1957; Hunt, 1959; Murray, 1965; Sleath, 1970; Liu, 1973], and it continues to be so today [e.g., Liu and Wen, 1997; Mizumura, 1998]. The general directions of pore water motion under a passing wave are illustrated in Figure 12.
Ignoring a thin transition zone, the so-called Brinkman layer [see McClain et al., 1977], the 3-D flow field is governed by simultaneous equations for the pressure $p$ and the pore water (Darcy) velocity vector $u$, i.e.,

\[ \nabla^2 p = 0 \]  \hspace{1cm} (23)

Darcy's law

\[ u = -\frac{k}{\rho g} \nabla p, \]  \hspace{1cm} (24)

where $k$ is permeability, $g$ is the gravitational constant, and $\rho$ is water density. With constant coefficients and a flat bottom, the solution following a wave is [Harrison et al., 1983]

\[ u_x = u_a e^{-\nu} \cos (\eta x - \omega t) \]  \hspace{1cm} (25a)

\[ u_z = -u_a e^{-\nu} \sin (\eta x - \omega t) \]  \hspace{1cm} (25b)

\[ u_y = 0, \]  \hspace{1cm} (25c)

where $x$ is the propagation direction of the waves, $y$ is lateral direction, $\eta$ is the wavenumber, $\omega$ is angular frequency, $a$ is amplitude, $h$ is water depth, $u_a$ is $\kappa \eta a/ (\cosh (\eta h))$, and, to a good approximation, $\omega = (g \eta \tanh (\eta h))^{1/2}$. Equation (25) also informs us that the effect of the waves falls exponentially with depth and is linearly proportional to the permeability.

Figure 11. Rapid burial of a pulse input of $^{137}$Cs into a sediment in a laboratory microcosm with head-down deposit feeders. The feeding distribution is given by the function $\gamma^*(x)$, which equals $f(x)$ in this text. The peak diminishes as it penetrates the feeding zone and part of the tracer is returned to the surface. The dotted line is the prediction from equation (22), whereas the solid line is the model with some added biodiffusion. Equation (22) accurately predicts the position of the tracer peak and the reappearance of material at the interface; however, a better fit to the data is obtained with the addition of minor mixing. From Robbins [1986].

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Figure 12. Illustration of the direction of pore water flow at a given depth in a sediment (shaded area) as a wave passes overhead. With kind permission from I. Webster.
The motions engendered by waves will also cause solute transport, as advective motions and possibly as hydrodynamic or rotational dispersion [see Webster and Taylor, 1992], a process first modeled by Riedl et al. [1983] and subsequently by Harrison et al. [1983]. Pore water measurements in permeable sediments are technologically difficult, so that application of 2-D or 3-D models is still not feasible. Those few studies of such pore waters have used 1-D models with either an enhanced diffusivity (dispersion) [e.g., Vanderborght et al., 1977; Rutgers van der Loeff, 1981; Lohse et al., 1996] or a nonlocal source or sink [Marinelli et al., 1998]. In addition, empty U-shaped burrows can act as important conduits for wave-driven flow in a sediment [Webster, 1992; Allanson et al., 1992; Ridd, 1996].

Shum [1992, 1993] and Shum and Sundby [1996] have produced a remarkable analysis of wave-induced transport when the bed surface is also rippled. Using conformal mapping and Fourier-series analysis, they calculated the pore water velocity analytically (example “particle” trajectories in Figure 13), then obtained the concentration field through conformal mapping and numerical integration of the solute conservation equation:

\[
\frac{1}{Fo} \frac{dc}{dt} + Pe \frac{c}{U} \nabla c - \nabla^2 c + Da \frac{dc}{dt} = 0,
\]  

(26)

where \(c\) is a dimensionless concentration (\(c = C/C_0\)), \(U\) is a dimensionless velocity (\(U = u/u_p\), where \(u_p\) is the local time-averaged velocity of the pore water), \(T\) is the period of the waves, \(L\) is the ripple length, \(Pe\) is the Peclet number (\(u_pL/D\)), \(Da\) is the Damköhler number (\(kL^2/D\)), and \(Fo\) is the Fourier number (\(D^2T/L^2\)). An example of the normalized (nondimensional) contours of \(c\) averaged over a wave period is displayed in Figure 14 for a rapidly decaying tracer in a highly advective dominated sediment.

The results in Figure 13 and 14 illustrate the strong effect of the ripples themselves in controlling both the flow and the solute exchange. In fact, Bernoulli-type pressure variations adjacent to bed forms (e.g., ripples, pits, etc.) and objects (e.g., shells, nodules, sessile fauna and flora, etc.), even in a steady flow, can drive significant local percolation of water [e.g., Thibodeaux and Boyle, 1987; Savant et al., 1987; Hutchinson and Webster, 1998] and substantial solute displacements [e.g., Huettel and Gust, 1992; Rutherford et al., 1995; Ziebis et al., 1996; Huettel et al., 1996, 1998].

The examples discussed above should convince the reader that most important aspects of traditional applied mathematics, at least as they relate to the calculus, can arise from the study of diagenetic processes. Yet if diagenesis is to constitute fertile ground as a basis for
modeling methods, it must also supply obvious examples of more modern problems considered by applied mathematicians. The goal of the next section is to provide such evidence.

4. DIAGENETIC MODELS OF MORE MODERN TYPE

4.1. Free-Boundary Problems

Many questions exist in science that involve locating the position of a point, or line, or surface that is not known a priori; for example, finding (1) the phreatic surface in hydrology, (2) the surface of a crystal in a solution as it grows, (3) the furthest infiltration of O₂ in injured tissue, or (4) the penetration distance of reactants into a catalytic pellet are all good examples. The mathematics of these problems is of sufficient interest to modern mathematicians to warrant at least three monographs [e.g., Fasano, 1983; Crank, 1984; Diaz, 1995] and scores of related research papers. Diagenesis has generated a number of examples of this class of problem, of which two are discussed below.

4.1.1. Example 6: Mean depth of bioturbation. Data on the depth of biological mixing of marine sediments [Boudreau, 1994] are characterized by a mean of about 10 cm (Figure 15), independent of the overlying water depth. Why? One possibility is that the intensity of mixing decreases with depth in the sediment as a direct function of the decreasing amount of food (metabolizable organic matter) \( G \) with depth, i.e., \( D_B \propto G \). The simplest assumption of this variety is that [Boudreau, 1998]

\[
D_B(G) = D^* G,
\]

where \( D^* \) is a constant food-based mixing coefficient with units of length squared per unit concentration or organic matter and unit time. Thus at steady state, constant porosity, and negligible burial, reactive organic matter (food) diagenesis is governed by the equation

\[
\frac{d}{dz} \left[ D^* G \frac{dG}{dz} \right] - kG = 0,
\]

Figure 14. Contour plots of the time-averaged concentration field of a tracer in the pore waters beneath a rippled bed for \( Pe = 100 \) and \( Da = 100 \) in equation (26). Adapted from Shum [1993].

Figure 15. Plot of the tracer-identified mixed-layer thickness \( L \) of marine sediments as a function of the overlying water-column depth (160 points). The dashed line is the worldwide mean of 9.8 ± 4.5 cm (1 standard deviation). Adapted from Boudreau [1998] with kind permission from the American Society for Limnology and Oceanography.
where \( k \) is the rate constant for decay, i.e., oxidation.

Equation (28) contains a negative feedback mechanism: Because \( G \) decays with depth, so will \( D_B(G) \); as \( D_B(G) \) decreases with depth, less \( G \) penetrates before decaying, so that \( D_B(G) \) decreases even more, and so on. There then exists an unknown depth \( L \), where \( G \) and \( D_B(G) \) disappear entirely; the problem is in locating this point (depth).

Statement of the problem is incomplete without boundary conditions. At the sediment-water interface we can assume that we know the organic matter concentration, i.e., \( G = G_0 \) at \( z = 0 \). The other boundary is the one of unknown position; however, at that point we know from logic that the concentration \( G \) is zero and that there is no diffusive flux of organic beyond that point, i.e.,

\[
G = 0 \\
\frac{dG}{dz} = 0 \quad z = L. \tag{29}
\]

While having two conditions at one point may appear to be overspecification, this extra information allows location of \( L \). The solution is

\[
G = G_0 \left[ 1 - \frac{z}{L} \right]^2, \tag{30}
\]

where

\[
L = 4 \sqrt{\frac{3D^*G_0}{8k}}. \tag{31}
\]

In order to calculate \( L \) with (31), we need estimates of \( D^*G_0 \) and \( k \). If data fitting results with constant \( D_B \) are assumed to represent the mean value of \( D^*G \), then \( D^*G_0 = 3D_B \). Also, past studies give us that \( D_B = 15.7 \ w^{0.6} \) [Boudreau, 1994] and that \( k = 3.0 \ w^{0.6} \) [Tromp et al., 1995], to arrive at \( L = 9.7 \) cm. Thus the food-feedback process is a viable mechanism for generating the observed mean mixing depths in sediments. Other 1-D free-surface models are given by Bouldin [1968], Jahnke [1982], Boudreau and Westrich [1984], Jahnke [1985], Wilkinson and Dampier [1990], and Cai and Sayles [1996].

4.1.2. Example 7: Oxygen beneath surficial objects (nodules). If an object, such as a manganese nodule [see Cronan, 1977; Calvert and Price, 1977], or a shell, or even a sessile organism is found at the sediment-water interface, its mere presence will alter the fluxes of solutes and solids between the overlying waters and the sediments. Solutes and solid particles cannot very well pass through the solid object, but must circumvent it.

Reactive organic matter (stoichiometric \( \text{CH}_2\text{O} \)) is supplied to the sediment from the water column, and the organic matter is mixed into the sediments by bioturbation. The organic matter also disappears from the system, as \( \text{CO}_2 \), by microbial decay, i.e.,

\[
\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}. \tag{32}
\]

Assuming a half-spherical object of radius \( r_0 \) (Figure 16), the conservation equation for organic matter \( G \) in a spherical coordinate system about the object is [Boudreau and Taylor, 1989]

\[
D_B \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial G}{\partial r} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial G}{\partial \theta} \right) \right] + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \phi} \left( \sin \theta \frac{\partial G}{\partial \phi} \right) = -kG = 0. \tag{33}
\]

The organic matter rains down at a known rate \( F \) on that portion of the sediment-water interface not occupied by the object, i.e.,
In addition, there is no flux of \( G \) through the object surface, \( r = r_0 \), in the sediment,

\[
\frac{\partial G}{\partial r} = 0 \quad 0 \leq \theta \leq \pi/2,
\]

and the concentration must remain finite, i.e., \( G \rightarrow \) finite at \( \theta = 0 \) and \( r \rightarrow \infty \).

The resulting solution is [see Özisik, 1980, chapter 4]

\[
G(r, \theta) = \frac{F}{D_B} \exp \left( -r \cos (\theta) \frac{k}{D_B} \right) \sum_{n=0}^{\infty} \frac{r_0}{r} K_{n+1/2} \left( r \frac{k}{D_B} \right) P_n(\cos (\theta)).
\]

An example of this solution is illustrated in Figure 17. Note that for the large hemisphere in the right column of Figure 17, the contours become highly compressed, so as to indicate that large objects have very little fast decaying organic matter beneath them.

Figure 17. Isogram (contours of concentration) of the solid organic matter, \( G \), field near a hemisphere generated with equation (36) by Boudreau and Taylor [1989]. Plots are for two different reactivities \( k \) of the organic matter and three object radii \( (r_0 = 1, 2, 3 \text{ cm}) \). Note that the more rapidly decaying organic matter disappears beneath a large object.
Reaction (32) will consume O$_2$, which must be supplied by molecular diffusion from the overlying water in the absence of irrigation. The spatial concentration of O$_2$ is governed by

$$D_0 \left[ \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial C}{\partial \theta} \right) \right] - kG = 0, \quad (37)$$

where $G$ is specified by (36). The first three of the boundary conditions on (37) regulate the concentration of O$_2$ at the sediment-water interface, the flux at the boundary conditions on (37) regulate the concentration where Berger et al. have been under development since the mid-1960s [e.g., Wilkinson and Dampier [1990], and Archer [1991a, b] with respect to carbonate geochemistry and pH. The hydrological and hydrothermal literatures also contain many discussions of DAEs in the context of similar geochemical problems [e.g., Rubin, 1983; Bahr and Rubin, 1987; Lichtner, 1988, 1992, 1993; Bahr, 1990; Friedly and Rubin, 1992]. Considerable attention has been paid to the solution of DAEs, particularly with numerics [e.g., Gear and Petzold, 1984; Hindmarsh and Petzold, 1995].

4.2.1. Example 8: Pore water pH in a Beggiatoa mat. To illustrate a DAE problem in early diagenesis, let us consider the pH in Beggiatoa mats (Plate 2 and Figure 19), as measured by Jørgensen and Revsbech [1983]. Bacteria can meet their metabolic demand for energy by oxidizing inorganic chemicals, like H$_2$S. This is known as chemolithothrophy. Such bacteria can aggregate in large numbers at the sediment-water interface to form mats, for example, Plate 2. Sharp gradients of O$_2$, H$_2$S, and pH can occur as a result of the intensity of the microbial redox reaction (Figure 19). Modeling of this reaction leads to DAEs [e.g., Boudreau, 1991].

Specifically, the metabolic reactions in the mat are

$$\text{H}_2\text{S} + 2\text{O}_2 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-} \quad (40a)$$
$$\text{HS}^- + 2\text{O}_2 \rightarrow \text{H}^+ + \text{SO}_4^{2-}. \quad (40b)$$

These reactions are responsible for the disappearance of sulfide and oxygen and the pH decline in the mat in Figure 19. In addition, the pore waters are buffered by dissociation of the weak acids held in solution in most natural waters, i.e.,

$$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+ \quad (41)$$
$$\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \quad (42)$$
$$\text{B(OH)}_3 + \text{H}_2\text{O} \leftrightarrow \text{B(OH)}_4^- + \text{H}^+ \quad (43)$$
$$\text{H}_2\text{S} \leftrightarrow \text{HS}^- + \text{H}^+ \quad (44)$$
$$\text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{H}^+. \quad (45)$$

These latter reactions are also fast and reversible.

At steady state, constant porosity, and no pore water advection, the conservation equations for all the species in reactions (40) through (45) are

$$D_0 \frac{d^2 \text{O}_2}{dz^2} - R_{\text{OS}} = 0 \quad (46)$$

where $R_{\text{OS}}$ is the consumption of O$_2$ from the organic matter solution.
Figure 18. Isogram (contours of concentration) of the dissolved O\textsubscript{2} field near a hemisphere generated through numerical solution of equations (37)–(39) by Boudreau and Taylor [1989]. Plots are for two different reactivities \(k\) of the organic matter and three object radii \(r_0 = 1, 2, 3\) cm. Note that O\textsubscript{2} is found preferentially beneath a large object with rapidly decaying organic matter.

\[
D_{\text{CO}_2} \frac{d^2[\text{CO}_2]}{dz^2} - R_{C1} = 0 \quad (47)
\]
\[
D_{\text{HCO}_3} \frac{d^2[\text{HCO}_3^-]}{dz^2} + R_{C1} - R_{C2} = 0 \quad (48)
\]
\[
D_{\text{CO}_3^-} \frac{d^2[\text{CO}_3^-]}{dz^2} + R_{C2} = 0 \quad (49)
\]
\[
D_{\text{B(OH)}_3} \frac{d^2[\text{B(OH)}_3]}{dz^2} - R_{B} = 0 \quad (50)
\]
\[
D_{\text{B(OH)_2}} \frac{d^2[\text{B(OH)}_2]}{dz^2} + R_{B} = 0 \quad (51)
\]
\[
D_{\text{H}_2\text{S}} \frac{d^2[\text{H}_2\text{S}]}{dz^2} - R_{S} = 0 \quad (52)
\]
\[
D_{\text{HS}} \frac{d^2[\text{HS}^-]}{dz^2} + R_{S} = 0 \quad (53)
\]
\[
D_{\text{H}_2\text{O}} \frac{d^2[\text{H}^+]}{dz^2} + R_{C1} + R_{C2} + R_{B} + R_{S} + 2R_{\text{OS}} + R_{w} = 0 \quad (54)
\]
\[
D_{\text{OH}^-} \frac{d^2[\text{OH}^-]}{dz^2} + R_{w} = 0, \quad (55)
\]

where \(R_{\text{OS}}\) is the net rate of the oxidation reactions (40a) and (40b), \(R_{C1}, R_{C2}, R_{B}, R_{S}\) and \(R_{w}\) are the net rates of
the reversible reactions (41) through (45), respectively, and the $D$ parameters are the respective species ionic/molecular diffusion coefficients.

Reactions (41) through (45) are not only reversible, they are also fast and, consequently, essentially at equilibrium at each point in the pore waters. Furthermore, our knowledge of their thermodynamics is much better than of their kinetics. This suggests a strategy wherein these equations are manipulated to eliminate the $R_{C1}, R_{C2}, R_B, R_S,$ and $R_W$ terms from the conservation equations [e.g., Olander, 1960; Otto and Quinn, 1971; Di Toro, 1976; Chang and Rochelle, 1982; Meldon et al., 1982; Gallagher et al., 1986; Versteeg et al., 1989; Bontozoglou and Karabelas, 1991; Wallin and Bjerle, 1990; Ochoa-Tapia et al., 1991; Wallin and Olausson, 1993]. The approach is called the local or partial equilibrium assumption. Doing so reduces this set of equations to the following (the first is identical to equation (46)):

$$2D_{H_2S} \frac{d^2[H_2S]}{dz^2} + 2D_{HS} \frac{d^2[HS^-]}{dz^2} - D_{O_2} \frac{d^2[O_2]}{dz^2} = 0$$

(58)

$$D_H \frac{d^2[H^+]}{dz^2} - D_{HCO_3} \frac{d^2[HCO_3^-]}{dz^2} - 2D_{CO_3} \frac{d^2[CO_3^-]}{dz^2}$$

$$- D_{B(OH)_3} \frac{d^2[B(OH)_3]}{dz^2} - D_{HS} \frac{d^2[HS^-]}{dz^2} + D_{O_2} \frac{d^2[O_2]}{dz^2}$$

$$- D_{OH} \frac{d^2[OH^-]}{dz^2} = 0.$$  

(59)

This is a set of five equations, i.e., implicit ODEs, for 10 unknown species distributions. In order to resolve the indeterminacy, the nonlinear algebraic equations (mass action laws) that govern reactions (41) through (45) at equilibrium are introduced as new simultaneous constraints, i.e.,

$$K_{C1}^*[CO_2] = [HCO_3^-][H^+]$$

(60)

$$K_{C2}^*[HCO_3^-] = [CO_3^{2-}][H^+]$$

(61)

$$K_{B}^*[B(OH)_3] = [B(OH)_3][H^+]$$

(62)

$$K_{S}^*[H_2S] = [HS^-][H^+]$$

(63)

$$K_{w}^* = [OH^-][H^+]$$

(64)

Plate 2. Bacterial mat of Beggiatoa (white areas) at the surface of a marine mud. The mats form where sulfide reaches the sediment-water interface, due to very high rates of sulfate reduction. A blue-and-white 6-inch ruler is present for scale. Photograph supplied to the author by R. Marinelli.
where the \( K^* \) parameters in these equations are the (stoichiometric) equilibrium constants.

The resulting set of differential equations, (46) plus (56)–(59), and the nonlinear algebraic equations, (60)–(64), must be solved simultaneously to obtain the predicted species distributions with depth in the mat. The particular solution depends on the form of \( R_{OS} \). For example, the model-predicted pH (solid line) and observed pH values from Figure 19 (squares) in the mat are displayed in Figure 20 when \( R_{OS} \) is approximated as a depth-dependent Gaussian about the \( O_2-\Sigma H_2S \) intersection point. Clearly, one obtains a very respectable prediction.

### 4.3. Inverse Problems

The models presented above all have one element in common; that is, given a model, it is solved, subject to initial and/or boundary conditions and parameter values, to produce a prediction (or hindcast) of the distribution of one or more sediment or pore water components. However, geochemists are often more interested in extracting values of parameters from data, rather than predicting data from parameter values. Parameter extraction is known in mathematics as an inverse problem. Examples of parameter estimation abound in the diagenetic literature.

Sediment accumulation rates (velocities) are derived by fitting appropriate solutions to (12), with \( D_B = 0 \) and \( \lambda \) known [see Berner, 1980], to observed depth profiles of radionuclides that are attached to the solids [e.g., Robbins and Edgington, 1975; Turekian and Cochran, 1978; Christensen, 1982]. Profiles of short-lived isotopes in the bioturbated zone of sediments have similarly proven to be useful in determining the value of the mixing parameter \( D_B \) [e.g., Guinasso and Schink, 1975; Nozaki et al., 1977; DeMaster and Cochran, 1982; Cochran, 1985; Pope et al., 1996; Mulsow et al., 1998]. Rate constants for various processes can also be determined by fitting solutions of simple forms of (11) to observed profiles of solutes or solid components [Berner, 1980]. For example, Rice [1986] derives nonlocal exchange rate constants from \(^7\)Be, while irrigation constants have been retrieved from dissolved \(^3\)H [Emerson et al., 1984], \(^{222}\)Rn [Smethie et al., 1981; Martin and Sayles, 1987], Br [Martin and Banta, 1992], and \(^{22}\)Na [Matisoff and Wang, 1998] solute profiles. Similarly, rate constants for geochemical reactions have also been estimated by fitting models to the distributions of minor components of the solids or pore waters [e.g., Berner, 1974, 1980; Murray and Grundmants, 1980; Emerson et al., 1985; van Raaphorst et al., 1990].

Mathematical research on methods of parameter estimation has a long history in applied mathematics, beginning with simple linear regression. Today, such research continues to be vibrant and has seen some original contributions from workers in the field of diagenesis [e.g., Officer and Lynch, 1982, 1983; Officer, 1982; Lynch and Officer, 1984; Banks and Rosen, 1987; Meile, 1999].

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**Figure 19.** Dissolved \( O_2 \), total dissolved sulfide, and pH profiles obtained by Jørgensen and Revsbech (1983), using microelectrodes, in the vicinity of a Beggiatoa mat sitting at the interface of a Danish coastal sediment. The interface is at the depth marked zero. Equations (46) and (56)–(64) describe the dynamics of these dissolved species in this mat. Reproduced with kind permission from the American Society for Microbiology.

**Figure 20.** Best visual prediction of the pH data from Figure 19 using an analytical solution to equations (46) and (56)–(64), obtained by Boudreau [1991]. Reproduced with kind permission of the Geochemical Society.
Another type of inverse problem emerges naturally from diagenesis; an accumulating sediment column records historical variations in solid sediment components, including tracer ratios like $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O that have been interpreted as a record of sea surface temperature, productivity, etc. In fact, such data are crucial to paleoceanographic and palaeoclimatic reconstructions. Yet the preserved record has been altered by diagenesis, particularly bioturbation, and is not a direct representation of the input signal. To reconstitute the original input to the sediment, the effects of diagenesis should be removed; that is, an appropriate diagenetic model needs to be run “backward” by feeding the data in and extracting the time-varying flux boundary condition at the sediment-water interface. This problem is closely related to the so-called inverse heat-conduction problem, wherein one attempts to derive an unknown heat flux at the surface of a material based on temperatures measured at various points in the interior of the material [e.g., Weber, 1981; Tandy et al., 1986; Raynaud and Beek, 1988; Murio and Roth, 1988; Scarpa and Milano, 1995]. Consider now a diagenetic example.

**4.3.1. Example 9: Unmixing heavy metal records.** For some solid components, biological mixing in the upper surface layer is the only appreciable diagenesis they undergo. Reconstruction of their input history to a sediment is possible by removing the mixing effects from their record in the sediment column. If the mixing can be considered to be infinitely fast in a surficial mixed layer of thickness $L$, then the concentration $B$ of a solid species, also subject to burial advection $w$, first-order decay, and time-dependent input at the sediment-water interface $J(t)$, is given by [Berger and Heath, 1968]

$$\frac{d\rho_m B}{dt} = \frac{J(t) - \text{change with time in mixed layer}}{L} - \frac{J_l}{\text{difference of input at top and output at bottom}} - \frac{\lambda \rho_m B}{\text{possible removal by decay}}, \tag{65}$$

where $\rho_m$ is the average density of sediment in the mixed layer and $\lambda$ is the rate constant for decay ($\lambda = 0$ for a stable species).

Christensen and Klein [1991] rewrite this last equation for the unknown flux, i.e.,

$$J(t) = L \rho_m \frac{dB}{dt} + (r + \lambda \rho_m)B, \tag{66}$$

where $r = w \rho_m$ is the mass accumulation rate (mass per unit area per unit time). Furthermore, data are usually obtained for layers of finite thickness; thus this last equation can be expressed in terms of the flux $J_l$ for a finite layer, i.e.,

$$J_l = \left(L \rho_m \left[ \frac{B_{i+1}}{t_{i+1}} \exp \left( \lambda \left( \bar{t}_i - \bar{t}_{i+1} \right) \right) - B_i \right] \right) + (r + \lambda L \rho_m) B_i \exp \left( \lambda (\bar{t}_i - t_m) \right), \tag{67}$$

where $t_i = (t_{i+1} + t_i)/2$; $t_i = m/r$; $m_i$ is the cumulative mass of sediment above the lower boundary of slice $i$; and $t_m$ is the time for deposition of the mixed layer, i.e.,

$$t_m = \frac{1}{r} \int_0^L \rho \ dz. \tag{68}$$

An example of the output from (67) for the stable Pb surface flux at a site in Lake Michigan is given in Figure 21. The uncorrected flux from the core is given by the dotted line, whereas the solid segments are the mixing-corrected fluxes with their uncertainties, indicated by the dashed lines. Clearly, the corrected record contains peaks and troughs not discernible in the original record; the latter can significantly underestimate or overestimate the actual inputs because mixing “smears” out the high-frequency variations. In addition, the timing of events is shifted to more recent dates. Improvements to this model are offered by Christensen and Karls [1996], Christensen and Goetz [1987], Christensen and Osuna [1989], Fukumori et al [1992], and Christensen and Karls [1996].

**4.3.2. Example 10: Model selection.** Even modest experience with models and data reveals two truisms. First, models usually contain a number of free parameters, and second, it is possible for different models to explain a given set of data equally well, at least in the sense of coefficients of determination, $R^2$. Faced with this conundrum, what is a modeler to do? This question has recently been addressed by Soetaert et al. [1996a] in the context of diagenetic modeling. These investigators were in possession of a set of $^{210}$Pb profiles from deepsea sediments in the North Atlantic. The $^{210}$Pb is supplied to the sediment surface by production from uranium series decay and can be transported in the sediment by burial, bioturbation, and subsurface egestion. They wished to establish what model “best” described these data from a hierarchy of models and specifically if nonlocal transport in the form of subsurface defecation (egestion) by infauna [Smith et al., 1986] was necessary to explain the data.

The models in question derive from the linear conservation equation:

$$D_B \frac{d^2B}{dz^2} - w \frac{dB}{dz} - \lambda C + S_p + Q - rC = 0, \tag{69}$$

models 1 and 2

models 4a and 4b and model 5

where $D_B$ is the biodiffusion coefficient (see example 1 above), $w$ is the burial velocity, $\lambda$ is the radioactive decay rate constant, $r$ is the rate constant for removal by
head-down deposit feeders (see example 4 above), $Q$ is the source rate by subsurface egestion (defecation), and $S_P$ is the source rate by in situ decay of parent radionuclides in the sediment. All these coefficients are treated as constants, at least piecewise, and are available as fitting parameters. The models are generated by retaining different combinations of terms, i.e., model 1 moves $^{210}$Pb by burial alone, while allowing it to be produced and to decay. Model 2 adds diffusive bioturbation, model 3 affixes subsurface egestion at a single depth, model 4a allows egestion over a finite zone, model 4b appends subsurface ingestion to model 3, and model 5 adjoins subsurface ingestion to model 4a.

The models are fit to the data by an iterative Marquardt-Levenberg algorithm, and the models are compared using a one-tailed $F$ test. The $F$ test is based on the $F$ parameter,

$$F = \frac{(SSR_i - SSR_j)df_j}{(df_i - df_j)SSR_j} \quad (70)$$

where $SSR$ is the sum of squared residuals for models $i$ or $j$ ($i \neq j$) and $df$ is the degree of freedom for a given model (i.e., number of observations – number of parameters – 1). The null hypothesis is that a more complex model does not decrease the variance, and this is rejected when the calculated $F$ value exceeds the critical value for the $F$ distribution.

The results of the model selection exercise are displayed in Figure 22. Model 3 is needed in five of the 17 cases, model 2 is sufficient in seven other cases, and model 1 is all that is required in the remainder. Models 4 and 5 provided no statistically justified improvements, although they formally provide better $R^2$ values. Thus 30% of the isotope profiles require some subsurface (nonlocal) transport, which is a surprise, as the organisms responsible for this behavior are not thought to be all that common in the deep sea. Berg et al. [1998] offer a generalization of this methodology to other diagenetic components and processes.

The foregoing examples hardly exhaust the diagenetic sources of mathematical inspiration. Nicolis [1995], for example, has utilized fractals to describe bioturbation, Boudreau [1986a] alludes to the potential for stochastic differential equations, Middelburg et al. [1996] and Soetaert et al. [1998] have made advantageous use of Monte Carlo simulations, and François et al. [2000] employ both particle lattice and automaton concepts to derive a new model for bioturbation. In addition, the solution of large systems of coupled, nonlinear diagenetic equations with disparate timescales, nonlocal transports, and singular points has become a topic of great interest to practitioners in this field. This has resulted in numerous advanced computer codes [e.g., Rabouille and Gaillard, 1991a, b; Park and Jaffé, 1996; Van Cappellen and Wang, 1995, 1996; Boudreau, 1996b; Dhakar and Burdige, 1996; Wang and Van Cappellen, 1996; Soetaert et al., 1996b; Hensen et al., 1997; Hunter et al., 1998; Kelly-Gerreyn et al., 1999]. However, at this point my allotted space has disappeared, and I probably tax my readers’ interest.
5. DÉNOUEMENT

Diagenesis encompasses the changes induced by biological, chemical, and physical phenomena in sediments, often superimposed and eliciting nonlinear feedbacks. The result is a field that offers rich possibilities and necessities for modeling. In a short 35 years the state of diagenetic theory has blossomed to include virtually all the models of classical applied mathematics, for example, ODEs, PDEs, integrodifferential equations, etc., and many more modern mathematical models, for example, free-boundary problems, differential-algebraic

Figure 22. Results from the model selection exercise conducted by Soetaert et al. [1996b] that compared the five models given in equation (69) with data from the Ocean Margin Experiment stations in the North Atlantic. Profiles that are a significantly better fit, i.e., that have superior $F$ test results (equation (70)) with model 3 that contains nonlocal transport, are boxed with a border; those adequately fit by model 1 are shaded below and to the right; the remaining profiles are best explained by model 2. Models 4 and 5 do not provide statistically better fits for any profile, as based on the $F$ test. The surprising finding is that 30% of these deep-sea sediments require nonlocal mixing in order to explain the observed $^{210}\text{Pb}$ depth distribution. Reproduced with kind permission from the *Journal of Marine Research.*
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