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GRAIN-SCALE STABLE ISOTOPE DISEQUILIBRIUM DURING FLUID-ROCK INTERACTION. 1: SERIES APPROXIMATIONS FOR ADVECTIVE-DISPERSIVE TRANSPORT AND FIRST-ORDER KINETIC MINERAL-FLUID EXCHANGE

R. ABART* and R. SPERB**

Institut für Mineralogie und Petrographie, ETH-Zentrum, CH-8092 Zürich, Switzerland

ABSTRACT. Stable isotope fronts provide lasting evidence of fluid-rock interaction. The processes involved in material transport and mineral-fluid exchange may be identified from an analysis of front geometries based on transport theory. For the interpretation of stable isotope fronts the distinction between equilibrium and disequilibrium scenarios is crucial. For fossil systems this distinction can be made only if two or more minerals are considered as stable isotope monitors simultaneously. We derive approximations that describe one-dimensional advective-dispersive transport and coupled first-order kinetic mineral-fluid exchange, where the various constituent minerals of the rock are allowed to have different exchange rates. The new formalism is an extension of transport theory that accounts for the polyphase nature of rocks and allows integration of isotopic information from several monitoring phases. Comparison of the geometries of stable isotope fronts monitored by different phases permits identification of departures from local equilibrium that occurred during fluid-rock interaction. Furthermore it permits distinction of the contributions of diffusion-dispersion and of kinetically controlled mineral-fluid exchange to the distension of an initially sharp front. If mineral-fluid exchange is kinetically controlled, this has an interesting implication for stable isotope thermometry in that the inter-mineral fractionations may vary as a function of space and time irrespective of the system temperature. The series approximations presented here provide a formal basis for the interpretation of such disequilibrium phenomena. In particular they facilitate extraction of quantitative relations among transport velocities, exchange rates, and the duration of fluid-rock interaction from front geometries.

INTRODUCTION

The fluid in the pore spaces of a rock has profound influence on the physical rock properties during metamorphism. In particular, the fluid phase

* Present address; Institut für Mineralogie-Kristallographie und Petrologie, Karl-Franzens-Universität Graz, Universitätsplatz 2, A-8010 Graz, Austria.

** Seminar für Angewandte Mathematik, ETH-Zürich, Fliederstrasse 23, CH-8092 Zürich, Switzerland.

plays an important role in material transport. In general, the pore fluid that was present during metamorphism is removed through compaction and textural evidence of fluid pathways that may have existed earlier is usually obliterated by continuous deformation and recrystallization before a metamorphic rock becomes amenable to petrographic observation. Fluid-rock interaction that occurred during metamorphism can usually be inferred only from indirect evidence such as anomalous mineralogical, chemical, and/or isotopic rock compositions. In this context stable isotope fronts are of special interest. Initially sharp fronts may be degraded and/or displaced by isotope transport in the pore fluid.[1] Material transport may then be monitored by the constituent minerals of the rock through mineral-fluid isotopic exchange. The geometry of an evolving stable isotope front depends on the mechanisms and the relative rates of the processes involved in transport and exchange.

If mineral-fluid exchange is "infinitely" rapid compared to material transport, then local equilibrium is maintained, and the front geometry is entirely determined by the extent and the mechanisms of material transport. In particular, the degradation and distension of an initially sharp front can be unambiguously ascribed to dispersion,[2] and the relative contributions of advective and dispersive transport can be estimated from the comparison of front displacement and distension. The formalism that describes advective-dispersive transport and coupled equilibrium exchange has been introduced into the geological literature by a number of authors (Hofmann, 1972; Fletcher and Hofmann, 1974; Bickle and McKenzie, 1987; Baumgartner and Rumble, 1988; among others). Based on the local equilibrium assumption, analytical solutions of the governing equations were repeatedly used to constrain transport mechanisms and integrated fluxes by inverse modeling of front geometries (Ganor, Mathews, and Paldor, 1989; Bickle and Baker, 1990; Jamtveit, Bucher-Nurminen, and Stijfhoorn, 1991; Todd and Evans, 1993; Cartwright, 1994; among others). The local-equilibrium concept is, however, in conflict with numerous observations of disequilibrium intermineral fractionations in rocks that experienced fluid-rock interaction (Taylor 1974, 1977; Taylor and Turi, 1976; Forester and Taylor, 1977; Taylor and Forester, 1979; Gregory and Taylor, 1981; Chriss and Taylor, 1986; Criss, Gregory, and Taylor, 1987; Abart, 1995; Barnet and others, 1996; among others). If mineral-fluid exchange is kinetically controlled and both material transport and mineral-fluid exchange occur at finite rates, then the system may depart from local equilibrium during fluid-rock interaction. In this case the geometry of an evolving front not only depends on the extent and the mechanisms of material transport, but it may also be modified significantly by mineral-fluid exchange. In particular, kinetically controlled mineral-fluid exchange contributes to front distension in addition to diffusive-dispersive processes (Lassey, 1988a; Lassey and Blattner, 1988; Bickle, 1992; Baker and

[1] Material transport by solid-state diffusion is several orders of magnitude slower than fluid-bound transport and will be disregarded in the following discussion.

[2] In this context the term "dispersion" describes the combined effects of molecular diffusion and hydrodynamic dispersion, which may be treated similarly in a Fickian framework.

Spiegelman, 1995). The kinetics of mineral-fluid isotopic exchange was discussed in detail by Cole and Ohmoto (1986). Cole, Ohmoto, and Lasaga (1983) derived a pseudo first-order rate law for surface-reaction controlled mineral-fluid isotopic exchange. The incorporation of linear kinetics into transport theory does not pose major problems to a numerical solution of the governing equations (for a review, see Bowman, Willet, and Cook, 1994), but it adds some complexity to an analytical treatment. So far, only several endmember scenarios have been solved analytically. A closed solution for pure diffusive tracer transport and coupled first-order kinetic mineral-fluid exchange was given by Crank (1975). An alternative scenario with pure advective tracer transport and coupled first-order kinetic mineral-fluid exchange was treated analytically by Lassey and Blattner (1988). The more general case of simultaneous advective-dispersive tracer transport and first-order kinetic mineral-fluid isotopic exchange was solved analytically by Ogata (1964) and by Lassey (1988b). The solutions given by the latter authors, however, have two limitations: On the one hand, they contain integrals that can only be evaluated numerically and are thus impractical for many purposes. On the other hand, the solutions are designed for scenarios where kinetically controlled mineral-fluid exchange only occurs between one monitoring phase and the pore fluid. It has been shown by Baker and Spiegelman (1995) that it is generally not possible to distinguish between the contributions to the distension of an initially sharp front from dispersive processes and from kinetically controlled mineral-fluid exchange, if the front is defined by the isotopic compositions of only one monitoring phase or by bulk rock compositions. This ambiguity with respect to the mechanisms of front distension severely limits the potential of inverse modeling based on front geometries. For the interpretation of front geometries the distinction between equilibrium exchange and departures from local equilibrium due to kinetically controlled mineral-fluid exchange is crucial. This distinction can generally be made only if the stable isotope fronts preserved by several monitoring phases and the systematics of the inter-mineral fractionations are considered. In this communication we present an approach that fully accounts for the polyphase nature of rocks and takes into consideration the systematics of inter-mineral fractionations. A similar approach has already been suggested by Barnett and Bowman (1995), who used numerical techniques to solve the governing equations. We present for the first time explicit expressions for advective-dispersive tracer transport and coupled first-order kinetic mineral-fluid exchange in a polyphase rock. Our formalism allows the solid-phase matrix of a porous rock to be treated as an aggregate comprised of a variety of constituent minerals, with different rates of mineral-fluid exchange.

In a companion paper (Eppel and Abart, 1997) this new formalism is applied to the analysis of the isotope signature preserved in the metasediments of the Cretaceous Palombini Formation at a Penninic-Lower Austroalpine tectonic contact in eastern Switzerland.

THEORY

One-dimensional Transport and Kinetic Exchange

The geometrical features of stable isotope patterns from coupled transport and kinetically controlled mineral-fluid exchange in a one-dimensional system are first derived qualitatively. Consider a hypothetical one-dimensional, semi-infinite system containing a rock composed of two mineral phases, *a* and *b*, and a pore fluid, *f*. Let the temperature be constant throughout the system. Initially the constituent minerals of the rock and the pore fluid are in isotopic equilibrium, and their isotopic compositions are constant throughout the system. At some stage the rock is juxtaposed to an external fluid reservoir. Let this reservoir be inexhaustible and well mixed so that the fluid composition at the interface between the external reservoir and the rock remains fixed at reservoir composition. If the isotopic composition of the reservoir fluid is different from the composition of the pore fluid in the rock, a sharp stable isotope front is established at the interface. This front may propagate into the rock by fluid advection, and it will be degraded by the combined effects of molecular diffusion, hydrodynamic dispersion, and mineral-fluid exchange. With respect to the relative rates of isotope transport and mineral-fluid exchange, three scenarios can be envisaged: If the constituent minerals of the rock do not exchange with the fluid at all, then an isotopic front will develop only in the pore fluid (fig. 1A). If, in an alternative scenario, the rates of mineral-fluid exchange are infinitely fast, then local equilibrium will prevail during fluid-rock interaction. Isotopic fronts will develop equally in the constituent minerals and in the pore fluid. In this case, the inter-mineral isotopic fractionations are exclusively a function of the system temperature, and they are constant throughout the system (fig. 1B). If, in a third scenario, mineral-fluid exchange takes place at finite rates, then the fronts monitored

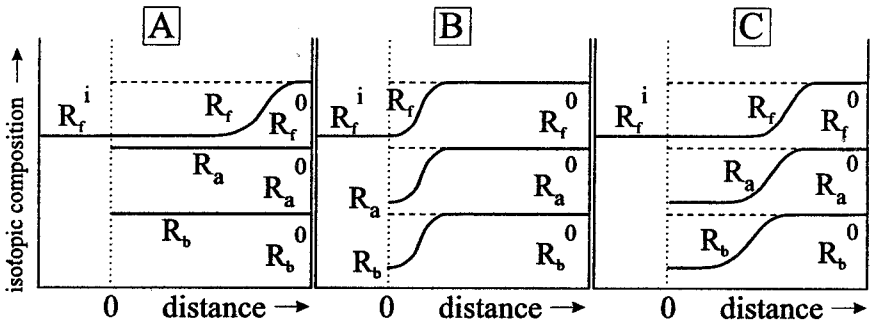

Fig. 1. Schematic illustration of the propagation of a stable isotope front in a hypothetical rock composed of minerals *a* and *b*, and the pore fluid *f*, after juxtaposition to a well mixed, inexhaustable external fluid reservoir; composition of the pore fluid is fixed to reservoir composition at the interface between the external reservoir and the rock; – initial situation indicated by dashed lines – propagation of isotope fronts shown by bold curves for non-reactive transport (A), instantaneous mineral-fluid equilibration (B), and kinetically controlled mineral-fluid exchange (C).

by the constituent minerals will lag behind the front in the pore fluid (fig. 1C), and they will be more strongly distended. As a consequence, the inter-mineral fractionations will show a systematic spatial variation, even if the temperature is constant throughout the system, and they will vary with time.

Governing equations

In modeling the isotopic effects of fluid-rock interaction, it is convenient to express the observed isotopic shifts as "normalized" isotopic compositions. The isotopic compositions of minerals are normalized to their initial compositions prior to fluid-rock interaction and to the compositions they would have in equilibrium with the externally derived fluid. The normalized isotopic composition of phase k is defined as:

$$R_k = \frac{\delta_k^{obs} - \delta_k^{init}}{\delta_k^{eq} - \delta_k^{init}},$$

where δ_k^{init} is the isotopic composition of phase k before fluid-rock interaction has started, δ_k^{eq} is the isotopic composition of phase k in equilibrium with the externally derived fluid, and δ_k^{obs} is the observed isotopic composition of

TABLE 1

Frequently used symbols

t	time	[s]
X	distance	[m]
D	dispersion coefficient	[m^2/s]
v	mean interstitial particle velocity	[m/s]
q	Darcy velocity	[m/s]
ϕ	porosity	
X_f	fraction of the exchanging element contained in the pore fluid	
X_k	fraction of the exchanging element contained in mineral phase k	
γ_k	partitioning of the exchanging element between mineral k and the fluid	
α_k	equilibrium isotopic fractionation factor between mineral k and the pore fluid	
K_k	overall rate of mineral-k fluid isotopic exchange	[1/s]
R_f	normalized isotopic composition of the pore fluid	
R_k	normalized isotopic composition of mineral k	
L	scaling distance	[m]
x	dimensionless distance	
τ	dimensionless time	
N_{Pe}	Peclet Number	
N_k^{DI}	Damköhler I Number of mineral k	
N_k^{DII}	Damköhler II Number of mineral k	

phase k. R_k takes values between 0 and 1 and is equivalent to the reaction progress variable as introduced by Myers and Prestwood (1951).

Assume a one-dimensional, semi-infinite system extending from $X = 0$ to $X = \infty$ containing a rock composed of M mineral phases k, with normalized isotopic compositions $R_k^0 = 0$ in isotopic equilibrium with a pore fluid of initially uniform normalized composition, $R_f^0 = 0$. Let the temperature be constant with time throughout the system. At $t = 0$ the rock is exposed to a well mixed, inexhaustible external fluid reservoir of isotopic composition $R_f^i = 1$. If the external fluid is connected to the pore fluid of the rock then isotopic fronts will develop in the pore fluid and the constituent phases of the rock. Let fluid advection and dispersion in the pore fluid account for the bulk of material transport, and let mineral-fluid isotopic exchange be controlled by first-order kinetics. The temporal evolution of such a system is formally described by the differential equations:

$$D\frac{\partial^2 R_f}{\partial X^2} - v\frac{\partial R_f}{\partial X} = \frac{\partial R_f}{\partial t} + \sum_{k=1}^{M} \gamma_k \frac{\partial R_k}{\partial t} \tag{1}$$

$$\frac{dR_k}{dt} = K_k(R_f \alpha_k - R_k), \tag{2}$$

which must satisfy the initial and boundary conditions:

$$\begin{aligned} R_f(X, 0) &= 0, \qquad R_k(X, 0) = 0 \qquad \text{for } X > 0 \\ R_f(0, t) &= 1, \qquad R_f(\infty, t) = 0 \end{aligned} \tag{3}$$

R_f and R_k are the normalized isotopic compositions of the pore fluid and mineral k, respectively. X and t are distance and time, D is the effective dispersivity, v is the mean interstitial particle velocity which is related to the Darcy velocity q through $v = q/\phi$, where ϕ is the volumetric porosity. The parameter γ_k is defined as the ratio X_k/X_f, where X_k and X_f represent the atomic fractions of the element whose isotopes are under consideration, hosted in mineral phase k and in the pore fluid. The kinetics of mineral-fluid isotopic exchange is described by a pseudo first-order rate law (Northrop and Clayton, 1966; Cole, Ohmoto, and Lasaga, 1983). This implies that mineral-fluid isotopic exchange is controlled by surface reaction and that intra-mineral diffusion does not significantly influence the rate of mineral-fluid exchange. K_k is the overall rate constant of exchange between mineral k and the fluid, and α_k is the equilibrium fractionation factor between mineral k and the fluid.

In eqs (1) and (2) isotope transport and mineral-fluid isotopic exchange are parameterized by a total of $M + 2$ system variables as a function of space and time coordinates. Transport is parameterized by the mean interstitial particle velocity, v, and by the dispersion coefficient, D. The rates of the M mineral-fluid exchange reactions are expressed by the M overall rate constants, K_k. The number of system parameters can be reduced if the equations are

rewritten in dimensionless form. This may be done by choosing an arbitrary scaling distance L and defining dimensionless distance as

$$x = \frac{X}{L}$$

The relative contributions of advection and diffusion-dispersion to isotope transport are described by the Peclet Number, defined as:

$$N_{Pe} = \frac{vL}{D}.$$

There are two possibilities to describe the interplay between transport and exchange (Damköhler, 1936; Boucher and Alves, 1959): The relative rates of the advective contribution to isotope transport and mineral-fluid isotopic exchange are expressed by the Damköhler I Number, defined as:

$$N_k^{DI} = \frac{K_k L}{v}.$$

The corresponding definition of dimensionless time is:

$$\tau = \frac{vt}{L}.$$

The Damköhler I Number is small if mineral-fluid isotopic exchange is slow relative to advective isotope transport, and it is large if the rate of mineral-fluid exchange is relatively fast. For instantaneous mineral-fluid equilibration, the Damköhler Number is infinity. For non-reactive advective transport, it is zero. The relative rates of transport and exchange may be expressed alternatively in terms of the Damköhler II Number. The Damköhler II Number compares the dispersive contribution of material transport to the rates of mineral-fluid exchange. It is defined as:

$$N_k^{DII} = \frac{K_k L^2}{D}.$$

In this case dimensionless time is given by:

$$\tau = \frac{Dt}{L^2}.$$

Out of the three dimensionless parameters, Peclet Number, Damköhler I Number, and Damköhler II Number, only two are independent variables. Two of these parameters are sufficient to describe the interplay of advective-dispersive transport and first-order kinetic mineral-fluid exchange. The choice of which parameter set to use to describe the system is arbitrary and does not

influence the analysis. In the following discussion transport and exchange are parameterized by N_{Pe} and N_k^D, where the choice of the definitions for N_k^D and τ remain unspecified.

Substitution of the above definitions into eqs 1 and 2 yields:

$$\frac{1}{N_{Pe}}\frac{\partial^2 R_f}{\partial x^2} - \frac{\partial R_f}{\partial x} = \frac{\partial R_f}{\partial \tau} + \sum_{k=1}^{M} \gamma_k \frac{\partial R_k}{\partial \tau} \tag{4}$$

$$\frac{dR_k}{d\tau} = N_k^D (R_f \alpha_k - R_k), \tag{5}$$

with initial and boundary conditions:

$$\begin{aligned} &R_f(x, 0) = 0, \qquad R_k(x, 0) = 0 \qquad \textit{for } x > 0 \\ &R_f(0, \tau) = 1, \qquad R_f(\infty, \tau) = 0 \end{aligned} \tag{6}$$

In eqs (4) and (5) coupled isotope transport and mineral-fluid exchange are described by a total of $M + 1$ system parameters. This set represents the minimum number of parameters required to describe the geometry of stable isotope patterns that may develop during fluid-rock interaction for which the initial and boundary conditions in eq (6) hold.

Series approximations.–Eqs (4) and (5) must be solved simultaneously. An analytical solution for the special case of $M = 1$ was given by Ogata (1964) and by Lassey (1988b). For the case where $M > 1$ we suggest solutions that take the form of infinite series. For computational purposes the convergence behavior of the series expansions is crucial. The behavior of the series depends on the contribution of kinetically controlled mineral-fluid exchange to the material balance in a control volume. The magnitude of this contribution depends on the modal abundances of the minerals with kinetically controlled exchange, on the mineral-fluid equilibrium fractionation factors, and on the corresponding Damköhler Numbers. The relative importance of kinetic exchange may be expressed by a parameter σ defined as:

$$\sigma = \sum_{k=1}^{M} \alpha_k \gamma_k N_k^D$$

If σ is small, then kinetically controlled mineral-fluid isotopic exchange has only minor influence on the isotopic composition of the pore fluid and on the propagation and distension of the isotope front in the pore fluid. If σ is large, then the isotopic composition of the pore fluid and the geometry of the isotope front that develops in the pore fluid are significantly influenced by mineral-fluid isotopic exchange. Two different series expansions have been developed that give good approximations for scenarios with relatively small effects of exchange kinetics on the material balance of the pore fluid.

Series approximation for $\sigma < 1$.–If the modal abundances of the phases with kinetically controlled mineral-fluid exchange and the corresponding

Damköhler Numbers are small, so that $\sigma < 1$, then the following series approximations may be applied:

$$R_f(y,\tau) = \frac{1}{2}\, e^{(\sqrt{N_{Pe}}/2)y} G\left(y, \tau \frac{\sqrt{N_{Pe}}}{2}\right) - \epsilon \sum_{k=1}^{M} \frac{\beta_k y e^{(\sqrt{N_{Pe}}/2)y - N_k^D \tau}}{4\omega_k} [B(y,\tau,-\omega_k) - B(y,\tau,\omega_k)] \quad (7)$$

$$R_k(y,\tau) = \frac{\alpha_k}{2}\, e^{(\sqrt{N_{Pe}}/2)y}\left[G\left(y,\tau,\frac{\sqrt{N_{Pe}}}{2}\right) - e^{-N_k^D\tau}\, G(y,\tau,\omega_k)\right] - \epsilon \frac{\alpha_k N_k^D y}{2}\, e^{(\sqrt{N_{Pe}}/2)y}\left[\beta_k T_k(y,\tau) + \sum_{l=1,l\neq k}^{M} \frac{\beta_l}{(\omega_k^2 - \omega_l^2)} F_k(y,\tau) + \frac{\beta_l}{(\omega_l^2 - \omega_k^2)} F_l(y,\tau)\right] \quad (8)$$

where

$$y = \sqrt{N_{Pe}}x, \qquad \beta_k = \frac{\gamma_k \alpha_k N_k^D}{\epsilon}, \qquad \omega_k = \sqrt{\frac{N_{Pe}}{4} - N_k^D},$$

and ϵ is an arbitrarily defined constant <1. The functions $B(y,\tau,s)$, $G(y,\tau,s)$, $Ex(y,\tau,s)$, $T_k(y,\tau)$, and $F_k(y,\tau)$ are defined as follows:

$$B(y,\tau,s) = e^{ys} erfc\left(\frac{y}{2\sqrt{\tau}} + s\sqrt{\tau}\right)$$

$$G(y,\tau,s) = B(y,\tau,s) + B(y,\tau,-s)$$

$$Ex(y,\tau,s) = exp\left[-\left(\frac{y^2}{4\tau} + s^2\tau\right)\right]$$

$$T_k(y,\tau) = \frac{1}{\omega_k^2}\left(\frac{\tau}{\pi}\right)^{1/2} Ex\left(y,\tau,\frac{\sqrt{N_{Pe}}}{2}\right) + \frac{1}{4\omega_k^3} e^{-N_k^D\tau}[B(y,\tau,\omega_k)(1 - \omega_k y - 2\omega_k^2\tau) + B(y,\tau,-\omega_k)(-1 - \omega_k y + 2\omega_k^2\tau)]$$

$$F_k(y,\tau) = \frac{1}{2\omega_k} e^{-N_k^D\tau}[B(y,\tau,-\omega_k) - B(y,\tau,\omega_k)] \quad (9)$$

Series approximation for large N_k^D.–If the modal abundances of the phases with kinetically controlled mineral-fluid exchange and the corresponding

Damköhler Numbers are large, so that $\sigma > 1$, then the following series approximations may be applied:

$$R_f(y, \tau) = \frac{1}{2} e^{(\sqrt{N_{Pe}}/2)y} G\left(y, \tau, \frac{\sqrt{N_{Pe}}}{2}\right) - \epsilon\left[\frac{y}{2}\left(\frac{1}{\pi\tau}\right)^{1/2} e^{(\sqrt{N_{Pe}}/2)} Ex\left(y, \tau, \frac{\sqrt{N_{Pe}}}{2}\right)\hat{\sigma}\right] \quad (10)$$

$$R_k(y, \tau) = \frac{\alpha_k}{2} e^{(\sqrt{N_{Pe}}/2)y}\left[G\left(y, \tau, \frac{\sqrt{N_{Pe}}}{2}\right) - e^{-N_k^D \tau} G(y, \tau, \omega_k)\right]$$

$$- \epsilon\left[\frac{\alpha_k N_k^D y}{4\omega_k} e^{(\sqrt{N_{Pe}}/2)y - N_k^D \tau}[B(y, \tau, -\omega_k) - B(y, \tau, \omega_k)]\hat{\sigma}\right], \quad (11)$$

where $\hat{\sigma} = \Sigma_{k=1}^{M} \alpha_k \gamma_k N_k^D / d_k$, with $d_k = \epsilon N_k^D$, and ϵ is an arbitrarily defined constant <1.

The series expansions from which eqs (7) to (11) are derived may be obtained in several ways. The methods of derivation as well as special cases, such as the steady-state solution and simplified solutions for the case where $M = 1$ and $N^D = N_{Pe}/4$ are described in the appendix. The expressions given here are good approximations for small values of dimensionless time and for scenarios where only a small fraction of the exchanging element is contained in the phases with kinetically controlled mineral-fluid exchange. Higher order correction terms must be considered, if alternative scenarios and long time duration of fluid-rock interaction are to be modeled. Higher order correction terms are, however, relatively complex expressions, and for systems where the bulk of the exchanging element is contained in phases with kinetically controlled mineral-fluid exchange, it may be necessary to develop alternative approximations.

Quality of approximations.–Eqs (7) to (11) are derived from infinite series expansions truncated after the first two terms. For the function $R_f = R_f(x, \tau)$ the first term of the series describes the shape of an isotopic front for non-reactive advective-dispersive transport. The second term introduces a first-order correction that accounts for the gains/losses of the isotopic tracer in the pore fluid due to kinetically controlled mineral-fluid isotopic exchange. For the function $R_k = R_k(x, \tau)$ the first term of the solution only accounts for exchange of mineral k and the pore fluid. Higher order terms introduce the effects of exchange between minerals l and the fluid, where $l \neq k$. In both cases, $R_f = R_f(x, \tau)$ and $R_k = R_k(x, \tau)$, the second term of the series is always negative, and successive terms have alternating signs. The true solution thus lies between the curves representing the series expansion truncated after the n^{th} and the $(n + 1)^{\text{th}}$ terms.

DISCUSSION

To illustrate the features of the stable isotope pattern that develops in the course of one dimensional advective-dispersive transport and coupled first-order kinetically controlled mineral-fluid exchange in a polyphase rock, we chose a hypothetical model system. Assume a rock composed of three minerals, *a*, *b*, *c* and a pore fluid *f*. Let the rates of mineral-fluid isotope exchange decrease in the order $K_a \gg K_b > K_c$, and let the corresponding

Damköhler numbers be $N_a^D = \infty$, $N_b^D = 5$, $N_c^D = 0.5$. Mineral abundances and porosity are such that 80 percent of the isotopic element under consideration is contained in the instantaneously exchanging mineral *a* and the pore fluid. Minerals *b* and *c* for which isotopic exchange is kinetically controlled contain 10 percent of the respective element each. Let transport be dominated by advection on the observational scale so that $N_{Pe} = 15$. The system is subject to the initial- and boundary-conditions given in eq (6). The normalized isotopic compositions of the three mineral phases and the pore fluid are shown as a function of dimensionless distance in figure 2A, B, and C for three different stages of fluid-rock interaction. In this coordinate frame the isotopic composition of phases in isotopic exchange equilibrium with each other coincide and the difference between their normalized isotopic compositions, henceforth referred to as the "normalized inter-mineral fractionation," is zero. If the normalized inter-mineral fractionation between two phases deviates from zero, the phases are out of isotopic exchange equilibrium. The systematics of the normalized inter-mineral fractionations in the hypothetical model system are illustrated in figure 2D, E, and F.

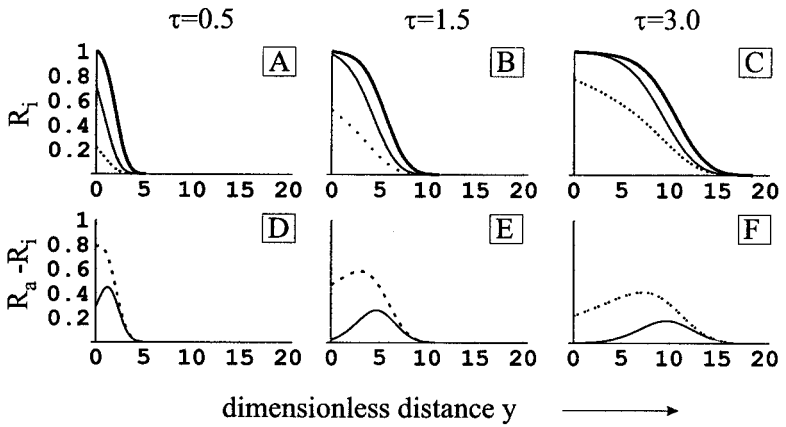

Fig. 2. Normalized stable isotope compositions and inter-mineral fractionations at three different stages of fluid-rock interaction (τ = 0.5, 1.5, 3.0) in a hypothetical rock comprised of minerals *a*, *b*, and *c*; modal mineral abundances are such that $\gamma_a = 0.8$, $\gamma_b = \gamma_c = 0.1$; material transport is by one-dimensional advective-dispersive transport with $N_{Pe} = 15$; mineral-fluid exchange is kinetically controlled with, $N_a^D = \infty$, $N_b^D = 2.5$, and $N_c^D = 0.5$; diagrams (A), (B), and (C): geometries of fronts monitored by mineral *a* (coincides with the front in the pore fluid) – heavy solid line, mineral *b* – thin solid line, and mineral *c* – dashed line; diagrams (D), (E), and (F): normalized inter-mineral fractionations between minerals *a* and *b* – solid line, and between minerals *a* and *c* – dashed line.

The geometries of the fronts recorded by the various monitoring phases of the hypothetical model system are significantly different from one another and generally do not coincide. For a given value of dimensionless time both the positions as well as the shapes differ if the fronts are monitored by phases with different N_k^D's. Only the front recorded by phase *a* coincides with the front in the pore fluid; that is, mineral *a* and the pore fluid are in local

equilibrium with each other. The "local equilibrium front" propagates farthest into the rock. The fronts recorded by phases *b* and *c* lag behind, and they are more strongly distended. The lag of fronts *b* and *c* with respect to the "local equilibrium front" as well as their additional distension are entirely due to the limited exchange rates of phases *b* and *c*. For each of the monitoring phases the relative contribution of kinetically controlled mineral-fluid exchange to front distension is different, and, as a consequence, the relation between relative front displacement and front distension is different for each front. Extraction of transport and exchange parameters from a stable isotope front gives meaningful results only if the degree of equilibration between the monitoring phase and the pore fluid during fluid-rock interaction is known. If the front is defined by the spatial variation of the compositions of only one monitoring phase or by bulk rock compositions, it is generally not possible to distinguish between equilibrium exchange and deviations from local equilibrium from front geometry (Lassey, 1988a; Bowman, Willet, and Cook, 1994; Baker and Spiegelmann, 1995). In such a case, the contributions to front distension of dispersive processes, on the one hand, and of kinetically controlled mineral-fluid exchange, on the other, can not be distinguished, and the interpretation of front geometries remains ambigous. This ambiguity is largely resolved and the potential for inverse modeling is greatly enhanced, if the fronts recorded by different monitoring phases are considered simultaneously. In particular, the systematics of the inter-mineral fractionations provide information on the extent of equilibration during fluid-rock interaction. Comparison of the front geometries recorded by different minerals allows extraction of quantitative relations among the relative rates of mineral-fluid exchange. If the N^D can be established for either one of the monitoring phases from independent evidence, all the transport and exchange parameters, that is N_{Pe} and all the remaining N_k^Ds can be quantitatively derived from front geometries by applying the above formalism along with standardized optimization procedures.

The effects of exchange kinetics on inter-mineral fractionations have interesting consequences for stable isotope thermometry. The normalized inter-mineral fractionations illustrated in figure 2D, E, F show significant deviations from the equilibrium value of zero across the isotopic front. They have a maximum that is shifted into the rock together with the front. By definition the temperature is constant with time throughout the system. The variation in the inter-mineral fractionations as a function of space and time therefore does not reflect any thermal structure; it is merely a consequence of different exchange rates of the various monitoring phases. If an isotopic front develops in a rock composed of minerals with kinetically controlled mineral-fluid exchange, a "wave" of disequilibrium fractionations propagates into the rock together with the front. The deviations from equilibrium fractionations are most pronounced during the incipient stages of fluid-rock interaction, and these disequilibrium phenomena degrade as fluid-rock interaction proceeds.

The influence of N_{Pe} and N_k^Ds on the geometry of stable isotope patterns is illustrated in figure 3. The normalized isotopic compositions of the fluid and the constituent minerals of the rock are plotted against dimensionless

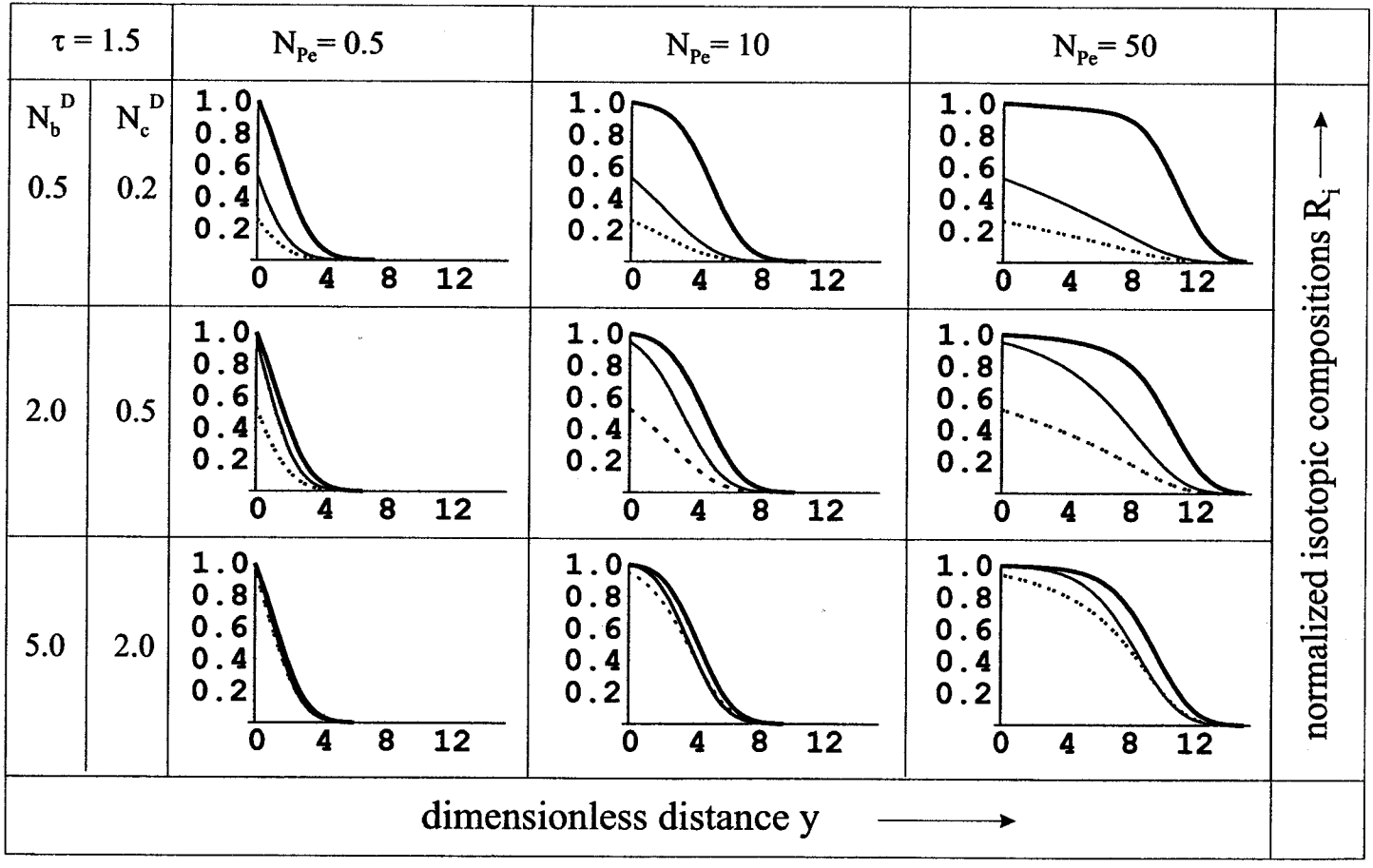

Fig. 3. Influence of the Peclet Number and Damköhler Numbers on the stable isotope patterns that may develop in the hypothetical model system of figure 2; normalized stable isotope compositions of minerals *a*, *b*, and *c* as a function of dimensionless distance *y* for a fixed value of dimensionless time $\tau = 1.5$; *a* and the pore-fluid – heavy solid lines, *b* – thin solid lines, *c* – dashed lines; N_{Pe} increases from left to right, N_k^{Da}s increase from top to bottom.

distance for a fixed value of dimensionless time. The Peclet Number increases from left to right; the Damköhler Numbers increase from top to the bottom of the figure. Significant deviations from local equilibrium occur only at low Damköhler Numbers. In this case, the fronts preserved by the different monitoring phases are clearly separated from one another. At high Damköhler Numbers the fronts from the different monitoring phases tend to coincide. For a given set of Damköhler Numbers the disequilibrium phenomena and front separation are more pronounced at high Peclet Numbers than at low Peclet Numbers.

The time evolution of the inter-mineral fractionations between phases a and b in a hypothetical model system is shown in figure 4. In this model case 90 percent of the exchanging element is contained in phase a with $N_a^D = \infty$ and in the pore fluid, and 10 percent of the respective element is hosted in mineral b, for which the mineral-fluid exchange rate is finite. The differences in the normalized isotopic compositions between a and b, that is the normalized $a - b$ fractionations are plotted against dimensionless distance for several values of dimensionless time. Note that in this figure the abscissa is scaled by a factor $1/\tau$, and the scaling is different for each of the individual $R_a - R_b$ curves within each diagram. As in the previous figure, the Peclet Number increases from left to right, and the Damköhler Number of mineral b increases from the top to the bottom of the figure. Significant departure from local equilibrium is predicted for small values of dimensionless time. In the initial stage $R_a - R_b$ decreases monotonically with distance from the system boundary. With increasing time a local maximum in $R_a - R_b$ develops. A "wave" of disequilibrium inter-mineral fractionations propagates into the rock together with the isotope front. At large Damköhler Numbers the maximum in $R_a - R_b$ decreases rapidly with time, and the $R_a - R_b$ curves are close to symmetrical around the maximum. For low Damköhler Numbers the maximum in $R_a - R_b$ degrades at a slower rate, and the curve is skewed around the maximum. This is particularly pronounced at high Peclet Numbers.

SUMMARY AND CONCLUSIONS

The understanding of the processes involved in fluid-rock interaction in fossil systems from an analysis of stable isotope fronts may be greatly enhanced, if two or more of the constituent minerals of a rock are considered as stable isotope monitors simultaneously. The formalism presented here fully accounts for the polyphase nature of rocks and allows integration of isotopic information from several minerals at a time. In general, the fronts preserved by the various monitoring phases of a rock have different geometries. The tracer-front as it propagates in the pore fluid is monitored without modification only by phases for which mineral-fluid equilibration is instantaneous. The "local equilibrium front" monitored by these phases propagates farthest. Stable isotope fronts that are monitored by phases with finite rates of

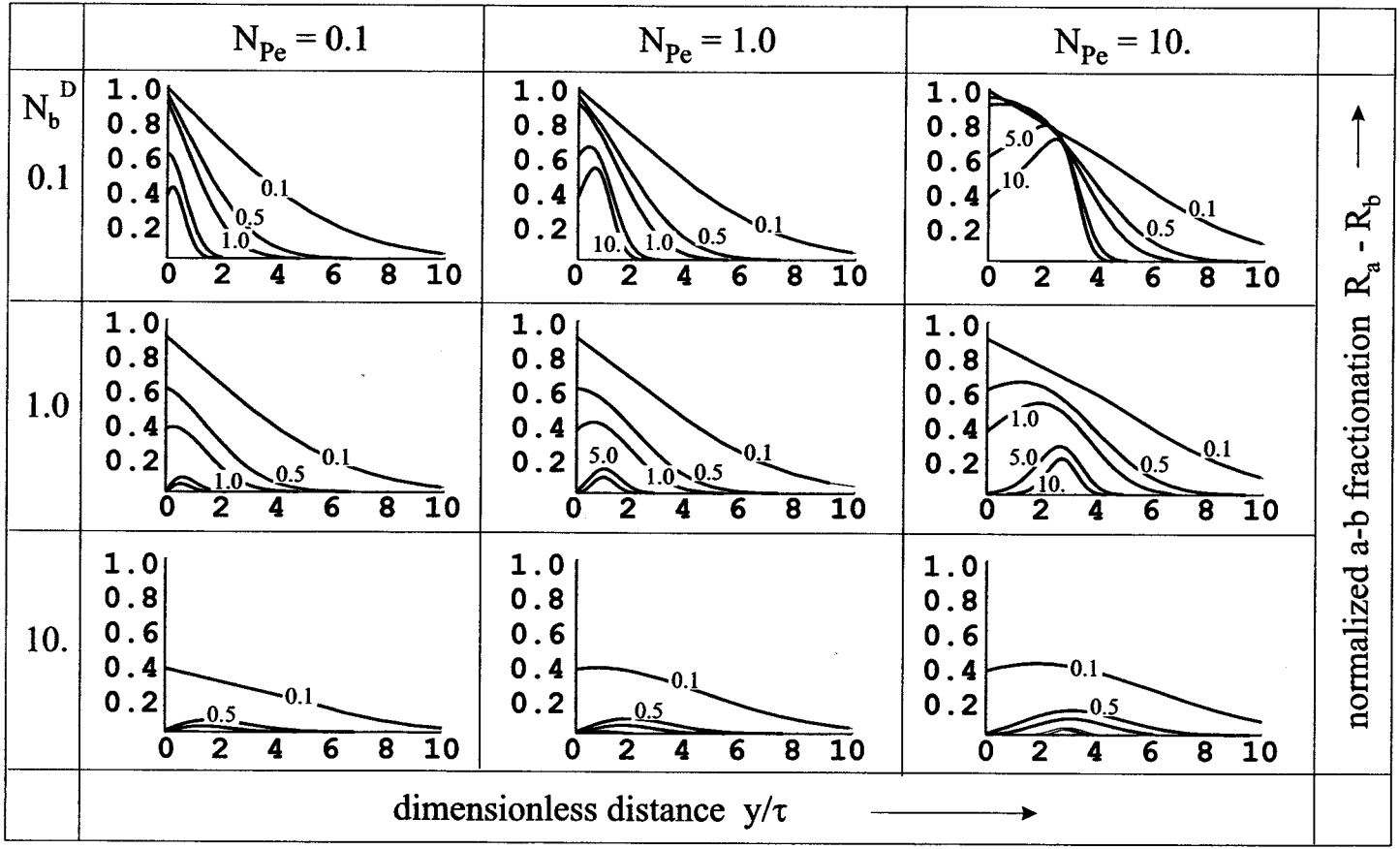

Fig. 4. Time evolution of the normalized inter-mineral fractionations, $R_a - R_b$ for different scenarios of fluid-rock interaction in a hypothetical rock comprised of two minerals a and b; 90 percent of the exchanging element contained in mineral a and the pore fluid, 10 percent of the exchanging element contained in mineral b; $N_a^D = \infty$, N_b^D increases from top to bottom; N_{Pe} increases from left to right; the numbers on the curves give the respective values of τ, dimensionless distance on the abscissa is scaled by a factor $1/\tau$.

mineral-fluid exchange lag behind the local equilibrium front, and they are more strongly distended. Comparison of the geometrical features of the fronts preserved by the various monitoring phases allows derivation of quantitative relations among the exchange rates of the respective phases, and it permits discrimination of the contributions to front distension of dispersion on the one hand, and of kinetically controlled mineral-fluid exchange on the other. As a consequence of differences in mineral-fluid exchange rates the inter-mineral fractionations will vary systematically as a function of space and time irrespective of the system temperature. In a rock composed of minerals with different exchange rates a "wave" of disequilibrium fractionations develops across a propagating front. The systematics of the inter-mineral fractionations contain information on deviations from local equilibrium that occur during fluid-rock interaction and thus provide a means to derive relations among transport velocities and mineral-fluid exchange rates. The geometries of stable isotope fronts preserved by the various constituent minerals of a rock contain information on the mechanisms and the relative rates of material transport and mineral-fluid exchange as well as on the duration of fluid-rock interaction. The explicit nature of the solutions presented here facilitates efficient analysis of observational data by standardized optimization procedures.

ACKNOWLEDGMENTS

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APPENDIX A

Method of solution using Laplace-transformation

For the subsequent derivations it is convenient to simplify the notation. The differential eqs (4) and (5) may be rewritten in the form:

$$\frac{1}{\nu}\frac{\partial^2 R}{\partial x^2} - \frac{\partial R}{\partial x} = \frac{\partial R}{\partial \tau} + \sum_{k=1}^{M} \gamma_k \frac{\partial r_k}{\partial \tau}$$

$$\frac{dr_k}{d\tau} = \delta_k (R\alpha_k - r_k), \tag{A-1}$$

with the obvious interpretations of R, r_k, and the parameters ν, α_k, γ_k, and δ_k. The initial and boundary conditions are:

$$R(x, 0) = 0, \qquad r_k(x, 0) = 0, \qquad \textit{for } x > 0$$
$$R(0, \tau) = 1, \qquad R(\infty, \tau) = 0 \tag{A-2}$$

Our aim is to expand the solution in powers of a small parameter ϵ which will be selected later on. The expansion of for example $R(x, \tau, \epsilon)$ will then be of the form:

$$R(x, \tau, \epsilon) = R_0(x, \tau) + \epsilon R_1(x, \tau) + \epsilon^2 R_2(x, \tau) + \ldots \tag{A-3}$$

and similar expansions hold for the $r_k(x, \tau, \epsilon)$. We will restrict our calculations to first-order approximations, that is, only the first two terms of the expansion will be used. A convenient way to calculate the necessary expansions is by using the Laplace-transforms.

Laplace Transforms

The Laplace-transforms of $R(x, \tau)$ and $r_k(x, \tau)$ are written as $\overline{R}(x, p)$ and $\bar{r}_k(x, p)$. Using the rules for Laplace-transforms (see, for example, Crank, 1975) the differential equations in (A-1) are reduced to:

$$\frac{1}{\nu}\overline{R}'' - \overline{R}' = p\overline{R} + p\sum_{k=1}^{M}\gamma_k\bar{r}_k$$

$$p\bar{r}_k = \delta_k(\overline{R}\alpha_k - \bar{r}_k) \tag{A-4}$$

Here the prime denotes d/dx. The boundary conditions for $\overline{R}$ become:

$$\overline{R}(0) = \frac{1}{p}, \qquad \overline{R}(\infty) = 0 \tag{A-5}$$

The equations in (A-4) are then reduced to

$$\frac{1}{\nu}\overline{R}'' - \overline{R}' = p\overline{R} + p\sum_{k=1}^{M}\alpha_k\gamma_k\delta_k\frac{1}{p+\delta_k}\overline{R} \tag{A-6}$$

or in abbreviated form:

$$\frac{1}{\nu}\overline{R}'' - \overline{R}' - a\overline{R} = 0 \tag{A-7}$$

The solution of (A-7) with boundary condition (A-5) has the form:

$$\overline{R}(x, p) = \frac{1}{p}e^{\lambda_1 x}, \tag{A-8}$$

where λ_1 is the negative root of the characteristic equation

$$\frac{1}{\nu}\lambda^2 - \lambda - a = 0.$$

That is

$$\lambda_1 = 1/2(\nu - \sqrt{\nu^2 + 4a\nu}), \tag{A-9}$$

with

$$a = p\left(1 + \sum_{k=1}^{M}\alpha_k\gamma_k\delta_k\frac{1}{p+\delta_k}\right).$$

The main problem is now to calculate the inverse Laplace-transform of $\overline{R}(x, p)$. Our procedure is as follows: If we have an expression of the form:

$$R(x, \tau, \epsilon) = R_0(x, \tau) + \epsilon R_1(x, \tau) + \ldots$$

then the transformed expression is:

$$\overline{R}(x, p, \epsilon) = \overline{R}_0(x, p) + \epsilon \overline{R}_1(x, p) + \ldots$$

We will develop explicit expressions $R_0(x, \tau)$, $R_1(x, \tau)$ from their transforms $\overline{R}_0(x, p)$, $\overline{R}_1(x, p)$. It will be clear from our calculations that we could give the corresponding terms for any order.

Expansions of the Laplace-transforms

We write the solution $\overline{R}(x, p)$ in the form:

$$\overline{R}(x, p) = \frac{1}{p} exp\left(\frac{\nu x}{2}\right) exp\left[-\sqrt{\nu} x \left\{\frac{\nu}{4} + p\left(1 + \sum_{k=1}^{M} \alpha_k \gamma_k \delta_k \frac{1}{p + \delta_k}\right)\right\}^{1/2}\right] \tag{A-10}$$

Expansion for $\delta < 1$.–We now set $\sqrt{\nu} x = y$ and $\alpha_k \gamma_k \delta_k = \epsilon \beta_k$, where ϵ is an arbitrarily defined constant <1 and define

$$f(y, p, \epsilon) = exp\left[-y\left\{\frac{\nu}{4} + p(1 + \epsilon S)\right\}^{1/2}\right], \tag{A-11}$$

with

$$S = \sum_{k=1}^{M} \beta_k \frac{1}{p + \delta_k}.$$

The Taylor expansion of $f(y, p, \epsilon)$ with respect to ϵ around $\epsilon = 0$ yields:

$$f(y, p, \epsilon) = f_0(y, p) + \epsilon f_1(y, p) + \ldots,$$

where

$$f_0(y, p) = exp\left[-y\left(p + \frac{\nu}{4}\right)^{1/2}\right] \tag{A-12}$$

$$f_1(y, p) = -exp\left[-y\left(p + \frac{\nu}{4}\right)^{1/2}\right] \frac{y}{2} \frac{p}{\left(p + \frac{\nu}{4}\right)^{1/2}} S. \tag{A-13}$$

Hence the first approximation of $\overline{R}(y, p)$ is

$$\overline{R}(y, p) = \overline{R}_0(y, p) + \epsilon \overline{R}_1(y, p)$$

with

$$\overline{R}_0(y, p) = exp\left(\frac{\sqrt{\nu}}{2} y\right) \frac{1}{p} exp\left[-y\left(p + \frac{\nu}{4}\right)^{1/2}\right] \tag{A-14}$$

$$\overline{R}_1(y, p) = -exp\left(\frac{\sqrt{\nu}}{2} y\right) exp\left[-y\left(p + \frac{\nu}{4}\right)^{1/2}\right] \frac{y}{2} \frac{1}{\left(p + \frac{\nu}{4}\right)^{1/2}} S. \tag{A-15}$$

We postpone the calculation of the inverse Laplace-transform to the next subsection and consider an alternative expansion of $\overline{R}(y, p)$ first.

Expansion for large δ_k^-.–In many practical situations, the δ_k may be rather large, so that we may set

$$\alpha_k \gamma_k \delta_k = e_k, \qquad \delta_k = \frac{d_k}{\epsilon}$$

Then $\overline{R}$ is rewritten as

$$\overline{R}(y, p) = \frac{1}{p} exp\left(\frac{\sqrt{\nu}}{2} y\right) exp\left[-y\left\{\frac{\nu}{4} + p\left(1 + \sum_{k=1}^{M} e_k \frac{\epsilon}{p\epsilon + d_k}\right)\right\}^{1/2}\right], \tag{A-16}$$

and we introduce similar to $f(y, p, \epsilon)$ now

$$g(y, p, \epsilon) = exp\left[-y\left\{\frac{\nu}{4} + p\left(1 + \sum_{k=1}^{M} e_k \frac{\epsilon}{p\epsilon + d_k}\right)\right\}^{1/2}\right] \tag{A-17}$$

The expansion of $g(y, p, \epsilon)$ now becomes

$$g(y, p, \epsilon) = g_0(y, p) + \epsilon g_1(y, p) + \ldots \tag{A-18}$$

with

$$g_0(y, p) = f_0(y, p) = exp\left[-y\left(p + \frac{\nu}{4}\right)^{1/2}\right] \tag{A-19}$$

$$g_1(y, p) = -exp\left[-y\left(p + \frac{\nu}{4}\right)^{1/2}\right] \frac{y}{2} \frac{p}{\left(p + \frac{\nu}{4}\right)^{1/2}} \sum_{k=1}^{M} \frac{e_k}{d_k} \tag{A-20}$$

The zero-order term is the same in the first and the second expansion. The first-order correction term now is:

$$\overline{R}_1(y, p) = -exp\left(\frac{\sqrt{\nu}}{2} y\right) exp\left[-y\left(p + \frac{\nu}{4}\right)^{1/2}\right] \frac{y}{2} \frac{1}{\left(p + \frac{\nu}{4}\right)^{1/2}} \hat{\sigma},$$

where $\hat{\sigma} = \Sigma_{k=1}^{M} (e_k/d_k)$. In all cases the corresponding terms for $\bar{r}_k$ are obtained through a multiplication by $\alpha_k \delta_k/(p + \delta_k)$ as we can see from the second equation in (A-4).

Calculation of the Inverse Laplace-transforms

For the calculation of the inverse Laplace-transforms, we use two basic relations which can be found in Crank (1975, p. 377, 378). We denote the inverse Laplace-transform by L^{-1}.

$$L^{-1}\left(\frac{1}{p - a} e^{-yp^{1/2}}\right) = \frac{1}{2} e^{a\tau}\left[e^{-y\sqrt{a}} erfc\left\{\frac{y}{2\sqrt{\tau}} - \sqrt{a\tau}\right\} + e^{y\sqrt{a}} erfc\left\{\frac{y}{2\sqrt{\tau}} + \sqrt{a\tau}\right\}\right] \tag{A-22}$$

It is convenient to introduce the functions

$$B(y, \tau, s) = e^{ys} erfc\left\{\frac{y}{2\sqrt{\tau}} + s\sqrt{\tau}\right\} \tag{A-23}$$

and

$$G(y, \tau, s) = B(y, \tau, s) + B(y, \tau, -s). \tag{A-24}$$

We remark that $G(y, \tau, s)$ will be real, even if the parameter s is imaginary. We now calculate the inverse of the terms $\overline{R}_0$ and $\overline{R}_1$ given in eqs (A-14) and (A-15). By the translation theorem for Laplace-transforms one has for arbitrary $f(\tau)$

$$L(e^{k\tau} f(\tau)) = \bar{f}(p - k)$$

Hence we have

$$L^{-1}\left(\frac{1}{p} exp\left[-y\left(p + \frac{\nu}{4}\right)^{1/2}\right]\right) = e^{-(\nu/4)\tau} L^{-1}\left(\frac{1}{p - \frac{\nu}{4}} exp\left[-yp^{1/2}\right]\right)$$

According to eq (A-22), we find then, using the notation introduced in (A-23) and (A-24), that the inverse of $\overline{R}_0(y, \tau)$ (eq A-15) is given by

$$R_0(y, \tau) = \frac{1}{2} e^{(\sqrt{\nu}/2)y} G\left(y, \tau, \frac{\sqrt{\nu}}{2}\right) \tag{A-25}$$

If we write $R_0(y, \tau)$ in terms of the original variables, we obtain the first term on the right hand side of eq (7). In the calculation of the inverse of $\overline{R}_1(y, p)$ given by eq (A-15), namely

$$\overline{R}_1(y, p) = -exp\left(\frac{\sqrt{\nu}}{2} y\right) exp\left[-y\left(p + \frac{\nu}{4}\right)^{1/2}\right] \frac{y}{2} \frac{1}{\left(p + \frac{\nu}{4}\right)^{1/2}} \sum_{k=1}^{M} \frac{\beta_k}{p + \delta_k},$$

it suffices to consider

$$h_k(y, p) = exp\left[-y\left(p + \frac{\nu}{4}\right)^{1/2}\right] \frac{1}{\left(p + \frac{\nu}{4}\right)^{1/2} (p + \delta_k)}.$$

We make use again of the translation theorem:

$$\begin{aligned} L^{-1}(h_k(y, p)) &= e^{-(\nu/4)\tau} L^{-1}\left(h_k\left(y, p - \frac{\nu}{4}\right)\right) \\ &= e^{-(\nu/4)\tau} L^{-1}\left(exp\left[-yp^{1/2}\right] \frac{1}{p^{1/2}\left(p + \delta_k - \frac{\nu}{4}\right)}\right) \end{aligned} \tag{A-26}$$

Expansion in partial fractions gives

$$\frac{1}{p^{1/2}\left(p + \delta_k - \frac{\nu}{4}\right)} = \frac{1}{2\left(\delta_k - \frac{\nu}{4}\right)}\left(\frac{2}{p^{1/2}} - \frac{1}{p^{1/2} - \left(\frac{\nu}{4} - \delta_k\right)^{1/2}} - \frac{1}{p^{1/2} + \left(\frac{\nu}{4} - \delta_k\right)^{1/2}}\right) \tag{A-27}$$

It is convenient to define $\omega_k = |(\tau/4) - \delta_k|^{1/2}$. At this point we can apply another basic inversion rule given in Crank (1975, p. 377, no. 12):

$$L^{-1}\left(\frac{1}{p^{1/2}+h}\,e^{-yp^{1/2}}\right) = \left(\frac{1}{\pi\tau}\right)^{1/2} exp\left[-\frac{y^2}{4\tau}\right] - h\,exp\,[hy + h^2\tau]erfc\left\{\frac{y}{2\sqrt{\tau}} + h\sqrt{\tau}\right\} \tag{A-28}$$

The combination of eqs (A-27) and (A-28) yields after some rearrangement

$$L^{-1}(h_k(y,p)) = \frac{1}{2\omega_k}\,exp\,[-\delta_k\tau](B(y,\tau,-\omega_k) - B(y,\tau,\omega_k)) \tag{A-29}$$

From eqs (A-29) and (A-15) the second term of expansion 7 follows.

We now calculate the terms of expansion 8. We write:

$$\bar{r}_k(y,p,\epsilon) = \bar{r}_k^0(y,p) + \epsilon\bar{r}_k^1(y,p) + \ldots \tag{A-30}$$

and use

$$\bar{r}_k^0(y,p) = \frac{\alpha_k\delta_k}{p+\delta_k}\,\bar{R}_0(y,p) \text{ and } \bar{r}_k^1(y,p) = \frac{\alpha_k\delta_k}{p+\delta_k}\,\bar{R}_1(y,p).$$

Hence we have

$$\bar{r}_k^0(y,p) = exp\left(\frac{\sqrt{\nu}}{2}y\right)exp\left[-y\left\{p+\frac{\nu}{4}\right\}^{1/2}\right]\frac{\alpha_k\delta_k}{p(p+\delta_k)}, \tag{A-31}$$

and the problem is to calculate

$$L^{-1}\left(exp\left[-y\left\{p+\frac{\nu}{4}\right\}^{1/2}\right]\frac{1}{p(p+\delta_k)}\right) = e^{-(\nu/4)\tau}L^{-1}\left(exp\,[-yp^{1/2}]\,\frac{1}{\left(p-\frac{\nu}{4}\right)\left(p+\delta_k-\frac{\nu}{4}\right)}\right).$$

Now

$$\frac{1}{\left(p-\frac{\nu}{4}\right)\left(p+\delta_k-\frac{\nu}{4}\right)} = \frac{1}{\delta_k}\left(\frac{1}{p-\frac{\nu}{4}} - \frac{1}{p+\delta_k-\frac{\nu}{4}}\right),$$

and we can apply the inversion formula (A-22). After some simplification, we arrive at:

$$r_k^0(y,\tau) = \frac{\alpha_k}{2}\,exp\left[\frac{\sqrt{\nu}}{2}y\right]\left(G\left(y,\tau,\frac{\sqrt{\nu}}{2}\right) - exp\,[-\delta_k\tau]\,G(y,\tau,\omega_k)\right), \tag{A-32}$$

which is the first term of expansion 8. It remains to invert

$$\bar{r}_k^1(y, p) = -\alpha_k \delta_k \exp\left(\frac{\sqrt{\nu}}{2} y\right) \exp\left[-y\left(p + \frac{\nu}{4}\right)^{1/2}\right] \frac{y}{2} \frac{1}{\left(p + \frac{\nu}{4}\right)^{1/2} (p + \delta_k)} \sum_{l=1}^{M} \frac{\beta_l}{p + \delta_l} \tag{A-33}$$

The translation theorem is applied once more, and we now need the partial fraction expansion of

$$\frac{1}{p^{1/2}\left(p + \delta_k - \frac{\nu}{4}\right)}, \qquad \delta_k \neq \frac{\nu}{4}$$

and

$$\frac{1}{p^{1/2}\left(p + \delta_k - \frac{\nu}{4}\right)\left(p + \delta_l - \frac{\nu}{4}\right)}, \qquad \delta_k \neq \delta_b \qquad \delta_k \neq \frac{\nu}{4}, \qquad \delta_l \neq \frac{\nu}{4}.$$

Now routine algebra gives

$$\frac{1}{p^{1/2}\left(p + \delta_k - \frac{\nu}{4}\right)} = \frac{1}{4\omega_k^3}\left(\frac{1}{(p^{1/2} - \omega_k)^2} - \frac{1}{(p^{1/2} + \omega_k)^2}\right)$$

$$+ \frac{1}{2\omega_k^4}\left(\frac{2}{p^{1/2}} - \frac{1}{p^{1/2} + \omega_k} - \frac{1}{p^{1/2} - \omega_k}\right) \tag{A-34}$$

So that the inversion formula (A-28) can be applied. We note that from (A-28) we find the inversion formula for

$$\frac{1}{(p^{1/2} + h)^2} e^{-yp^{1/2}}$$

by simply using the fact that

$$\frac{e^{-yp^{1/2}}}{(p^{1/2} + h)^2} = -\frac{\partial}{\partial h}\left(\frac{1}{p^{1/2} + h} e^{-yp^{1/2}}\right).$$

This gives the inversion formula 17 (p. 378) in Crank (1975). After some rearrangement we find the inverse:

$$L^{-1}\left(\exp\left[-y\left(p + \frac{\nu}{4}\right)^{1/2}\right] \frac{1}{\left(p + \frac{\nu}{4}\right)^{1/2} (p + \delta_k)^2}\right) = T_k(y, \tau) \tag{A-35}$$

where we have introduced the abbreviations

$$T_k(y, \tau) = \frac{1}{\omega_k^2}\left(\frac{\tau}{\pi}\right)^{1/2} Ex\left(y, \tau, \frac{\sqrt{\nu}}{2}\right) + \frac{1}{4\omega_k^3} e^{-\delta_k \tau}$$

$$[B(y, \tau, \omega_k)(1 - \omega_k y - 2\omega_k^2 \tau) + B(y, \tau, -\omega_k)(-1 - \omega_k y + 2\omega_k^2 \tau)] \tag{A-36}$$

and

$$Ex(y, \tau, s) = exp\left[-\left(\frac{y^2}{4\tau} + s^2\tau\right)\right]. \tag{A-37}$$

For $M = 1$ the inversion formula (A-35) leads to the second term in eq (8). For $M > 1$ and $\delta_k \neq \delta_l$ for $k \neq l$ and $\delta_k \neq (\nu/4)$ for $k = 1 \ldots M$, the second type of term involving $(1/[p^{1/2}(p - \omega_k^2)(p - \omega_l^2)])$ must be taken into account. The partial fraction expansion of this term is:

$$\frac{1}{p^{1/2}(p - \omega_k^2)(p - \omega_l^2)} = \frac{1}{\omega_k^2\omega_l^2 p^{1/2}} + \frac{1}{2\omega_k^2(\omega_k^2 - \omega_l^2)}\left[\frac{1}{p^{1/2} - \omega_k} + \frac{1}{p^{1/2} + \omega_k}\right] + \frac{1}{2\omega_l^2(\omega_l^2 - \omega_k^2)}\left[\frac{1}{p^{1/2} - \omega_l} + \frac{1}{p^{1/2} + \omega_l}\right] \tag{A-38}$$

Setting

$$F_k(y, \tau) = \frac{1}{2\omega_k} e^{-\delta_k\tau}(B(y, \tau, -\omega_k) - B(y, \tau, \omega_k)) \tag{A-39}$$

we can write the inverse of $\bar{r}_k^1(y, p)$ as

$$r_k^1(y, \tau) = -\alpha_k\delta_k \frac{y}{2} exp\left[\frac{\sqrt{\nu}}{2} y\right] \cdot \left[\beta_k T_k(y, \tau) + \sum_{l=1, l\neq k}^{M} \frac{\beta_l}{(\omega_k^2 - \omega_l^2)} F_k(y, \tau) + \frac{\beta_l}{(\omega_l^2 - \omega_k^2)} F_l(y, \tau)\right] \tag{A-40}$$

Finally we consider the second type of expansion described by eq (A-17). The zero order term for $R(y, \tau)$ is the same for this expansion. We only need the inversion of $(1/p)g_1(y, p)$ given in eq (A-20), and this is by eq (A-28).

$$\begin{aligned} L^{-1}\left(\frac{1}{p} g_1(y, p)\right) &= -\frac{y}{2} e^{-(\nu/4)\tau} L^{-1}\left(e^{-y p^{1/2}} \frac{1}{p^{1/2}}\right)\hat{\sigma} \\ &= -\frac{y}{2} e^{-(\nu/4)\tau}\left(\frac{1}{\pi\tau}\right)^{1/2} exp\left[-\frac{y^2}{4\tau}\right]\hat{\sigma} \\ &= -\frac{y}{2}\left(\frac{1}{\pi\tau}\right)^{1/2} Ex\left(y, \tau, \frac{\sqrt{\nu}}{2}\right)\hat{\sigma}, \end{aligned} \tag{A-41}$$

which explains the second term in eq (10). The corresponding terms for $r_k(y, \tau)$ are easy to obtain now: The zero-order term is the same as in the first expansion, and the first-order correction term, $r_k^1(y, p)$ coincides up to a constant with the term $h_k(y, p)$ whose inversion is given in relation (A-29). This explains the terms in eq (11).

The calculation of second-order correction terms shows that they are positive in both series expansions, and higher-order correction terms have alternating signs. This means that the exact solution of $R(y, \tau)$ must lie between the curves $R_0(y, \tau)$ and $R_0(y, \tau) + \epsilon R_1(y, \tau)$ for $y \in (0, \infty)$ and fixed $\tau > 0$. All higher correction terms can be expressed in terms of our basic inverses given by eqs (A-22) and (A-28) and their derivatives with respect to the parameters a and h.

Special Cases

The steady state solution.–From equation (A-1) we obtain for the steady state:

$$\frac{1}{\nu}\frac{\partial^2 R}{\partial x^2} - \frac{\partial R}{\partial x} = 0$$

$$\delta_k(R\alpha_k - r_k) = 0, \tag{A-42}$$

For the boundary conditions

$$R(0) = 1, \qquad |R(\infty)| \neq \infty \tag{A-43}$$

this requires that $R(x) = 1$ and $R \cdot \alpha_k = r_k$, that is, bulk and local mineral-fluid equilibrium.

The case $M = 1$, $\delta = \nu/4$, $\varsigma < 1$.–The solutions for the special case are somewhat simpler than the solutions for the general case. They are obtained from the Laplace transforms. The expression for $R_0(y, \tau)$ is the same as for the general case. The Laplace transform of $R_1(y, p)$ is:

$$\overline{R}_1(y, p) = -\beta_k \frac{y}{2} e^{(\sqrt{\nu}/2)y} \frac{e^{[-y(p+(\nu/4))^{1/2}]}}{\left(p + \frac{\nu}{4}\right)^{3/2}} \tag{A-44}$$

Application of the translation theorem yields

$$R_1(y, \tau) = -\beta_k \frac{y}{2} e^{(\sqrt{\nu}/2)y - (\nu/4)\tau} L^{-1}\left[\frac{e^{-yp^{1/2}}}{p^{3/2}}\right] \tag{A-45}$$

Using the tables of Crank (1975) the back-transformation is directly obtained:

$$R_1(y, \tau) = -\beta_k \frac{y}{2} e^{(\sqrt{\nu}/2)y}\left[2\left(\frac{\tau}{\pi}\right)^{1/2} e^{-(y^2/4\tau)} - y\, erfc\left(\frac{y}{2\sqrt{\tau}}\right)\right] \tag{A-46}$$

The corresponding expression for $\bar{r}_k^0(y, p)$ is:

$$\bar{r}_k^0(y, p) = e^{(\sqrt{\nu}/2)y} \frac{1}{\left(p + \frac{\nu}{4}\right)p} e^{[-y(p+(\nu/4))^{1/2}]} \tag{A-47}$$

Application of the translation theorem yields:

$$r_k^0(y, \tau) = e^{(\sqrt{\nu}/2)y - (\nu/4)\tau} L^{-1}\left[\frac{e^{-yp^{1/2}}}{p\left(p - \frac{\nu}{4}\right)}\right], \tag{A-48}$$

which can be transformed back to:

$$r_k^0(y, \tau) = \frac{2}{\nu} e^{(\sqrt{\nu}/2)y}\left[G\left(y, \tau, \frac{\sqrt{\nu}}{2}\right) - e^{-(\nu/4)\tau} G(y, \tau, 0)\right] \tag{A-49}$$

The expression for $\bar{r}_k^1(y, p)$ is:

$$\bar{r}_k^1(y, p) = -\frac{\beta_k}{\left(p + \frac{\nu}{4}\right)} \frac{y}{2} e^{(\sqrt{\nu}/2)y} \frac{e^{-y\sqrt{p+(\nu/4)}}}{\left(p + \frac{\nu}{4}\right)^{3/2}} \tag{A-50}$$

After translation this is:

$$r_k^1(y,\tau) = -\frac{\beta_k y}{2} e^{(\sqrt{\nu}/2)y-(\nu/4)\tau} L^{-1}\left[\frac{e^{-yp^{1/2}}}{p^{5/2}}\right], \tag{A-51}$$

which can be transformed back to:

$$r_k^1(y,\tau) = -\frac{2\beta_k}{\nu} e^{(\sqrt{\nu}/2)y-(\nu/4)\tau} i^3 erfc\left(\frac{y}{2\sqrt{\tau}}\right)\tau^{3/2}, \tag{A-52}$$

where $i^3 erfc$ is the triple integral over the complementary error function and can be written in terms of explicit functions (see Crank, 1975).

SERIES EXPANSION WITHOUT LAPLACE-TRANSFORMS

We go back to the differential equations in (A-1) noting that the second equation can be solved in terms of R:

$$r_k(x,\tau) = \alpha_k\delta_k \int_0^\tau e^{-\delta_k(\tau-s)} R(x,s)\,ds. \tag{A-53}$$

Then one can use (A-53) in the first equation of (A-1) to derive a single equation for $R(x,\tau)$ which becomes:

$$\frac{1}{\nu}\frac{\delta^2 R}{\partial x^2} - \frac{\partial R}{\partial x} = \frac{\partial R}{\partial \tau} + \sum_{k=1}^{M} \alpha_k\gamma_k\delta_k R - \sum_{k=1}^{M} \alpha_k\gamma_k\delta_k^2 \int_0^\tau e^{-\delta_k(\tau-s)} R(x,s)\,ds. \tag{A-54}$$

Setting

$$\sigma = \sum_{k=1}^{M} \alpha_k\gamma_k\delta_k, \qquad \text{and } d(\tau) = \sum_{k=1}^{M} \alpha_k\gamma_k\delta_k^2 e^{-\delta_k\tau}$$

we first put eq (A-54) into the form

$$\frac{\partial R}{\partial \tau} - \frac{1}{\nu}\frac{\delta^2 R}{\partial x^2} + \frac{\partial R}{\partial x} + \sigma R = \int_0^\tau d(\tau - s) R(x,\tau)\,ds. \tag{A-55}$$

One can make a further reduction by setting

$$R(x,\tau) = exp\left[\frac{\nu}{2}x - \left(\frac{\nu}{4} + \sigma\right)\tau\right] \cdot U(x,\tau), \tag{A-56}$$

which leads to the differential equation

$$\frac{\partial U}{\partial \tau} - \frac{1}{\nu}\frac{\delta^2 U}{\partial x^2} = \int_0^\tau \delta(\tau - s) U(x,s)\,ds, \tag{A-57}$$

with

$$\delta(s) = exp\left[\left(\frac{\nu}{4} + \sigma\right)s\right] d(s),$$

and a new boundary condition

$$U(0,\tau) = exp\left[\left(\frac{\nu}{4} + \sigma\right)\tau\right], \qquad U(\infty,\tau) = 0, \tag{A-58}$$

and the same initial condition

$$U(x, 0) = 0. \tag{A-59}$$

Finally we can absorb the parameter ν by chosing a new space variable $y = \sqrt{\nu}x$. Defining the parabolic operator

$$P = \frac{\partial}{\partial \tau} - \frac{\partial^2}{\partial y^2} \tag{A-60}$$

We can write the differential equation in short form as

$$PU = \int_0^\tau \delta(\tau - s) U(y, s)\, ds. \tag{A-61}$$

Assume now that $\delta(\tau)$ contains a small parameter ϵ so that we can set

$$\delta(\tau) = \epsilon \hat{\delta}(\tau) \tag{A-62}$$

and

$$U(y, \tau, \epsilon) = U_0(y, \tau) + \epsilon U_1(y, \tau) + \epsilon^2 U_2(y, \tau) + \dots \tag{A-63}$$

One then compares powers of ϵ in A-61, and this leads to the following iteration scheme:

$$\begin{aligned} PU_0 &= 0 \qquad y \in (0, \infty), \tau > 0 \\ U_0(0, \tau) &= exp\left[\left(\frac{\nu}{4} + \sigma\right)\tau\right], \qquad U_0(\infty, \tau) = 0 \\ U_0(y, 0) &= 0 \qquad y > 0 \end{aligned} \tag{A-64}$$

$$PU_{k+1} = \int_0^\tau \hat{\delta}(\tau - s) U_k(y, s)\, ds,\ k = 0, 1, 2, \dots \tag{A-65}$$

with homogeneous boundary conditions for $U_k(y, \tau)$, $k \geq 1$. At this point we can apply a general formula. The solution of the diffusion problem on $(0, \infty)$ with a source term, namely

$$\begin{aligned} PV &= q(y, \tau) \qquad y \in (0, \infty) \qquad \tau > 0 \\ V(0, \tau) &= 0, \qquad V(\infty, \tau) = 0 \\ V(y, 0) &= 0 \qquad y > 0 \end{aligned} \tag{A-66}$$

is given (for reasonable $q(y, \tau)$) by

$$V(y, \tau) = \int_0^\tau \int_0^\infty K(y, \eta, \tau - s) q(\eta, s)\, d\eta ds, \tag{A-67}$$

where the associated "Green's function" or "heaf kernel," $K(y, \eta, \tau)$, is given by

$$K(y, \eta, \tau) = \frac{1}{2\sqrt{\pi\tau}} \left\{ exp\left[-\frac{|y - \eta|^2}{4\tau} \right] - exp\left[-\frac{|y + \eta|^2}{4\tau} \right] \right\}. \tag{A-68}$$

The solution of (A-64) may be found by Laplace transform, and one is led to

$$U_0(y, \tau) = \frac{1}{2} exp\left[\left(\frac{\nu}{4} + \sigma\right)\tau\right] G\left[y, \tau \sqrt{\frac{\nu}{4} + \sigma} \right], \tag{A-69}$$

where $G[y, \tau, s]$ is defined in (A-19) and (A-20). For $\sigma = 0$, eqs (A-69) and (A-56) lead to expression (A-25) for $R_0(y, \tau)$. All higher terms $U_k(y, \tau)$ can then be calculated by integration using formula (A-67). A straightforward but lengthy calculation shows that we arrive at the same expressions found by Laplace-transforms.

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