LONG-TERM FLOW/CHEMISTRY FEEDBACK IN A POROUS MEDIUM WITH HETEROGEOUS PERMEABILITY: KINETIC CONTROL OF DISSOLUTION AND PRECIPITATION

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ABSTRACT. The kinetics of dissolution and precipitation is of central importance to our understanding of the long-term evolution of fluid flows in crustal environments, with implications for problems as diverse as nuclear waste disposal and crustal evolution. We examine the dynamics of such evolution for several geologically relevant permeability distributions (models for en-echelon cracks, an isolated sloping fractured zone, and two sloping high-permeability zones that are close enough together to interact). Although our focus is on a simple quartz matrix system, generic features emerge from this study that can aid in our broader goal of understanding the long-term feedback between flow and chemistry, where dissolution and precipitation is under kinetic control. Examples of thermal convection in a porous medium with spatially variable permeability reveal features of central importance to water-rock interaction. After a transient phase, an accelerated rate of change of porosity may be used with care to decrease computational time, as an alternative to the quasi-stationary state approximation (Lichtner, 1988). Kinetic effects produce features not expected by traditional assumptions made on the basis of equilibrium, for example, that cooling fluids are oversaturated and heating fluids are undersaturated with respect to silicic acid equilibrium. Indeed, we observe regions of downwelling oversaturated fluid experiencing heating and regions of upwelling, yet cooling, undersaturated fluid. In sloping high-permeability zones, upwelling causes deposition along the upper surface of the channel leading to flow which rises less vertically with time. In the long term, this change in slope of the flow may also lead to the onset of oscillatory behavior near the surface. Downwelling in sloping high-permeability zones tends to become more vertical with time, due to buoyancy effects and dissolution at the core of the downwelling zone. The location of the basal stalk of thermal plumes rising from the heated lower boundary is inherently unstable. This stalk migrates with time, as the core of the flow generally clogs via precipitation, while kinetic effects cause the edges of the stalk to dissolve. When oscillatory convection is present, the amplitudes of oscillation generally increase with time in near-surface environments, whereas amplitudes tend to decrease over long times near the heated lower boundary. Runaway dissolution can be moderated by shifts in the locations of saturation state reversals. This is especially true when kinetic rates are “slow.” “Fast” kinetics encourages the runaway dissolution regime. We examine the scaling behavior of characteristic length scales, of terms in the solute equation, and of the typical deviation from equilibrium, each as a function of the kinetic rate parameters. Many of these features are viewed as generic and of significance for a wider range of geologic environments than the quartz system considered.

INTRODUCTION

Fluid motion in the Earth’s crust and the chemistry of the fluid contribute to the dynamical evolution of near-surface environments by controlling dissolution and precipitation of minerals, which in turn leads to changing porosity, permeability, and flow structures. The kinetics of water-rock interaction and the influence of spatially heteroge-
neous permeability are of prime importance to our understanding of such evolution. These factors must be understood to make progress in fields as diverse as hazardous waste migration and the formation of ore deposits. Complete characterization and exact modeling of a particular environment are never possible. However, we may build up the intuition necessary to understand a broad range of physical systems by studying the results of well chosen models. Up to now, very few examples of kinetic modeling in heterogeneous systems exist in the literature.

Although full review of flow and reaction in the Earth’s crust is beyond the scope of this paper, we offer some key references that provide essential background on the fundamental processes and a context for our study. The collection of papers in Lichtner, Steefel, and Oelkers (1996) and the review by Person and others (1996) summarize recent modeling and theory of crustal fluid flows. Phillips (1991) provides a nice introduction to the coupling of fluid flow and water/rock reactions that affect the porosity and permeability fields. Further background is available from textbooks, monographs, review collections, and conference proceedings. Additional background in the field of groundwater and porous media flow theory, some of which include heat transfer and modeling, is readily available (Bear, 1972, 1979; de Marsily, 1986; Domenico and Schwartz, 1990; El-Kadi, 1995; Hornung, 1997; Kaviani, 1995; Parnell, 1994; Zijl and Nawalany, 1993). For more emphasis on reactive transport in porous media, see Dracos and Stauffer (1994), Lichtner, Steefel, and Oelkers (1996), Ortoleva (1994), and Phillips (1991). For general background on fluid/rock interaction in the Earth’s crust see Barnes (1997) and Fyfe, Price, and Thompson (1978). The specific influence of fractures is discussed in Committee on Fracture Characterization and Fluid Flow (1996).


More recently, a number of review papers have been published (Bethke, 1989; Bjorlykke, 1993; Furlong, Hanson, and Bowers, 1991; Garven, 1995; Konikow and Mercer, 1988; Lichtner, Steefel, and Oelkers, 1996; Lowell, 1991; Mangold and Tsang, 1991; Person and others, 1996; Ungerer and others, 1990; Yeh and Tripathi, 1989). Recent research developments have been far reaching (Ague, 1998; Ague and Brimhall, 1989; Aharonov and others, 1995; Aharonov and Rothman, 1996; Aharonov, Spiegelman, and Kelemen, 1997; Baumgartner and Ferry, 1991; Bethke, 1985; Chen and others, 1990; Ge and Garven, 1992; Hayba and Ingebritsen, 1994; Hoefner and Fogler, 1988; Lichtner, 1996; Lichtner and Biino, 1992; Liu and Narasimhan, 1989a,b; Ludvigsen, Palm, and McKibbin, 1992; Merino, Nahon, and Wang, 1993; Merino, Wang, and Deloule, 1994a,b; Novak, Schechter, and Lake, 1989; Ortoleva and others, 1987a,b; Pruess 1987, 1991; Raffensperger and Garven, 1995a,b; Sanford and Konikow, 1989; Spiegelman, 1993; Steefel and Lasaga, 1990, 1992, 1994; Steefel and MacQuarrie, 1996; Steefel and Van Cappellen, 1990; Wells and Ghiorso, 1991; Weng, Wang, and Merino, 1995; Yeh and Tripathi, 1991; to name a few).

Although kinetically based modeling is more fundamental, most modelers have used an equilibrium approach. A number of studies of two-dimensional convection in porous media flows have used the local equilibrium (LEQ) approximation. For example, Ludvigsen, Palm, and McKibbin (1992), Palm (1990), and Wood and Hewett (1982) used this approximation in their studies of natural (and sloping) convection with quartz dissolution and precipitation leading to porosity changes over time. Raffensperger and
Garven (1995b) assume LEQ in their multicomponent model related to uranium ore deposits. Although models based on LEQ have successfully described many observations, we wish to understand the conditions under which this traditional approach is inadequate and to understand the impact of kinetic control on the long-term evolution of crustal fluid/rock systems.

We stress that the key feature of kinetic control of fluid/mineral reactions makes our work distinct from many of the approaches cited above. Models that include kinetic control of mineral dissolution and precipitation have been developed only recently, and we are just beginning to explore the implications of kinetic control in multidimensions. Kinetic effects have been included in a number of one-dimensional (1D) models. Lasaga and Rye (1993) present an analytical model of metamorphic systems. Martin and Meunier (1995) present a 1D model for kinetically controlled quartz cementation. Other theoretical studies examine the conditions required for use of LEQ versus kinetics (Knapp, 1989; Lichtner, 1993) and details of the quasi-stationary state approximation for isothermal systems (Lichtner, 1988, 1991). Kinetic effects on permeability changes in a 1D quartz matrix were discussed by Wells and Ghiorso (1991), and this work was extended to include effects of matrix thermal expansion by Lowell, Van Cappellen, and Germanovich (1993). Kinetic effects in a multimineralic 1D flow-through system have been studied by Soler and Lasaga (1996a) relevant to bauxite formation. Soler and Lasaga (1996b) also extended this formulation to two dimensions, with infiltration at the upper surface. For a general introduction to the importance of kinetic control in geological systems, see Lasaga (1984, 1998).

Steefel and Lasaga (1992, 1994) examined two-dimensional thermal convection in a multimineralic system under kinetic control. General aspects of geochemical self organization (Ortoleva and others, 1987a) are also important to flow/reaction coupling. Permeability changes leading to the reactive-infiltration instability at dissolution fronts (Ortoleva and others, 1987b; Steefel and Lasaga, 1990) can occur even for isothermal systems. The effects of isolated high-permeability zones in a two-dimensional quartz matrix under kinetic control have been examined for thermal convection (Bolton, Lasaga, and Rye, 1996) and for forced-flux injection (Bolton, Lasaga, and Rye, 1997).

The initial bifurcations of nonlinear thermal convection in porous media without reactions or heterogeneous permeability are of interest in themselves and have been previously well documented (Caltagirone, 1975; Elder, 1967a,b; Frick and Müller, 1983; Kvernold and Tyvand, 1979; Or, 1989; Rosenberg and Spera, 1992; Steen and Aidun, 1988). Flow in the Earth’s crust can also be driven by compaction and topographic effects (see Bethke, 1989; Garven, 1995; Person and others, 1996). Analysis of convection in sloping permeability zones has also been an active area of research (Bories and Combarnous, 1973; Criss and Hofmeister, 1991; Davis and others, 1985; Fisher, Becker, and Narasimhan, 1994; Gouze, Couedrain-Ribstein, and Bernard, 1994; Gentthon and others, 1990; Kvernold and Tyvand, 1976; López and Smith, 1995, 1996; Ludvigsen, Palm, and McKibbin, 1992; Powers and O’Neill, 1986; Wood and Hewett, 1982). In addition to the focus on sloping layers, some of these studies specifically examined various permeability distributions and the interplay between topographic and thermal convective effects.

Our focus here is on the long-term evolution of a quartz matrix system where dissolution and precipitation are governed by kinetic processes. We also wish to understand the first-order influence of fracture-filled zones on the evolution of porosity and permeability in a heterogeneous system. To this end, we use a formulation that captures the most important aspects of fractured zones, namely, compared to the low-permeability matrix surrounding such zones, crack-like or fractured, can have higher permeability and lower surface area to fluid volume ratios. Such factors tend to favor faster fluid flows (via higher permeability) and less rapid water/rock exchange (via...
lower surface areas), both of which make kinetics especially important in and around such zones. The subgrid-scale grain model of a partially occluded spherical close pack of grains developed by Bolton, Lasaga, and Rye (1996) serves this purpose well for moderate porosities. We also present results for low porosities for which the grain model is based on cubes bounded by fluid-filled tubes.

A host of complicating factors exists in natural systems. By examining the influence of a small number of processes we hope to build up intuition about the influence of each process. Additional features can be included systematically in models, thereby making it possible to comprehend the influence of each factor. As our focus is to understand the important influence of the kinetics and spatially variable permeability on the evolution of flows driven by thermal convection, we have left out other potentially important factors (for example, compaction, pressure solution, anisotropic permeabilities, multiphase flows, hierarchical features of porosity and permeability, et cetera).

Little is known about the long-term changes of porosity and permeability for multidimensional systems in which the mineral dissolution and precipitation is under kinetic control. Clearly, the flow rate and saturation state of the fluid will change as the permeability changes, and the rate of change of the permeability will depend on the flow and chemistry. This coupling will be strongly influenced by all the relevant rates governing the system (rates of reaction, heat flow, flow of mass, with additional dependencies upon permeability, temperature, mineral surface areas, et cetera). Multimineralic systems generally have smaller mineral surface areas for a given mineral in a given volume of fluid. Spatial heterogeneities in the placement of mineral assemblages will also influence fluid chemistry. Both these factors would favor disequilibrium behavior compared to the monomineralic case we consider in this paper.

Major changes in permeability between discrete fractures and a more uniform matrix would be expected to exhibit large spatial changes in the degree of departure from equilibrium. Our present formulation allows permeability contrasts of up to about 100 across the domain. We use a continuously varying permeability to capture the first-order influence of heterogeneous permeability. Low-permeability convective systems with weak thermal forcing will have flow rates, thus favoring near equilibrium behavior, if the mineral surface areas are large, and if the kinetic rate constants are not too slow. Given these factors and the desire to understand the full range of behavior from near equilibrium to far from equilibrium, we purposely chose to examine the upper range of observed permeabilities. This study extends the work of Bolton, Lasaga, and Rye (1996) on thermal convection and water/rock exchange in a quartz matrix to longer time scales, where the significant permeability changes over time noticeably affect the flow field, and shifts in saturation state are also apparent.

FORMULATION

To simulate the flow of crustal fluids we use a model that includes changes in fluid chemistry, permeability, temperature, and fluid flow, all coupled in a self-consistent way. For this we use the numerical model of Bolton, Lasaga, and Rye (1996). (We dub this model QTZFLOW, which is a special case of a more general multimineralic model we developed called KINFLOW). An extended summary of the formulation is in app. A. The fluid is a dilute aqueous solution of silicic acid. The rate of reaction between the solid quartz phase and the solution is governed by the experimentally determined kinetics of Rimstidt and Barnes (1980). The more rapid homogeneous dissociation reactions of water and silicic acid are assumed to be in local equilibrium, based on temperature-dependent equilibrium constants. Low-temperature systems yield dilute solutions, and by use of primary and secondary species and charge balance, a single solute equation may be derived for the “total” concentration of silicic acid. The solute equation includes advection, diffusion, and the kinetic source term.
The quartz grains are allowed to grow or dissolve, which links the fluid chemistry to the permeability changes. One subgrid-scale grain model is based on a spherical close pack of grains (Martin and Meunier, 1995, present a similar subgrid-scale grain model based on other packing arrangements.). (Another based on fluid-filled tubes is discussed in app. C). Given a local spherical close pack radius $R_0$, overgrowth occurs on the grain faces exposed to the fluid. The formulation corrects for the volumes and surface areas occluded during such growth and yields an effective local grain radius $R_N$ (slightly larger than $R_0$, both in meters). The rate of change of the effective grain radius with time is given by

$$\frac{dR_N}{dt} = -\nabla \cdot \left(k_0 A_c \right)$$  \hspace{1cm} (1)

where $t$ is time (in sec), $k_0$ is a kinetic rate term (in moles*m$^{-2}$*sec$^{-1}$), $\nabla \cdot$ is the molar volume (in m$^3$ of quartz/mole), and $A_c$ is unity. In some examples herein, we artificially accelerated the rate of change of grain radii with time by using $A_c > 1$. This procedure is related to but distinct from the quasi-stationary state approximation of Lichtner (1988, 1991). Limitations in values of $A_c$ are discussed in app. B. The initial values of $R_0$ and $R_N$ were variable in space and are denoted $R_0^I$ and $R_N^I$, respectively. The ratio between the effective radius and the touching close pack radius was initially uniform and corresponded to a “half-occluded” state, where the effective radius is midway between the close pack radius and the radius at which the smallest holes in the structure would pinch off. For the grain model based on spheres, the Kozeny-Carman equation (see Bear, 1972, p. 165-166) was used to relate the permeability $k$ (in m$^2$) to the porosity fraction ($\phi$) and had the form:

$$k = \frac{(R_0^I)^2}{45} \left( \frac{\phi^3}{(1 - \phi)^2} \right)$$  \hspace{1cm} (2)

This basic form of $k(\phi)$ is quite appropriate for sandstones. Other similar forms may better represent some details of the low-porosity limit (compare du Plessis and Roos, 1994; von Bargen and Waff, 1986). Unless otherwise stated, all our references to porosity will assume the porosity fraction, rather than percent. The surface area to fluid volume ratio and the porosity can be calculated analytically from the model. Small values of $R_0^I$ yield low permeabilities and high surface area to fluid volume ratios. High-permeability zones were created by imposing zones of larger $R_0^I$ than the background. These zones also have smaller surface area to fluid volume ratios than the background. In this way, the zones of large grain size capture the two most important aspects of crack-like or fractured zones (high permeability and low surface area to fluid volume ratios).

To complete a dynamical model, we must also include a formulation for the evolution of temperature and the flow. Temperature is governed by a heat equation, including the effects of advection and conduction. Temperature changes often lag changes in solute concentration due to the significant thermal inertial of the water/rock system. Although conservation of mass in a water saturated porous medium must account for dissolution and precipitation, our modeling up to now has indicated that the Darcy velocity $q$ (in m/s) is essentially divergence free for the regimes considered. Darcy’s law naturally accounts for heterogeneous permeability and buoyancy effects and is given by Bear (1972):

$$q = -\frac{1}{\mu} \cdot k \cdot (\nabla P + \rho g \hat{k})$$  \hspace{1cm} (3)
where the gravitational acceleration \( g \) is downward (in m/s\(^2\)), \( \hat{k} \) is the vertical unit vector (upward and nondimensional), \( \mathbf{k} \) is the intrinsic permeability tensor (in m\(^2\)), \( P \) is pressure (in kg/m/s\(^2\)), \( \rho_f \) is the fluid density (in kg/m\(^3\)), and \( \mu \) is the temperature-dependent dynamic viscosity of the fluid (in kg/m/s, which was taken from Bruges, Latto, and Ray, 1966). For this study, we considered isotropic permeability (permeability which is the same in all directions) for which the permeability tensor may be replaced by a scalar. Even so, the scalar permeability, \( k \), is heterogeneous (it varies from place to place). We consider “slow” spatial variations in permeability rather than random fields. We used an equation of state for water which includes both thermal expansion and the minor effect of solutes on the fluid density. Future models will include anisotropic permeability and more general equations of state, dependent also on pressure and salinity. For the two-dimensional system considered and for the slow dissolution and precipitation rates, one can eliminate pressure and (within the Boussinesq approximation) use a stream function equation for the flow which naturally accounts for the production of vorticity by buoyancy effects (Norton and Knight, 1977).

The system of coupled nonlinear partial differential equations are solved on a finite difference grid. The stream function equation is solved by a spectral-transform technique. The spectral-transform method has a long history. It was used by Moore and Weiss (1973) and Jarvis and McKenzie (1980) to solve Poisson equations in two-dimensional convection problems. More recently, Christensen and Harder (1991) applied this method to the problem of three-dimensional convection with variable viscosity. The stream function equation for our model has the form of a Poisson equation, and thus we can take advantage of the superior efficiency of the spectral-transform method. Some iteration is required for this method in our case due to spatially variable permeability. The heat and solute equations are solved by third-order upwinding for the advection term. This scheme has less numerical dispersion than first-order schemes and is more efficient (although sometimes less accurate) than flux-limiting and particle-tracking schemes. An implicit-iteration secant method was used for the kinetic source term in the solute equation, which otherwise could severely limit the allowable time step sizes. The use of total concentration necessitates iteration at each node and time step, accomplished by a Newton-Raphson method. We used constant temperature thermal boundary conditions at the upper and lower boundaries, while no-flux conditions were applied at the lateral sides. No-flux conditions were applied for the solutes at all boundaries. For more details of the formulation, see app. A and Bolton, Lasaga, and Rye (1996).

RESULTS

Our main goal is to elucidate the “fully coupled” long-term behavior of the flow and chemistry in a heterogeneous system under kinetic control, where the chemistry affects the flow and vice versa. We consider several examples of thermal convection driven by isothermal upper and lower boundaries of different temperatures. These simulations illustrate the behavior of differing permeability distributions of geologic relevance. The maximum permeabilities used in the high-permeability zones are more representative of fractured zones than undisturbed sandstones. Even so, wide ranges of permeabilities have been reported for sandstones. Kinetic control is more important for conditions such as high permeabilities, low surface areas of mineral grains, rapid fluid flows, multimineralic systems, and where lithologies change. We consider generic permeability fields in order to build up our intuition about what kinds of behavior one can expect. The time scale for changes in the permeability of the low temperature systems considered is much longer than the convective turnover time. Once a statistically stationary state is reached, we may artificially “accelerate” the rate of change of effective grain radii with time. We have thoroughly tested the use of such an acceleration factor (as discussed in app. B). It is
essential to integrate the system long enough before such an acceleration is used to avoid any influence of the transient effects. Acceleration factors of 1000 were found generally acceptable for these low-temperature systems.

Our focus is on a range of parameter space where kinetic control is important. A number of factors can cause the system to evolve closer to equilibrium than exhibited by our examples, including globally lower permeabilities (or flow velocities), “faster” kinetics, and larger surface area to fluid volume ratios. By contrast, tendencies toward greater disequilibrium would be favored by larger permeability contrasts (accompanied by locally faster flows), by slower kinetic rates, and by multimineralic systems which typically would have lower surface area to fluid volume ratios for each contributing mineral than our monomineralic study.

The results of these simulations have important implications for our understanding of geologic systems, some of which we summarize here before discussing the details. Deep convecting systems likely maintain oscillatory thermal boundary layers, especially near high-permeability zones. Over the long term, such oscillations may diminish at the lower boundary for moderate Rayleigh numbers, yet increase in magnitude near the upper boundary (compare simulation L1). Near-surface environments of geologic systems are especially prone to precipitation, and thereby a record of oscillatory convection would be recorded by mineral zonation adjacent to high-permeability zones. A variety of mechanisms has been proposed for the formation of oscillatory banding in minerals (for example, as the sphalerite banding described in McLimans, Barnes, and Ohmoto, 1980), including mechanisms involving hydrofracturing and fluid pulsation. The oscillatory convection we describe is one more mechanism that could lead to such banding, and it is compatible with the banding and fluid mixing scenario described by Canals and others (1992).

Part of the convecting domain follows the conventional wisdom that upwelling is associated with cooling of an oversaturated fluid (silicic acid with respect to quartz), while downwelling is associated with warming of an undersaturated fluid. However, significant regions violate such commonly held notions. Dynamics of fluid motion account for some of these differences, while in other regions kinetics is critical to the failure of conventional wisdoms. Due solely to the dynamics of thermal convection, the entry zones of upwelling plumes draw fluid upward while it is being heated. Similarly, near the upper cold boundary, as fluid turns downward, it is being cooled. Undersaturated fluid that is warming emanates downward from the upper boundary in the cores of downwelling plumes. Because of kinetic effects, such zones are normally lined with downwelling, heating oversaturated fluid. Similarly, peripheral to upward moving plumes (cooling and oversaturated at their cores) are layers of upward moving undersaturated fluid that is cooling, as discussed below.

Kinetic control of dissolution and precipitation is associated with unexpected saturation states lining plumes that emanate from the thermal boundary layers. The cores behave as expected from equilibrium considerations, although the rates of dissolution and precipitation cannot be properly recovered from models of local equilibrium. The edges of such plumes have saturation states opposite to expectations based on local equilibrium. Plumes tend to fix themselves on pre-existing zones of high permeability. However, near the lower heated boundary, the location of the plume stalk is inherently unstable. Although this phenomenon could have been expected on the basis of equilibrium concepts, it is accentuated by kinetic effects. Figure 1A illustrates the region of upwelling from a heated lower boundary. Dashed lines represent fluid parcel trajectories as they converge on a (stippled) high-permeability zone. The core of such an upwelling plume stalk is cooling and oversaturated with respect to quartz, as would be expected from models based on equilibrium. The oversaturated fluid will precipitate quartz which tends to clog the high-permeability zone. This in itself would destabilize the plume stalk.
location, but kinetic effects significantly reinforce the instability. The core of the upwelling plume is lined with zones of undersaturated fluid which cools as it rises (gray regions labeled VCU in fig. 1A). Cooling undersaturated fluid can only be understood by considering kinetics, which delays the recovery of the expected saturation state. This kinetically controlled undersaturated zone implies dissolution along the edges of the plume stalk. As the plume stalk core clogs via precipitation, the edges experience dissolution and permeability increases, thereby accentuating the lateral migration of the plume, which could move to the left or the right. Alternatively, the flow could bifurcate around the clogging core.

Downwelling plumes from the upper cold boundary are also lined by unexpected saturation states. These zones (DHO in gray in fig. 1B) contain downwelling, heating, yet oversaturated fluid. Oversaturated fluid experiencing heating could only be present with kinetic control. These regions line the edges of the downwelling plume cores of undersaturated, heating fluid. Thus the cores of both upwelling and down-welling plumes contain the saturation state expected on the basis of equilibrium, but such plumes are lined by regions of the opposite saturation state, where a kinetic description is critical. These issues are discussed further below.

Precipitation leads to decreasing permeability, whereas dissolution leads to increasing permeability (for our monomineralic system). In an undersaturated zone (for example, in the core of downwelling plumes where the fluid is warming and undersaturated), the increase in permeability arising from dissolution generally leads to faster fluid motion. With faster flow, one could expect greater disequilibrium, thereby causing faster

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Fig. 1. A cartoon depicting flow and unexpected saturation states (gray) extant near thermal boundary layers. The lightly stippled region is a high-permeability zone. Dashed curves represent streamlines. (A) The region of upwelling from a lower heated boundary. The core of the plume stalk is upwelling, cooling, and oversaturated (VCO). This region is lined by zones of upwelling, cooling, yet undersaturated fluid (VCU in gray), whose presence would not be expected unless kinetics are taken into account. Lateral migration or bifurcation of the plume stalk is expected due to decreasing permeabilities in the core and increasing permeabilities of the rims. (B) The region of downwelling from a cold upper boundary. The core of the downwelling plume is heating and undersaturated (DHU). This region is lined by zones of downwelling, heating, yet oversaturated fluid (DHO in gray), whose presence would not be expected unless kinetics are taken into account.
dissolution and the possibility of “runaway” dissolution. Although some aspects of this sequence are observed in our simulations, the real runaway regime can be avoided owing to other moderating influences. For one thing, as the flow becomes more rapid, cooler fluid is brought in, which under some circumstances has the potential of slowing the local dissolution rate. Downwelling plumes are generally near regions where the saturation state reverses. As the flow becomes more rapid, the fluid drawn in from the sides is less undersaturated, or even oversaturated. For “slow” kinetics, we view this latter process to be the prime moderator of the potential runaway regime.

We now turn to the simulations, whose most important parameters are summarized in table 1. The initial permeability distributions were chosen to extract the generic behavior of some important geologic environments. Simulation L1 contains three isolated high-permeability zones, arranged in space in a way similar to en-echelon cracks or fractured zones. L2 has a single sloping high-permeability zone with both upwelling and downwelling occurring in the same zone. This represents an isolated fault zone filled with fractures. L3 has two isolated sloping high-permeability zones, with flow up one of these “fractured” zones and down the other. Such behavior could be common where two fault zones are close enough to interact and to take advantage of preferred flow “channels.” Fault zones can be thick and associated with high permeabilities as envisioned by our applications. Alternately, they can be thin and filled with low permeability gouge (Freeze and Cherry, 1979, p. 474). Other parameter values and details of the boundary conditions are given in Bolton, Lasaga, and Rye (1996). Each case utilizing the grain model based on spheres was initiated with a close-pack touching radius grain size of $R_0^I = 0.4 \text{ mm}$ in most of the domain. $R_0^I$ was ramped up to a maximum of $2 \text{ mm}$ in the centers of high-permeability zones. Although most of the simulations were performed at high resolution (129 by 139 grid points for the horizontal and vertical directions, respectively) some of the details at the plume centers may be slightly under-resolved. Toward the end of this paper we explore the implications of increasing the kinetic rate parameters that force the system to be closer to equilibrium (the lower resolution runs L4 through L8).

**Convection Simulation L1**

This simulation highlights the effects of long-term feedback between the flow and chemistry for a regime of moderately oscillatory convection. Three isolated high-

### Table 1

Summary of the simulations

<table>
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<th>Case</th>
<th>$T_{top}$ (K)</th>
<th>$T_{bot}$ (K)</th>
<th>$\Delta T$ (K)</th>
<th>$L_x$ (m)</th>
<th>$L_z$ (m)</th>
<th>Grain Model</th>
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</table>

Summary of simulation parameters with temperatures in Kelvin and domain sizes in meters. The parameter M > 1 represents cases run with artificially “fast” kinetics (see text). Simulations L1 through L3 had 129 grid points in the horizontal and 139 in the vertical, whereas the remaining simulations were run with 65 by 59 nodes [horizontal by vertical]. The symbol pos refers to grain models based on partially occluded spheres, while tec cases were based on tube-edged cubes. The pos cases were initiated with a spatially uniform porosity fraction (0.1159863), with min ($R_0^I$) = 0.4 mm in most of the domain, and with max ($R_0^I$) = 2 mm in the high-permeability zones. The tec cases were initiated with an initial porosity fraction of 0.00485 (that is 0.485 percent) and nucleation densities of 1.37 mm in most of the domain, while ranging up to 6.87 mm in the high-permeability zones.
permeability zones were placed as shown in figure 2A (zones A, B, and C) which serve as a model for large-scale en-echelon cracks or a series of isolated fractured zones. The domain was 500 m in depth and 1000 m in lateral extent, with a 25 K temperature difference between the upper and lower boundaries. Such a temperature gradient is on the high side of average but not at all unrealistic, especially in the oceanic crust (compare discussion on p. 227 of Fyfe, Price, and Thompson, 1978, as well as Garland, 1979, and Stacey, 1977). In this paper we focus on fluid flow driven by thermal convection, so we chose depths and temperature gradients to yield Rayleigh numbers above the onset

![Permeability and surface areas used as initial conditions for simulation L1](image)

**Fig. 2.** Permeability and surface areas used as initial conditions for simulation L1. (A) Three isolated high-permeability zones (zones A, B, and C). The permeability contour labels are $10^{12}$ times their values in m$^2$. (Except in and near the high permeability zones, this simulation has the background permeability of $7.1 \times 10^{-12}$ m$^2$). (B) The surface area to fluid volume ratio in m$^2$/m$^3$ (in most of the domain the background value is $A_f/V_f = 3.2 \times 10^{-4}$ m$^{-1}$).
values for thermal convection in porous media \((Ra_c = 4\pi^2\text{ for onset})\). The Rayleigh number for a uniform porous media is defined as

\[
Ra = \frac{\rho g \alpha k H (\Delta T)}{\mu \lambda^*}
\]

with fluid density \(\rho\), gravitational acceleration \(g\), thermal expansion coefficient \(\alpha\), permeability \(k\), layer depth \(H\), temperature difference between the upper and lower boundaries \(\Delta T\), dynamic viscosity \(\mu\), and thermal diffusivity \(\lambda^*\).

The surface area to fluid volume ratio is shown in figure 2B. In addition to an initial constant vertical temperature gradient, a sinusoidal thermal perturbation was superimposed to initiate upwelling in the center of the domain. Snapshots at six different times are shown in figure 3 for a variety of fields. The first four frames summarize the transient behavior. By the time of frame 5, the system has reached a statistically stationary state (in our usage, a statistically stationary state is one which may have embedded time dependence, but whose statistical and harmonic properties are essentially time independent). This is not, however, a steady (time independent) state as most fields oscillate with time, especially near the high-permeability zones. Figure 4 shows various fields as a function of time at the centers of the three high-permeability zones, spanning a time range up to frame 5 of figure 3.

As the transient regime has been discussed in detail for similar systems in Bolton, Lasaga, and Rye (1996), in this paper we just briefly summarize the key aspects of this time period. Oscillations occur in the thermal boundary layers near the upper and lower high-permeability zones. In the initial \(\sim 40\text{ yrs}\), plumelets (small-scale plumes) fall frequently and rapidly through the high-permeability zone \((A)\). The rapid oscillations associated with these plumelets are barely discernible in the first part of the transient in figure 4. After several turnover times, the oscillations become more uniform and less frequent. The evolution to a statistically stationary state took \(\sim 1000\text{ yrs}\). During this time, the dominant oscillation frequency at the upper boundary (above zone \(A\)) is more than twice that of the dominant frequency observed at the lower boundary (near zone \(C\)). Causes for this difference are discussed in Bolton, Lasaga, and Rye (1996). The waveforms at zones \((B)\) and \((C)\) are almost purely sinusoidal, while two frequencies have significant amplitude at location \((A)\). At higher Rayleigh numbers, the dynamics tend to be more chaotic. As is notable in figure 3 (part B, frame 1), the fastest flows are initially observed in the high-permeability zones \((\text{flows are fastest where streamlines are most closely spaced})\). With time, the central thermal plume becomes well established, leading to enhanced flow in zone \((B)\), via “thermal channelization.” Eventually, the thermal plume shifts so as to feed directly into zone \((C)\) \((\text{by frame 5 of fig. 3})\). Above zone \((A)\) there is a persistent “feeder” plume of downwelling cool fluid.

Significant changes in porosity and permeability occur on long time scales. The structure of the porosity changes \((\text{part D of fig. 3})\) are roughly inverted images of the relative saturation states shown in part \((E)\) \((\text{oversaturation is associated with decreasing porosity})\). The relative departure of silicic acid from equilibrium may be defined as the nondimensional number:

\[
\tilde{c}_{Si} = \frac{c_{Si} - c_{Si,eq}}{c_{Si,eq}}
\]

where \(c_{Si}\) represents the concentration of silicic acid \((\text{that is, } c_{H_4SiO_4}\text{ in molarity units: moles/L})\), and \(c_{Si,eq}\) is the temperature-dependent equilibrium concentration of \(H_4SiO_4\). We call this \(\tilde{c}_{Si}\) the “relative silicic acid concentration” or its relative saturation state: it is positive when the fluid is oversaturated in silicic acid, and it is negative for undersaturated concentrations. Note that the downwelling edges of the domain are undersaturated
Fig. 3. Snapshots of several fields at six different times for simulation L1. Permeability contours are dashed (at values $50, 100, \text{and } 150 \times 10^{-12} \text{ m}^2$) in parts (A) and (C). (A) temperature, (B) stream function, (C) silicic acid concentration, (D) porosity change over a finite time interval (expressed in units of porosity fraction change per million years), (E) relative silicic acid concentration $\tilde{c}_{\text{Si}}$ as defined in eq 5. Time of each frame (elapsed from startup), the time interval associated with part (D), the ranges of $\tilde{c}_{\text{Si}}$, and porosity changes over the interval are: (1) $\sim 3.2 \text{ yrs (interval } \sim 3.2 \text{ yrs), } \tilde{c}_{\text{Si max}} = 0.38, \tilde{c}_{\text{Si min}} = -0.11, \phi_{\text{max}} = 4.7 \times 10^{-5}, \phi_{\text{min}} = -1.0 \times 10^{-5}$; (2) $\sim 16 \text{ yrs (interval } \sim 13 \text{ yrs), } \tilde{c}_{\text{Si max}} = 0.34, \tilde{c}_{\text{Si min}} = -0.27, \phi_{\text{max}} = 5.8 \times 10^{-5}, \phi_{\text{min}} = -7.3 \times 10^{-5}$; (3) $\sim 48 \text{ yrs (interval } \sim 16 \text{ yrs), } \tilde{c}_{\text{Si max}} = 0.30, \tilde{c}_{\text{Si min}} = -0.15, \phi_{\text{max}} = 7.9 \times 10^{-7}, \phi_{\text{min}} = -6.9 \times 10^{-7}$; (4) $\sim 140 \text{ yrs (interval } \sim 95 \text{ yrs), } \tilde{c}_{\text{Si max}} = 0.17, \tilde{c}_{\text{Si min}} = -0.17, \phi_{\text{max}} = 4.9 \times 10^{-4}, \phi_{\text{min}} = -2.5 \times 10^{-5}$; (5) $\sim 1100 \text{ yrs (interval } \sim 250 \text{ yrs), } \tilde{c}_{\text{Si max}} = 0.18, \tilde{c}_{\text{Si min}} = -0.10, \phi_{\text{max}} = 8.7 \times 10^{-3}, \phi_{\text{min}} = -6.6 \times 10^{-3}$; (6) $\sim 760000 \text{ yrs (interval } \sim 250000 \text{ yrs), } \tilde{c}_{\text{Si max}} = 0.18, \tilde{c}_{\text{Si min}} = -0.17, \phi_{\text{max}} = 0.012, \phi_{\text{min}} = -0.0050$. 

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Fig. 3 (continued)
(and therefore dissolving). With time, the lower part of the main upwelling plume shrinks to form a stalk-like structure, especially apparent in the silicic acid concentration field (fig. 3C). The core of the main plume stalk is oversaturated and is a zone of precipitation. Also, note that the lines of saturation state reversal (thick curves in fig. 3E), though dynamic, approach the downwelling domain edges and approach the lower main plume stalk (forming a mushroom shape). The center of zone (A) is usually oversaturated. However, just above this zone is a region of persistent undersaturation. In addition to this undersaturated region, the dominant dissolution zones occur: (1) at the downwelling edges, (2) near the bottom left and right of the domain, and (3) on the lateral edges of the main upwelling plume stalk.

Time-dependent flows can occur for a variety of geologic systems. When local convection is embedded in a large-scale convection pattern, oscillations in thermal, compositional, and fluid velocity fields can be expected. Above zone (A) and below zone (C) are regions especially susceptible to oscillations. The long-term evolution of the system increases the permeability near the lower boundary, but for this modest Rayleigh number, oscillations never occur at the bottom except near zone (C), and even there, the boundary layer instabilities eventually cease.
We now classify regions of the flow/reaction system according to properties of the saturation state, the flow direction, and the sense of the thermal gradient in the flow direction. These classifications are critical to understanding which domains can be understood only by including kinetic effects. The domain may be divided into eight distinct types of regions. Furthermore, the location of each region has a rather generic spatial arrangement, showing important similarities between each simulation. To shorten our discussion, we adopt a three letter code, for example VCO. The first letter indicates the sense of the vertical component of the Darcy velocity (V = vertically upward, D = downward). The second letter indicates whether the fluid is experiencing heating or cooling in the flow direction (H = heating, C = cooling) and is calculated from the sign of $\mathbf{q} \cdot (\nabla T)$, that is the Darcy velocity dotted into the temperature gradient. The third letter indicates whether the fluid is oversaturated or undersaturated with respect to the equilibrium concentration of silicic acid (O = oversaturated, U = undersaturated). Thus VCO indicates upward moving oversaturated fluid experiencing cooling. The eight possibilities are summarized in table 2, along with the color code used in figure 5. Figure 5A shows one snapshot of this classification for simulation L1 (with similar views for simulations L2 and L3 in parts B and C). Following a fluid parcel from the core of an upwelling plume stalk near the bottom boundary and moving around the circulation
Fig. 4. At the centers of the high-permeability zones (A) (solid), (B) (short dash) and (C) (long dash): Figure parts: (A) Darcy velocity magnitudes in meters/year, (B) temperatures in Celsius, (C) silicic acid concentration in micromoles/liter, (D) the relative silicic acid concentration ($\tilde{c}_\text{Si}$). The abscissa is time after startup in units of years. All for simulation L1.
path back to the stalk, the typical sequence observed is: VCO $\rightarrow$ DCO $\rightarrow$ DHO $\rightarrow$ DHU $\rightarrow$ VHU $\rightarrow$ VCU $\rightarrow$ VCO. Of course there are variations to this theme, and not all fluid parcels travel through the core of the plume stalk. DCU and VHO are the least often observed states in our simulations. This is likely due to the usual correlation of downwelling with heating (and upwelling with cooling) and the usual correlation of heating with undersaturation (and cooling with oversaturation), thus pairing of two unusual states is rarely observed.

We observe significant regions in the flow/reaction system which would not exist unless kinetics were important. The VCU and DHO states violate the conventional wisdom based on equilibrium. Indeed, cooling yet undersaturated fluid is commonly observed lining the edges of upwelling plumes (compare VCU in green in fig. 5). Oversaturated fluid experiencing heating commonly lines cores of downwelling plumes (DHO). The extent of this zone is also significant near the lower-side exit of high-permeability zones near the surface. The regional structure of the periphery of high-permeability zones near the surface is especially complex when oscillations are present: Around zone (A) (the upper-left high-permeability zone of fig. 5A) all eight regional types are represented. Because of the oscillatory nature of this region, the locations of the regional boundaries are dynamic in time. Saturation state reversals along with oscillatory precipitation leading to quartz zonation are expected, as discussed in some detail by Bolton, Lasaga, and Rye (1996).

We now turn to a discussion of the long-term evolution of the flow/reaction system. After the end of the time sequence shown in figure 4, we used an acceleration factor $A_t = 1000$, applied to the right-hand side of eq (1) (see app. B for further details). Figure 6 shows the subsequent evolution of various fields at the centers of the high-permeability zones. The abscissa is in accelerated time. In order to calculate oscillation periods locally in time, the periods deduced from the accelerated time scale must be divided by the acceleration factor (1000). For this case, the oscillation magnitudes at the upper high-permeability zone (A) increase with time for each of the fields, while the dominant periods experience little change (other simulations we have performed showed significant increases of the oscillation period at the upper boundary). However, the oscillatory nature at locations (B) and (C) diminishes with time, slowly evolving on the time scale of the permeability changes. While the temperature slowly rises in zone (C), the silicic acid saturation state reverses. These changes are associated with a slight shift of the plume stalk location, as discussed further below. The eventual loss of oscillations near the bottom boundary is possibly associated with the stalk migration. While the high-permeability zone can promote oscillatory behavior early in the evolution, later, as the stalk is more centered on zone (C), fluid is drawn in more from below than from the side.

In figure 7, we present the spatial distribution of the porosity at the end of the transient phase and at the end of the simulation. The porosity fields at these two times have quite similar structure, although the magnitude of changes are much larger at the end. The dominant zones of long-term dissolution are: (1) the cores of the downwelling plumes (which for this case are at the left and right edges of the domain), (2) near the bottom boundary where undersaturated downwelling fluid experiences significant heating, (3) on the sides of zone (C) where kinetics delay saturation state recovery, and (4) just above zone (A) where a persistent undersaturated feeder plume exists. Dominant regions of net precipitation occurred: (1) near the upper boundary where upwelling undersaturated fluid is cooled by the boundary, (2) in the lower and upper parts of the main plume stalk (not much porosity change happens in the center of zone (C), as low surface areas inhibit significant exchange), and (3) just below zone (A), where the fluid is downwelling, yet oversaturated, and kinetic effects are critical.

As many regions within the flow system are oscillatory, in order to understand the long-term evolution of the velocity and silicic acid relative saturation states, we must
average over several cycles of the oscillations and compare such averages for time periods after the transient phase and at the end of the simulation. Figure 8 shows the time average of \( \tilde{c}_{\text{Si}} \) (see eq 5), which we denote by \( \tilde{c}_{\text{Si}} \). Also shown is the standard deviation experienced over several oscillations. These quantities are shown for two times (one after the transient phase, and the other at the end of the simulation). Figure 8E shows the difference between the initial and final averages. The overall structure of \( \tilde{c}_{\text{Si}} \) in parts (A) and (B) are very similar, although the deviation from equilibrium increased somewhat with time. Parts (C) and (D) indicate that the oscillations initially are most pronounced around zones (A) and (C), while eventually the oscillatory nature disappears near the bottom. Part (E) indicates how the long-term feedbacks have changed the local saturation states. Indeed, the dissolution zones at the edges become more undersaturated, as do the regions near the bottom boundary at the left and right of the domain. As we will see, these zones also experience modest long-term increases in the velocity magnitudes. The difference shown in part (E) is dominated by changes near zone (C), associated with the plume stalk migration.

The long-term changes in the velocity field are generally coupled to relative permeability changes caused by dissolution and precipitation. We define the Darcy velocity magnitude by \( q = q \cdot q \). In figure 9, we show the Darcy velocity magnitude time averages \( q \), standard deviations of \( q \) normalized by \( q \), and the difference of averages for the same two times compared in figure 8. Part (C) indicates that the major zones of time dependence are initially above zone (A), below zone (C), and in the high-velocity region connecting these zones. Thus, many significant oscillations in flow magnitude occur along the main flow channel, although part (D) shows that eventually most of the oscillations in velocities are confined around zone (A). Part (E), when compared to figure 7B, indicates that most major dissolution zones experienced some increase in velocity magnitudes. The major change in part (E) is around zone (C), where the plume stalk shifted to the right. Velocity increases near the bottom of the domain have been noted by a number of previous studies.

The location of the plume stalk is inherently unstable. Figure 10 shows the streamlines before and after the long-term sequence. The upwelling, oversaturated fluid at the core of the plume stalk causes precipitation, which eventually clogs the channel. In addition, the edges of the stalk are undersaturated (compare VHU, VCU, and DHU regions of fig. 5A), causing local dissolution, and relative permeability increases. The plume stalk can then be expected to move dynamically to one side or another, or even to

Table 2

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCO</td>
<td>upwelling, cooling, oversaturated</td>
<td>light blue</td>
</tr>
<tr>
<td>DCO</td>
<td>downwelling, cooling, oversaturated</td>
<td>violet</td>
</tr>
<tr>
<td>DHO</td>
<td>downwelling, heating, oversaturated</td>
<td>pink</td>
</tr>
<tr>
<td>DHU</td>
<td>downwelling, heating, undersaturated</td>
<td>light-brown</td>
</tr>
<tr>
<td>VHU</td>
<td>upwelling, heating, undersaturated</td>
<td>yellow</td>
</tr>
<tr>
<td>VCU</td>
<td>upwelling, cooling, undersaturated</td>
<td>green</td>
</tr>
<tr>
<td>DCU</td>
<td>downwelling, cooling, undersaturated</td>
<td>dark gray</td>
</tr>
<tr>
<td>VHO</td>
<td>upwelling, heating, oversaturated</td>
<td>white</td>
</tr>
</tbody>
</table>

Eight distinct types of regions exist. We adopt a three letter code, for example, VCO. The first letter indicates the sense of the vertical component of the Darcy velocity \( V = \text{upward}, D = \text{downward} \). The second letter indicates whether the fluid is experiencing heating or cooling in the flow direction \( H = \text{heating}, C = \text{cooling} \) and is calculated from the sign of \( q \cdot (\nabla T) \), that is the Darcy velocity dotted into the temperature gradient. The third letter indicates whether the fluid is oversaturated or undersaturated with respect to the equilibrium concentration of silicic acid \( O = \text{oversaturated}, U = \text{undersaturated} \). Thus VCO indicates upward moving fluid that is experiencing cooling and is oversaturated. Also shown is the color code used in figure 5.
Fig. 5. Regions, as defined in table 2. For simulations (A) L1 at time 760000 yrs, (B) L2 at time 1800000 yrs, and (C) L3 at time 2000000 yrs.
Fig. 6. As figure 4, but in accelerated time (see text). In part (C), the trace for location (B) is barely discernible (nearly horizontal below the mean of trace A).
bifurcate (as was the case for simulation C5 of Bolton, Lasaga, and Rye, 1996). These dynamic effects of the flow/reaction feedback have important consequences for geologic systems.

**Convection Simulation L2**

Sloping faulted zones are commonly observed in near-surface environments. Sloping fractured zones can be characterized by relatively high permeability and low surface area to fluid volume ratios. High-permeability zones may be isolated or may exist in close proximity to others, cases we model in simulations L2 and L3, respectively. Isolated high-permeability conduits of sufficient width can support both upwelling and

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Fig. 7. Porosity fraction (color scale and solid contours) and stream function (dashed) for simulation L1. A thick contour is shown for the porosity fraction used as an initial value (0.115963). (A) For time: 1200 yrs, with porosity fraction thin contours at 0.11597, 0.11598, 0.11599, and 0.1160; (B) for time: 760000 yrs, with porosity fraction thin contours at 0.10, 0.11, 0.12, 0.13, 0.14, and 0.15.
Fig. 8. Various views of the relative saturation state $\tilde{c}_s$ for simulation L1. (A) Time average before acceleration (at time 1200 yrs); (B) Time average after acceleration (at time 760000 yrs); (C) standard deviation before acceleration; (D) standard deviation after acceleration; (E) change of average relative saturation: part (B) minus part (A). In parts (C) and (D) the contour levels are at 0.001, 0.005, 0.01, 0.05, and 0.1.
downwelling in the same “channel,” which should be the case for some fault zones. A considerable body of literature exists for similar types of fluid flows in sloping fluid-filled channels with impenetrable edges and constant temperature boundaries, in which case nondimensional Grashof numbers characterize many of the transitions (Nagata and Busse, 1983). By contrast, the porous media problem is governed by different equations and boundary conditions compared to such simple fluid-filled channel flows. The high-permeability channel we consider does not have constant-temperature boundaries, nor do the edges satisfy “no-penetration” conditions. Simulation L2 was initiated with the same range of grain radii as the last simulation. The domain was 200 m in depth and 800 m in width, with convection driven by a 10 K temperature difference between the upper and lower boundaries. For the low temperatures and simple chemistry considered in these simulations, thermal effects on the density field far outweigh the influence of the

Fig. 8 (continued)
Fig. 9. As figure 8, except for the Darcy velocity magnitudes. Parts (C) and (D) were normalized by parts (A) and (B), respectively. (For simulation L1.)
solutes. Because of this, the flow up along the upper side of the sloping zone is relatively warm, and the downwelling flow on the lower side is relatively cool (with some leakage along both sides of the high-permeability zone). The upflow is of somewhat larger magnitude than the downflow due to the temperature dependence of the viscosity.

A variety of fields is shown in figure 11, with the location of the high-permeability zone also indicated. These are shown at three different times: early, long after the transient effect has disappeared, and at the end of the simulation (corresponding to almost 2 my). During this time, the porosity fraction changed by \( \pm 20 \) percent from the initial value of near 0.116. After the first 100 yrs, most fields change monotonically throughout most of the domain. The transient effects were nearly removed after 400 yrs, although we did not apply acceleration \( (A_c > 1) \) until 800 yrs into the simulation. Further changes occurred on the slower timescale of the permeability changes. By comparing...
parts (A) and (C) of figure 11, we note that the thermal field is much more diffuse than the solute field, in accordance with their differing diffusivities. Most of the flow is confined to the high-permeability zone (as is more apparent in velocity magnitude figures discussed below), although some fluid leaves this zone, especially near its upper and lower edges. If the simulation had been performed with larger permeability contrasts between the bulk of the matrix and the high-permeability “channel,” then even more of the flow would have been confined to the “channel.”

By comparing figure 11D and E, we note a number of features similar to simulation L1. First of all, most of the upper half of the domain is oversaturated, with porosity decreasing, while most of the lower half is undersaturated, with increasing porosity. The downwelling plumes have undersaturated cores, and this saturation state broadens with depth in much of the downwelling zones. The oversaturated core of the upwelling plume is extremely narrow (even somewhat under-resolved). A kinetic description is crucial for the dissolution that occurs on the edges of upwelling plumes and is likely a generic feature of convecting systems. The dominant dissolution occurred in zones near the bottom, directly below regions of downwelling. In addition, major dissolution occurred on the periphery of the upwelling plume (as was also the case for simulation L1). The dominant zone of precipitation is just below the upper part of the high-permeability zone, where oversaturated fluid plunges downward, and kinetic effects are also critical (see below). Within the high-permeability zone, the downwelling fluid is being heated and makes a transition from an oversaturated to an undersaturated state midway down the channel.

The regional breakdown shown in figure 5B exhibits many generic similarities to simulation L1. The core of the upwelling plume is oversaturated and cooling [state VCO]: This plume is layered by undersaturated cooling fluid [VCU], with VHU surrounding these zones near the bottom boundary. As fluid reaches the upper end of the channel and plunges downward, the VCO → DCO → DHO → DHU sequence is again observed. Simulation L2 is shallow enough to avoid the onset of boundary layer oscillations, at least for the time duration we investigated. If such oscillations were to commence, the region just between the upper boundary and the top of the high-permeability zone is the most susceptible to such oscillations.

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Fig. 10. Overlay of stream function contours before (dashed, at time 1200 yrs) and after the long-term run (solid, at time 760000 yrs). [For simulation L1].
The long-term changes for this single sloping channel may be subtle, but they reveal important principles applicable to geologic systems. Figure 12 summarizes these changes. In part (A), we show the porosity distribution at the end of the simulation. The initial porosity was uniform throughout the domain, so that the image nicely shows the porosity change in color. The porosity field changes are also directly proportional to the relative changes in the permeability field for the grain model based on partially-occluded spheres (for $\phi_{\text{init}} \sim 0.116$ we have $\delta k / k \sim 28 \phi$, where $k$ is the permeability, $\phi$ is the porosity fraction, and $\delta$ indicates a change from an initial value). Part (B) shows a normalized change of the silicic acid saturation state ($F_{\text{avg}c}$) over the long term, defined from:

$$\Delta c = c_{\text{Si:final}} - c_{\text{Si:initial}}$$

$$F_{\text{avg}c} = \frac{\Delta c}{\text{avg}(\text{abs}(\Delta c))}$$

where $\text{avg}$ indicates a global mean over the domain, and $\text{abs}$ denotes an absolute value. The dark arcuate zone on the upper part of the domain indicates that in this region the fluid has become more oversaturated over the time interval. This is related to an overall shift in the upwelling part of the channel flow to the left. The oversaturated upper surface of the channel gradually clogs via precipitation. Meanwhile, as we will see, the plume stalk also shifts to the left, making the upper zone of the channel closer (in a fluid trajectory sense) to the main source of fluid high in silicic acid concentration. This arcuate zone is then somewhat unusual—even though the region is clogging, changes in the plume stalk location allow the fluid near the surface to become even more oversaturated. Parts (C) and (D) of figure 12 show the velocity magnitudes ($q = (\mathbf{q} \cdot \mathbf{q})^{1/2}$) before and after the accelerated sequence, respectively. These fields appear very similar, yet an important shift toward the left is indicated by the normalized fractional change $F_{\text{avg}q}$ found from:

$$\Delta q = q_{\text{final}} - q_{\text{initial}}$$

$$F_{\text{avg}q} = \frac{\Delta q}{\text{avg}(\text{abs}(\Delta q))}$$

This fractional change is shown in figure 12E. Velocity magnitudes along the (clogging) uppermost surface of the channel have decreased, while increasing at a slightly lower part of the channel (which had been dissolving in much of the lower part of the channel). Meanwhile, the magnitude of flow velocities down the lower surface of the channel decreased. Part of the downwelling fluid is shunted off toward the core of the thermal plume downwelling from the upper surface, where eventual undersaturation and dissolution lead to increasing velocity magnitudes (the vertical dark zone near $x = 200$ m in fig. 12E). Another zone of increasing velocity magnitudes is just to the right of the base of the high-permeability zone (around $x = 550$ m, $z = 20$ m). Here, persistent undersaturation leads to large increases in permeability. In part (F), we show an overlay of the velocity magnitudes before and after the long-term sequence, which highlights these subtle, but important, changes. Flow fields expected to be steady over short time scales must change over long time scales due to the feedback between the flow, the chemistry, and the permeability changes.

Convection Simulation L3

Geologic systems often contain high-permeability zones close enough to allow interaction between them. When fluid travels up one system of conduits and down another, we may expect generic behavior somewhat different from the last simulation containing a single high-permeability zone. The interacting high-permeability (for
Fig. 11. Snapshots of several fields at three different times for simulation L2. Permeability contours (at values 50, 100, and $150 \times 10^{-12} \text{ m}^2$) are dashed in parts [A] and [C]. [A] Temperature; [B] stream function; [C] silicic acid concentration; [D] porosity change over a finite time interval (expressed in units of porosity fraction change per million years); [E] relative silicic acid concentration $\tilde{c}_\text{Si}$. Time of each frame (elapsed from startup), the time interval associated with part [D], the ranges of $\tilde{c}_\text{Si}$ and porosity changes over the interval are: [1] $\sim 16$ yrs (interval $\sim 16$ yrs), $c_{\text{Si,max}} = 0.20$, $c_{\text{Si,min}} = -0.077$, $\phi_{\text{max}} = 6.3 \times 10^{-4}$, $\phi_{\text{min}} = -1.4 \times 10^{-4}$; [2] $\sim 820$ yrs (interval $\sim 250$ yrs), $c_{\text{Si,max}} = 0.17$, $c_{\text{Si,min}} = -0.089$, $\phi_{\text{max}} = 2.4 \times 10^{-4}$, $\phi_{\text{min}} = -3.0 \times 10^{-4}$; [3] $\sim 1800000$ yrs (interval $\sim 63$ yrs), $c_{\text{Si,max}} = 0.19$, $c_{\text{Si,min}} = -0.084$, $\phi_{\text{max}} = 6.9 \times 10^{-4}$, $\phi_{\text{min}} = -8.5 \times 10^{-4}$. 
example, fractured) zones of this simulation (L3) reveal features that may be of central importance to a whole range of geologic systems, including long-term changes of the dynamics that follow as a direct consequence of the kinetics of dissolution and precipitation. The two sloping high-permeability zones are dashed in figure 13. In other respects this simulation was initiated with parameters similar to simulation L2, except that a thermal perturbation was applied to initiate upwelling in the channel on the right and downwelling on the left. Figure 13 (frame 1, parts A-E) shows a variety of fields soon after startup. The ensuing transient phase passed through a rather complicated sequence which included Rayleigh-Taylor type instabilities within each channel, where dense fluids lay above buoyant fluids, leading to overturning in several places along each channel. Eventually, enough time had passed to allow heat to diffuse from the “fractured” zones into (or out of) the surrounding matrix, generally inhibiting the local gravitational instabilities. The thermal, silicic acid concentration and velocity magnitudes appeared to be in steady state within 100 yrs. The more sensitive relative silicic acid saturation state required about 300 yrs to recover from the transient effects. By 600 yrs, the system was steady to within less than 0.1 percent of the initial variations. Frame 2 of figure 13 shows the fields at this time. We then continued the simulation (using an acceleration factor $A_c = 1000$) up to a time equivalent of 2 my, at which time the fields
Fig. 12. Various measures of the long-term changes for simulation L2. (A) Final porosity, with dashed stream function. The solid curve is a contour of the initial porosity. (B) $F_{avg\Delta\psi}$ as defined in eq 7. For this case $avg(\text{abs} (\Delta\psi)) = 0.0051$. (C) Darcy velocity magnitudes before the long-term segment.
Fig. 12(D) Darcy velocity magnitudes after the long-term segment. (E) $F_{avg|\Delta q}$ as defined in eq 9. For this case $\text{ave} (\text{abs} (\Delta q)) = 0.27 \text{ m/yr}$. (F) Overlay of the Darcy velocity magnitudes before (dashed) and after (solid) the long-term segment. These compare velocities between times into the simulation of 820 and 1800000 yrs. The isolated lobes appear where flow has become faster. The lower left portion of the “channel” became slower.
Fig. 13. Snapshots of several fields at three different times for simulation L3. Permeability contours are dashed (at values 50, 100, and $150 \times 10^{-12}$ m$^2$) in parts (A) and (C). (A) Temperature; (B) stream function; (C) silicic acid concentration; (D) porosity change over a finite time interval (expressed in units of porosity change per million years: with unequally spaced contour intervals at $\pm 0.00125$, $\pm 0.0025$, $\pm 0.005$, $\pm 0.01$, $\pm 0.02$, $\pm 0.04$, and a thick curve for 0); (E) relative silicic acid concentration $\tilde{c}_{\text{Si}}$. Time of each frame elapsed from startup, the time interval associated with part (D) in parentheses, the ranges of $\tilde{c}_{\text{Si}}$ and porosity changes over the interval are: (1) $\sim 3.2$ yrs (interval $\sim 3.2$ yrs), $\tilde{c}_{\text{Si,max}} = 0.15$, $\tilde{c}_{\text{Si,min}} = -0.15$, $\phi_{\text{max}} = 2.0 \times 10^{-4}$, $\phi_{\text{min}} = -1.1 \times 10^{-4}$; (2) $\sim 620$ yrs (interval $\sim 100$ yrs), $\tilde{c}_{\text{Si,max}} = 0.20$, $\tilde{c}_{\text{Si,min}} = -0.15$, $\phi_{\text{max}} = 3.5 \times 10^{-4}$, $\phi_{\text{min}} = -2.4 \times 10^{-4}$; (3) $\sim 2000000$ yrs (interval $\sim 200000$ yrs), $\tilde{c}_{\text{Si,max}} = 0.21$, $\tilde{c}_{\text{Si,min}} = -0.14$, $\phi_{\text{max}} = 0.0086$, $\phi_{\text{min}} = -0.0037$. 
were as shown in frame 3. During this time period thermal structures developed in such a way as to favor the onset of local convection above the “upflow” channel. Oscillations there probably initiate soon after the last frame shown, as was observed in simulations using somewhat larger acceleration parameters than those we present here.

By comparing the porosity changes and relative silicic acid saturation state (in fig. 13D and E), we note that the dominant oversaturation and precipitation occur at the outflow zone of the “upflow” channel. In fact, most of the precipitation occurs where the fluid is moving downward. Another major region of oversaturation is around the entry zone of the “downflow” channel. Much of this oversaturated region would not exist without including kinetic effects. This is clearly seen in figure 5C—where the eight categories defined earlier have spatial arrangements similar to previous simulations. The major dissolution region is near the bottom of the “downflow” channel (compare fig. 5C with fig. 13D:3 around (x, z) = (450 m, 25 m)).

The long-term changes revealed by this simulation have rather interesting consequences for crustal fluid flows in sloping aquifers. These changes are illustrated in figure 14. In part (A), we show the final porosity distribution. The porosity change from the initial constant value of ~0.116 has nearly the same spatial structure as the relative permeability change for the subgrid-scale grain model utilized (\(\delta k/k \sim 28\delta\phi\)) for this
Fig. 14. Various measures of the long-term changes for simulation L3. (A) Final porosity, with dashed stream function and solid curve for the initial porosity; (B) final permeability, with dashed stream function, (permeability contours at 33, 66, 100, 133, 166, and 200 m²); (C) $F_{\text{var,2d}}$ as defined in eq 7, along with the final stream function.
Fig. 14(D) $F_{\text{vel,q}}$ as defined in eq. 9; (E) overlay of the Darcy velocity magnitudes before (dashed) and after (solid) the long-term segment. The downwelling plume on the left steepens, while the upwelling plume on the right becomes less steep, and the flow slows in the upper zones, while becoming faster near the bottom; (F) Overlay of the stream function contours before (dashed) and after (solid) the long-term segment. These compare various quantities between times into the simulation of 620 and 2000000 yrs. The distal ends of the plume cores have shifted to the left, both for the left-side downwelling plume and the right-side upwelling plume.
In part (B), we show the final permeability. Permeabilities generally decreased in the upper half of the domain and increased in the lower half, but some of the significant regions of change could not have been predicted without kinetics. Parts (C) and (D) of figure 14 show the normalized changes in saturation state and velocity magnitudes ($F_{ave}^0$, $H_{ave}^0$, and $q_{ave}^0$, respectively). The most significant changes we observe in these are, in fact, associated with features best visualized in parts (E) and (F), which are overlays of the velocity magnitudes and the stream function at two different times (before and after the accelerated sequence). The flow down the left-hand channel steepens (becomes more vertical) with time. This is due in part to the fact that the downwelling fluid is dense and undersaturated in the core of the downwelling plume. The ensuing dissolution is most favorable on the lower side of the high-permeability zone. The potential of runaway dissolution is moderated by the increased draw of oversaturated fluid from the edges of the high-permeability zone. The flow rates increase along the bottom of the channel. They are decreasing in the entry zone at the top ($x, z = (100 m, 175 m)$) and along the upper surface of the lower part of the channel ($x, z = (325 m, 50 m)$). One new feature near the latter location is the development of closed circulation displaying the sequence $VCO \rightarrow DCO \rightarrow DHO \rightarrow DHU \rightarrow VHU \rightarrow VCU \rightarrow VCO$ (compare fig. 5C). The upflow part of this closed circulation is moving faster than was previously observed at this location. This small scale internal feature probably developed as a direct consequence of kinetic effects and illustrates the complexity that can develop even for slowly evolving simple models of flow and reaction.

In the right-hand “upflow” channel, precipitation clogs the upper half of the zone, causing circulation to become less vertical and shifting the main flow to the left significantly. This is apparent in parts (D), (E), and (F) of figure 14. The flow lines also begin to fan out to the right starting midway up the channel (diverging streamlines).

Scaling Issues in Relation to “Faster” Kinetics

One could ask whether kinetic control is really important to the long-term evolution of such convective systems. We explore this issue by comparing simulations performed using the experimentally derived values (Rimstidt and Barnes, 1980) with simulations that used kinetic rate prefactors made artificially larger. Systems are rarely “at” equilibrium, although some may be very close to equilibrium. The measure of deviation from equilibrium used above (in eq 5) was the relative “concentration” $c_{Si}$ (with $c_{Si} = \frac{c_{Si}}{c_{Si:eq}}$). Concentrations close to equilibrium are characterized by $\text{abs}(c_{Si}) \approx 1$, where abs denotes the absolute value. Note that $c_{Si} = 1$ is, in fact, a very substantial deviation from equilibrium with $c_{Si} = 2c_{Si:eq}$. The solute concentration (in our case silicic acid concentration) is intimately linked to the flow velocity, the thermal gradients, the kinetic rates, and the surface area to fluid volume ratio. Disequilibrium is favored by rapid flow in strong thermal gradients, with low surface areas available for exchange and slow kinetic rates. More general cases are influenced by changes in lithology. Although we have admittedly chosen permeabilities in the high range of normal to highlight kinetic control even for large scale systems, we can easily extend the model to faster kinetics.

Some key factors related to kinetic control are revealed by examining a balance between the advection and reaction terms of the solute equation. One may solve for the steady, one-dimensional balance of advection and reaction in a uniform medium (as has often been discussed, for example, Knapp, 1989). Here we use the notation of Bolton, Lasaga, and Rye (1997). For a constant Darcy velocity magnitude $q$, we may write the diffusion-free, steady-state limit of the concentration gradient in terms of

$$ q \frac{\partial c_{Si}}{\partial z} = R_{\text{min}} = \frac{A_r}{V_f k_b} \frac{1 \text{ m}^3 \text{ bulk}}{10^3 \text{ L bulk}} $$

(10)
Here, \( q \) is the Darcy velocity, \( c_{Si} \) is the concentration of silicic acid (in molarity), \( z \) is the spatial coordinate in the flow direction, \( R_{min} \) is the rate of production of silicic acid from quartz (in units of moles/(bulk volume in liters)/s), \( \phi \) is the porosity fraction (volume of fluid-filled pores/bulk volume), \( A_f \) is the surface area between the solid and fluid phases (with units of \( \text{m}^2 \)), and \( V_f \) is the fluid volume (in units of \( \text{m}^3 \)). The unit conversion is necessary as our reference volume for concentration is liters, while the \( A_f \), \( V_f \), and \( k \) reference meters. Also, for dilute solutions and unit water activities,

\[
k_q = k_q^{\text{RB}} \left( 1 - \frac{c_{Si}}{c_{Si,eq}} \right). \tag{11}
\]

The temperature-dependent kinetic rate parameters \( k_q^{\text{RB}} \) and \( k_q \) have units of \( \text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \), and \( c_{Si,eq} \) is the temperature-dependent concentration of silicic acid in equilibrium with quartz. In the above expression, we have ignored the small effect of dissociation of silicic acid. We find it useful to define

\[
k_{\text{eff}} = \frac{A_f}{V_f c_{Si,eq}} \left[ \frac{1 \text{ m}^3 \text{ bulk}}{10^3 \text{ L bulk}} \right] = \frac{R_{min}}{\phi(c_{Si} - c_{Si,eq})} \tag{12}
\]

as a generalized rate with units of \( \text{s}^{-1} \). Note that the first form given for \( k_{\text{eff}} \) shows that it is independent of \( c_{Si} \). We also define \( v = u_f = q/\phi \) as the average velocity of fluid in the pores. Then the steady equation for balance of advection and reaction can be written as

\[
v \frac{\partial c_{Si}}{\partial z} = k_{\text{eff}} (c_{Si,eq} - c_{Si}) \tag{13}
\]

For an injection concentration of \( c_0 \) at \( z = 0 \), the solution of (13) is

\[
c_{Si} = c_{Si,eq} + (c_0 - c_{Si,eq}) \exp \left( -\frac{z}{\delta} \right) \tag{14}
\]

where we have assumed isothermal, constant matrix property conditions, and

\[
\delta = \frac{v}{k_{\text{eff}}} = q \left( \frac{A_f}{V_f c_{Si,eq}} \left[ \frac{1 \text{ m}^3 \text{ bulk}}{10^3 \text{ L bulk}} \right] \right)^{-1}. \tag{15}
\]

We also find it convenient to define

\[
L_5 = \frac{3v}{k_{\text{eff}}} = 3\delta \tag{16}
\]

The characteristic distance \( L_5 \) is the distance for which the silicic acid concentration would recover to within 5 percent of equilibrium given some injection concentration (for example, \( c_0 \)) in an isothermal matrix of constant properties (see discussion in Lasaga, 1998, where his \( x_{min} \) of eq 3.95 is our \( L_5 \)). Note that the characteristic distances \( L_5 \) and \( \delta \) exhibit direct proportionality with the Darcy velocity \( q \) and inverse proportionality with the porosity \( \phi \), \( (A_f/V_f) \), and \( (k_q^{\text{RB}}/c_{Si,eq}) \) through \( k_{\text{eff}} \). This dependence has broad implications to reactive flows in porous media. Suppose simulation results with lower permeability resulted in flow velocities 10 times smaller than one of our cases. These characteristic distances would not change if the surface area to fluid volume ratio were also decreased by a factor of 10. The distances \( L_5 \) and \( \delta \) also depend on temperature through \( k_q^{\text{RB}} \) and \( c_{Si,eq} \). This result can be applied to other minerals primarily through a change of the kinetic rate term, as long as the kinetics are linear. For simulation L3, we had \( L_5 \) between 1000 and 2000 m in the high-permeability zones and between 10 and 100 m in most of the rest of the domain. This distance \( L_5 \) can vary from millimeters to kilometers. We wish
to emphasize that multimineralic systems that include changes in lithology at scales smaller than the local L₅ would not be expected to reequilibrate. We expect that kinetic effects for such heterogeneous multimineralic systems would be very important even for much lower permeabilities than what has been considered in this paper. For a discussion of nonlinear rate dependences and the inclusion of diffusion, see Lasaga and Rye (1993) and Lasaga (1998). Although we have presented only a one-dimensional analysis with an imposed injection concentration, the local readjustments made for the two-dimensional case follow similar local trends. Our convection simulations do not involve any injection concentrations, but spatial changes in c₅₆ are created by spatial changes in temperature and the temperature dependence of the equilibrium concentration.

One measure of kinetic control that relates to the above discussion is the advective Damköhler number

$$Da_{A} = \frac{k_{e} L}{v}$$

where v is the average fluid velocity in the pores (related to the Darcy velocity magnitude by $v = q/\phi$), L is a length scale, and $k_{e}$ is the effective kinetic rate parameter defined above (with units of $s^{-1}$). Damköhler numbers have often been used to characterize the relative importance of chemical reaction rates versus advective or dispersive fluxes. The nondimensional Damköhler numbers can also be viewed as ratios of time scales, ratios of rates, or ratios of various terms in the solute equation. Typically, a length scale must be chosen to specify fully the magnitude of a Damköhler number. Similar choices of length scales are usually necessary for defining other nondimensional numbers, such as the Peclet, Reynolds, and Rayleigh numbers. A variety of length scales may be defined for convective flow simulations in a porous medium, including the layer depth, the size of an imposed heterogeneity in the permeability field, the grid node spacing, the grain size, or the gap size of the fluid filled pores. Although any of these could be used in a definition of a Damköhler number, we turn the question around and compute the length scale for which the Damköhler number is near unity. Regarding the advective Damköhler number defined above ($Da_{A}$), large values are interpreted as kinetic rates being much faster than advective effects, which implies a system close to equilibrium. On the other hand, small $Da_{A}$ could be far from equilibrium as advective rates outweigh effective kinetic rates. An approximate balance of advective and reactive rates would be implied for Damköhler numbers near unity. Solving for $L_{5}$ when $Da_{A} = 1$ yields

$$L_{5} = \frac{v}{k_{e}} = \delta = \frac{L_{5}}{3}$$

In a qualitative sense, at scales much smaller than this $L_{5}$, one could expect little recovery toward equilibrium if a system were perturbed away from equilibrium, whereas at much larger scales than this $L_{5}$ one would expect the system to have had a chance to come close to equilibrium.

Although the use of the “quasi-stationary state (QSS) approximation,” as discussed by Lichtner [1988, 1991, 1993], is valid when the advective term $[q(\partial c_{56}/\partial z)]$ is balanced by the reaction term ($R^{min}$) and would have performed with acceptable accuracy for the calculation of the silicic acid concentration during the later parts of simulations L2 and L3, its use probably would not be appropriate for the oscillatory dynamics of simulation L1. Furthermore, use of the QSS approximation would not have been appropriate when attempting to distinguish the differences in the long-term behavior caused by artificial changes in the kinetic rates (discussed below). In the quasi-stationary state approximation, the partial derivative of concentration with respect to time is dropped from the solute equation. For negligible porosity changes with time, this leads to a balance
between advection, diffusion, and the kinetic source term. This approximation is often
made for geologically relevant problems to save computational time. If one retains the
local time derivative term in the solute equation small time steps are required for stable
advective Courant numbers unless implicit methods are used. Implicit methods have
been used in our codes for the kinetic source term, but we wished to retain the local time
derivative needed to describe properly the oscillatory dynamics. In order to extend our
calculations to the geologic time scales desired for the simulations, we used a different
approach (see app B).

The balance between solute equation terms described above can be generalized to
other mechanisms operative in this system. We introduce a variety of characteristic rates
and time scales \( \tau \) in table 3. The rate \( f_{eff} = k_{eff} \) has already been introduced in eq 12.
The rates \( f_c, f_r, f_s, \) and \( f_d \) are simply the terms of the solute equation for \( c_{Si} \) normalized by
\( c_{Si} \) itself (other normalizations are possible). When the advective term balances the
reaction term, one would have \( f_c + f_r = 0 \). Within the QSS approximation one would
have a balance equivalent to \( f_c + f_r + f_d = 0 \). The solute equation is equivalent to \( f_c = f_r +
f_c + f_d \) for the case of vanishing \( f_c \). In the regime of our simulations, we observe an
approximate balance of \( f_c \) and \( f_r \). We usually observe the order

\[
|f_{eff}| \gg |f_c| \gg |f_r| \gg |f_d| \gg |f_k|. \tag{19}
\]

Some of our simulations had \( |f_k| > |f_d| \). The fact that \( |f_k| \ll |f_d| \) justifies our omission of the
time dependence of the porosity in the solute equation. The ordering of \( f_k \) and \( f_d \) could
depend somewhat on the subgrid-scale grain model. The fact that reactive and advective
rates are nearly in balance would support the use of the QSS approximation as a
reasonable approximation in most regions. In our case, any mismatch of \( f_c \) and \( f_r \) is
locally nearly balanced by \( f_c \). The ordering of \( |f_r| > |f_d| \) is different from the QSS
approximation. The nonisothermal nature and at times oscillatory nature of our flow
system is at odds with the basic assumptions of the QSS approximation. The rates and

| Table 3 |

Characteristic rates and time scales

<table>
<thead>
<tr>
<th>Rate</th>
<th>Meaning</th>
<th>( 1/\tau )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_{eff} = k_{eff} )</td>
<td>( \frac{A_1 k_{eff}^{RB}}{V_f c_{Si,eq}} \left[ \frac{1 \text{ m}^3 \text{ bulk}}{10^3 \text{ L bulk}} \right] = \frac{1}{\tau_{eff}} )</td>
<td></td>
</tr>
<tr>
<td>( f_c = \frac{R_{min}}{\phi c_{Si}} = \frac{1}{\tau_c} )</td>
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</tr>
<tr>
<td>( f_r = \frac{-q \cdot \nabla c_{Si}}{\phi c_{Si}} = \frac{1}{\tau_r} )</td>
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</tr>
<tr>
<td>( f_s = \frac{\delta c_{Si}}{\delta t} c_{Si} = \frac{1}{\tau_s} )</td>
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<td></td>
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<tr>
<td>( f_d = \frac{D \nabla^2 c_{Si}}{c_{Si}} = \frac{1}{\tau_d} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( f_k = \frac{\delta k}{\delta t} k = \frac{1}{\tau_k} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( f_{fs} = \frac{\delta \phi}{\delta t} \phi = \frac{1}{\tau_{fs}} )</td>
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</table>
time scales introduced above make most physical sense when some quantity can grow exponentially from zero or decay toward zero. This is obviously true for $f_k$, $f_v$, and $f_{	ext{eff}}$. The physical nature of $f_{	ext{eff}}$ has already been discussed.

It is of interest to note that the advective Damköhler number is just a rescaled version of $f_{	ext{eff}}/k_v$ with a length scale naturally coming from gradients of $c_{\text{Si}, \text{eq}}$. One problem with such a ratio is that $f_v$ vanishes wherever $\mathbf{q} \cdot \nabla c_{\text{Si}}$ vanishes, causing $D_{\text{A}}$ to diverge. Similar problems occur in many other ratios of rates, making visualization of spatial variations of nondimensional ratios problematic. Of more interest is the spatial variation of the rates themselves, and how these rates scale with increasing kinetic rates.

To probe how the systems under consideration depend on the relative magnitude of the kinetic rate parameters, we made the kinetic rates artificially fast by imposing

$$k_{q, \text{model}} = M k_{q, \text{actual}} \tag{20}$$

where $k_{q, \text{actual}}$ is the experimentally derived kinetic source term defined above, and $M$ is a multiplier. With $M = 100$ the kinetic rates are 100 times faster than the experimentally observed value (for a given temperature and departure from equilibrium). Of course when this kinetic rate prefactor increases, one expects the deviation from equilibrium to decrease. The scaling behavior of this dependence is also discussed below.

The two-dimensional heterogeneous reactive transport for the nonlinear systems we deal with have no analytical solutions. For such cases we must evaluate what resolution is required more empirically and separately for each case considered. As an example of one of our convergence tests, note figure 15, which shows the relative silicic acid concentration $\tilde{c}_{\text{Si}}$ defined in eq 5 and the stream function for a comparison of two different resolutions (case L3: $129 \times 139$ nodes in part A and case L4: $65 \times 59$ nodes in part B). The quantity $\tilde{c}_{\text{Si}}$ is a particularly good variable for such testing as it depends on the resolution of the flow velocities, the temperature, and the silicic acid concentration simultaneously. These results compare quite well. The simulations L1 through L3 were computed at high resolution, but to explore further tendencies as function of $M$ we needed to use lower resolution to save computational time.

Convection simulations L4, L5, and L6—Simulation L4 was identical to L3 (including the initial conditions) except we used lower resolution. While L4 used $M = 1$, we made the kinetic rates artificially fast in simulations L5 ($M = 10$) and L6 ($M = 100$) which were computed with otherwise identical initial and boundary conditions. Figure 16 shows the results for these simulations after 2 my of simulation time with L4, L5, and L6 shown in parts (A), (B), and (C), respectively. Frames 1 (row 1) show the relative saturation $\tilde{c}_{\text{Si}}$ (in color) along with contours of the stream function and a bold contour which indicates the location of fluid in equilibrium with quartz. The fluid flow is up the “channel” on the right and down on the left. Increasing the rate of reaction shows how a system closer to equilibrium would behave. Frames 2 image the porosity fraction change over the simulation. There is a dramatic increase in porosity near the bottom of the downwelling “channel” on the left (near $(x, z) = (400, 25)$m). The velocity magnitude is imaged in frame 3 along with contours of the silicic acid concentration. As $M$ increases there is a large increase in flow velocity where the porosity has most increased. Surprisingly, even though the larger $M$ cases are closer to equilibrium, the factors moderating the potential runaway regime are no longer operative. For large $M$ a runaway regime ensues. Much larger changes in porosity, permeability, and fluid velocities begin, especially in the lower part of the left-hand high-permeability zone where the matrix is dissolving. This indicates that runaway regimes are favored by increasing the kinetic rates (at least for these monomineralic systems). As the runaway dissolution develops, our choice of resolution becomes too coarse. Also note that the silicic acid concentration $c_{\text{Si}}$ becomes more diffuse as $M$ increases. This is due to how $c_{\text{Si}}$ approaches $c_{\text{Si}, \text{eq}}$ with increasing $M$ and the fact that $c_{\text{Si}, \text{eq}}$ is a slave to the more diffuse temperature field.
Figure 17 shows the spatial distribution of various quantities for simulation L4. The rates $f_\nu$ and $f_r$ are practically identical except for sign, with the most intense magnitudes of these rates occurring where fluid exits the high-permeability zones and interacts with the larger surface area, smaller grained background matrix. The sign of $f_\nu$ is the same as that of $\tilde{c}_\text{Si}$ and $c_\text{Si}/H_{11002}c_\text{Si}$:eq. Most of the subtle imbalance of $f_\nu$ and $f_r$ is expressed in $f_\sigma$ (note that this field is more that two orders of magnitude smaller that $f_\nu$). The diffusive rates $f_d$ are, of course, most intense near the high gradient zones of $c_\text{Si}$ near the ends of the high-permeability zones. The rates $f_k$ and $f_\beta$ associated with the time dependence of the permeability and the porosity changes appear similar in form to $f_\nu$ but are several orders
Fig. 16. Columns (A), (B), and (C) are for simulations L4, L5, and L6, which used M = 1, 10, 100, respectively, all after 2 my of simulation time. Frame (row) 1 images $c_{\text{Si}}$ (in color), along with contours of the stream function and a bold contour which indicates the location of fluid in equilibrium with quartz. Frame 2 images the porosity fraction change over the simulation from its initial value (0.1159863) in units of porosity fraction change per million years (bold contour indicating no net change) along with thin contours of permeability (at 10, 50, and $100 \times 10^{-12}$ m$^2$. Additional contours at 500 and 1000 are shown for the runaway regime for M = 10 and 100. Frame 3 images the Darcy velocity magnitudes in m/yr, along with contours of $c_{\text{Si}}$ (at 120, 130, 140, 150, and 160 µmol/L).
of magnitude smaller. We also image the absolute deviation from equilibrium and the surface area to fluid volume ratios.

Figure 18 shows the spatial distribution of $L_5$ [as defined in eq 16], along with its logarithm and $k_{\text{eff}} = f_{\text{eff}}$ for simulations L4, L5, and L6 (for $M = 1, 10$, and $100$). Recall that the length $L_5$ is the length over which a perturbation in the solute concentration would come back to within 5 percent of equilibrium, if all factors were constant in the flow direction. Of course the system is heterogeneous and far from isothermal, even so, this characteristic length is a good physical descriptor. The characteristic length shows similar forms in each, but the magnitudes drop dramatically as $M$ increases. There is also some concentration of larger lengths toward the bottoms of the high-permeability zones with increasing $M$. For the experimentally derived rate ($M = 1$) the flow in the high-permeability zones does not converge much toward equilibrium as $L_5$ is much greater than the “channel” length. Even the larger rates ($M = 10, 100$) show significant distances for $L_5$ in the channels. The logarithmic view of $L_5$ shows that even the background low-permeability region would support nonequilibrium flow for up to $100$ m for $M = 1$ and up to $10$ m for $M = 10$. For $M = 100$, most of the domain would come to within 5 percent of equilibrium after it flowed between a few centimeters and a meter within the low-permeability region. The kinetic rate factor $k_{\text{eff}}$ increases linearly with $M$. Both this factor and the flow velocities influence the magnitude of $L_5$. Frame 3 also shows the stream function contours progressively concentrating in the runaway zone as $M$ increases.

Of considerable interest is the scaling behavior of the characteristic rates as a function of $M$. Figure 19 shows such scaling derived from calculations made at the end of simulations L4, L5, and L6. The values shown are the maxima and the averages of the magnitudes of the characteristic rates over the entire two-dimensional computational domain. Note the general trend of $|f_{\text{eff}}| \gg |f_s| \approx |f_r| \gg |f_{\text{dir}}| \gg |f_k| \approx |f_{\text{fl}}|$. Regarding the dependence on $M$, we have already discussed the simple linear dependence of $k_{\text{eff}}$ on $M$. The diffusive rates $f_d$ generally decrease with increasing $M$ as $c_{\text{Si}}$ approaches $c_{\text{Si:eq}}$, which is slaved to a diffuse temperature distribution. As such, we would expect $f_d$ eventually to become independent of $M$ for sufficiently large $M$. The modest increases in $f_k$ and $f_{\text{fl}}$ probably reflect the tendency toward runaway dissolution as $M$ increases.

The scaling behavior of the deviation from equilibrium.–The scaling behavior of the absolute deviation from equilibrium is shown in figure 20. The same trend is observed for the ratios $k_{\text{eff}}/f_s$ and $k_{\text{eff}}/f_r$ due to the near balance of $f_s$ with $f_r$ and the difference in the definition of $k_{\text{eff}}$ and $f_r$. In addition to the result for simulations L4, L5, and L6 ($M = 1, 10$, and $100$) for the grain model based on partially-occluded spheres (pos), we also show results for simulations L7 and L8 ($M = 1$ and $100$, discussed further below) for the grain model based on tube-edged cubes (tec). The exponent “a” for the scaling of the deviation from equilibrium of the form

$$ (c_{\text{Si}} - c_{\text{Si:eq}}) \sim M^{-a} $$

for the various cases is shown in table 4. The averages of $c_{\text{Si}} - c_{\text{Si:eq}}$ over the domain fall more rapidly with $M$ than do the maxima. Both grain models show similar values and trends (although the tec case was not computed for $M = 10$). We attempted to find analytical estimates to describe this scaling behavior with $M$ for simple nonisothermal flows. We examined the dependence on sinusoidal temperature variations in a closed loop (leading to Floquet solutions) and for linear thermal changes in space. The simple solute equation for both nonisothermal cases leads to intractable integrals. This failure of analytical estimates for the scaling behavior point again to the importance of numerical solutions of these complex flow systems. Certainly more work is necessary to understand the theoretical reasons for the scaling behavior of the deviation from equilibrium for nonisothermal flows.
Fig. 17. Various quantities at the end of simulation L4. In each case we show solid permeability contours for $k = 10^{-10}$, $10^{-9}$, $10^{-8}$ m$^2$. The color images have scale bars indicating the magnitudes. Each of the characteristic rates is in yr$^{-1}$, and is defined in Table 3. (A) $f_v$; (B) $f_r$; (C) $f_s$; (D) $f_d$; (E) $f_k$; (F) $c_{Si}$; (G) $c_{Si:eq}$ in μmol/L; (H) $A_f/V_f$ in m$^{-1}$, along with dashed stream function contours.
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Fig. 18. Characteristic lengths and rates after 2 my of simulation time for simulations L4, L5, and L6, which used M = 1, 10, 100, in columns (A), (B), and (C), respectively. Frame [row] 1 images L4 (in meters) on a linear scale, while frame 2 is the log10 transform of the same. Frame 3 images the rate $k_{\text{eff}}$ (in yr$^{-1}$), along with streamlines. Each image includes a dashed permeability contour (at $k = 50 \times 10^{-12}$ m$^2$).
Convection simulations L7 and L8.—The previous simulation (L1-L6) were all based on partially-occluded spherical (pos) close pack for the subgrid-scale grain model. We now turn to simulations based on tube-edged cubes (as described in app. C). This grain model is valid for smaller porosities than the pos model. Figure 21 shows the initial conditions used for simulations L7 and L8 for the nucleation density, the grain dimension, and the surface area to fluid volume ratio. Also shown is the temperature distribution along with the stream function and permeability conditions after the end of the transient phase. This simulation has a lower overall permeability distribution than simulations L1 to L6, is larger in vertical extent, and is forced by a smaller mean vertical temperature gradient.
We contrast results for \( M/H_11005 \) (simulation L7) and \( M/H_11005 \) (artificially faster kinetics for simulation L8) in figures 22 through 27. Figure 22 shows the thermal field along with contours of the stream function and permeability fields at the end of the simulations (nearly 2 my). By comparing the stream function contours we note that both cases show increasing velocities in the dissolving part of the downwelling "channels" and decreasing velocities and fanning out of the flow lines in the upwelling "channel" on the right arising from precipitation. Both these effects are more pronounced for \( M/H_11005 \)

**TABLE 4**

<table>
<thead>
<tr>
<th></th>
<th>pos</th>
<th>tec</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( M \in (1,10) )</td>
<td>( M \in (10,100) )</td>
</tr>
<tr>
<td>max (( c_{Si} - c_{eq} ))</td>
<td>0.45</td>
<td>0.76</td>
</tr>
<tr>
<td>ave (( c_{Si} - c_{eq} ))</td>
<td>0.75</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Scaling exponents "a" for the deviation from equilibrium of the form

\[
(c_{Si} - c_{eq}) \sim M^a
\]

Here, pos stands for the grain model based on partially-occluded spheres from simulations L4, L5, and L6 (\( M = 1, 10, \) and 100), while tec stands for the grain model based on tube-edged cubes from simulations L7 and L8 (\( M = 1 \) and 100). Scaling for both domain maxima and domain averages are shown.
Fig. 21. (A) The nucleation density used for simulations L7 and L8 in the form of log10(N) (where N is the number of grains per m³); (B) the grain dimension d (in mm); (C) the surface area to fluid volume ratio (expressed as log10(Af/Vf in m⁻¹)); (D) temperature in Celsius (color), stream function contours (solid), and the permeability k (dashed at k = 1, 5, 10⁻¹² m²). The value of 10 barely appears at the center of the two high-permeability zones. Simulation time is 2450 yrs.
Fig. 22. Parts (A) and (B) show the temperature (T) in Celsius while parts (C) and (D) show the silicic acid concentration in µmoles/L. Parts (A) and (C) on the left are for simulation L7 with $M_{1}/H_{11005}$1, while parts (B) and (D) on the right are for simulation L8 with $M_{1}/H_{11005}$100. In this figure and in figures 23 through 27, the stream functions are shown with solid lines, while the dashed contours bound the high-permeability zones (at $k_{1}/H_{11005}(1, 5, 10, 50, 100)$). Simulation time is $1.82 \times 10^{6}$ yrs.

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Fig. 23. Parts (A) and (B) show the deviation of the silicic acid concentration from equilibrium in μmoles/L while parts (C) and (D) show the relative silicic acid concentration $\tilde{c}_{\text{Si}}$. Parts (A) and (C) are for $M/H = 1000$ while parts (B) and (D) are for $M/H = 100$. See also the caption for figure 22.
Fig. 24. Parts (A) and (B) show the porosity change over the course of the simulation (from an initial value of 0.00485). Porosity is a fraction, not a percent. Parts (C) and (D) show the Darcy velocity magnitudes in m/yr. Parts (A) and (C) are for M/H11005 while parts (B) and (D) are for M = 100. See also the caption for figure 22.
Fig. 25. Parts (A) and (B) show the rate parameter \( k_{\text{eff}} \) in units of yr\(^{-1}\). Parts (C) and (D) show \( \log_{10} L \) in meters. Parts (A) and (C) are for \( M = 1 \), while parts (B) and (D) are for \( M = 100 \). See also the caption for figure 22.
Fig. 26. Parts (A) and (B) show the reaction rate parameter $f_r$ in units of $\text{yr}^{-1}$. Parts (C) and (D) show the rate parameter $f_s$ in units of $\text{yr}^{-1}$, which is a measure of the local time dependence of the silicic acid concentration. Parts (A) and (C) are for $M = 1$, while parts (B) and (D) are for $M = 100$. See also the caption for figure 22.
than for \( M = 1 \). The thermal fields are quite similar for both cases. Part (A) shows that the dissolution affects the permeability in a broad region around the “toe” of the downwelling channel, while part (B) \((M = 100)\) shows more dramatic permeability increases that are more localized at the very bottom of the high-permeability zone. Parts (C) and (D) contrast the silicic acid concentration for \( M = 1 \) and 100, respectively. Although the plumes are quite intense for \( M = 1 \), as the rate increases, \( c_{\text{Si}} \) tends to be more diffuse as \( c_{\text{Si,eq}} \) is slaved to the thermal field.

Figure 23 shows the absolute (top) and relative (bottom) deviations from equilibrium for \( M = 1 \) on the left and \( M = 100 \) on the right. As noted before, there is a dramatic decrease in deviations from equilibrium as the rate multiplier \( M \) increases. For \( M = 1 \), there is more of a tendency to concentrate the large deviations from equilibrium near the ends of the “flow channels,” while for \( M = 100 \) the slight deviations from equilibrium show only small increases along the flow channels. Figure 24 parts (A) and (B) show the
porosity changes from the initial value (of 0.00485) for the contrasting rates. (We centered the color scale on white. Nowhere does the porosity become negative, but modest decreases from 0.00485 do occur in and around the upwelling “channel” on the right-hand side.) The Darcy velocity magnitudes shown in parts (C) and (D) again point toward intense dissolution and flow enhancement in the lower regions of the downwelling channel and less intense upflow resulting from increases in $M$.

The characteristic rates $k_{\text{eff}}$ in parts (A) and (B) of figure 25 again show simple scaling with $M$. As was the case for simulation L4, simulation L7 with $M = 1$ exhibits a characteristic distance for recovery to equilibrium $L_5$ much longer than the flow channel and even up to 100 m in the background, low-permeability matrix. For $M = 100$, $L_5$ is on the order of tens of meters in the flow channels and on the order of a meter or less in the low-permeability region. The reactive rate term $f_r$ is shown in figure 26. Had we shown $f_r$, it would have again nearly duplicated $f_\text{d}$ except for sign. Also shown is the rate $f_s$, which exhibits a simple and intriguing structure for $M = 100$.

The scaling behavior of the characteristic rates shown in figure 27 for the tube-edged cube (tec) grain model is very similar in form and magnitude to that of figure 19 which was for the spherically based model. The main difference is that $f_d$ for the tec case is an order of magnitude smaller. The scaling behavior of $c_{Si} - c_{Si,\text{eq}}$ was previously discussed. We find that these results indicate that the scaling behavior is quite independent of the grain model for most of the characteristic rates.

**CONCLUDING REMARKS**

We have found that kinetic effects can be important in significant regions for crustal fluid flows in near-surface environments. This is especially true when high-permeability zones that serve as flow “channels” are present. Although our focus was on the quartz matrix system, many of the features present in these simulations are quite general and may even be accentuated for some multiminerical systems. The long-term flow reaction feedback changes the preferred flow “channels” over time. In sloping high-permeability zones, precipitation in upwelling regions forces the flow to become less vertical, while dissolving downwelling zones become more vertical. The saturation state expected on the basis of local equilibrium assumptions is often not observed near high-permeability zones. This is particularly true when flow rates are “large” and kinetics are “slow.” Plumes leaving thermal boundary layers are lined with kinetically controlled regions of the saturation state opposite from their cores. This would not be expected on the basis of a local equilibrium model. In plumes upwelling from a heated lower boundary, this kinetic effect contributes to an instability of the plume stalk location, forcing lateral migration. Complex internal recirculation can develop near sloping flow channels. Oscillatory boundary layers can produce rich dynamics for deep convecting systems, especially around near-surface high-permeability zones containing upwelling fluid. Real “runaway” dissolution was present only when the kinetic rates were made artificially high. For the cases we studied using the experimentally derived kinetic rates, modest increases in velocity occur in dissolving regions, but shifts in saturation state boundaries moderate what could have become a runaway regime. Such moderation may not always be operative. We expect that lower permeability systems of large vertical extent (deep systems) and faster kinetics may more often fall into a runaway regime. The scaling behaviors of a number of characteristic rates and length scales have been examined. The absolute deviation from equilibrium does not seem to follow a simple scaling law. As many aspects of the long-term evolution depend upon the deviation from equilibrium, we recognize the need for additional theoretical analysis of scaling laws for nonisothermal, kinetically controlled reactive flow systems.

Other factors must eventually be assessed for their relative importance, including the effects of nucleation kinetics, compaction, and fracture mechanics of the solid matrix,
and multimineralic systems. Minerals such as calcite, with its decreasing solubility with increasing temperature, could reverse some of the trends with upwelling and downwelling flows. Isotropic exchange between minerals and fluids is another ripe field for modeling studies, for which comparison with numerous field studies could be performed. Although our focus here has been on the basic phenomena and mechanisms influenced by kinetic control of dissolution and precipitation, our future models will also include more realistic treatments of dispersion, anisotropic permeability, dual porosity, et cetera. Additional work should assess the influence of pressure on the solubility and kinetics of quartz matrix systems. More efficient and accurate numerical methods must also be sought.

Different initial permeability distributions should also be investigated. Although we presented three generic permeability structures, some of the features would be changed by varying the background permeability and the width of the high-permeability zone. Our focus has been on shallow upper crustal environments where the aqueous phase is below the boiling point. Deeper systems, which span the critical point of CO2-water mixtures, remain as exciting new horizons for future modeling of reactive multiphase fluid flows. Systematic variation of these fields is beyond the scope of this paper.

**ACKNOWLEDGMENTS**

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**APPENDIX A**

**Mathematical formulation**


\[
\text{SiO}_2(s) + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4(aq).
\]  

The dissociation of water and silicic acid (H$_4$SiO$_4$) were also considered, but these reactions were assumed to be in equilibrium. We partition the system into primary and secondary species (compare Reed, 1982; Lichtner, 1985; Kirkner and Reeves, 1988). This partitioning, along with charge balance, leads to a solute equation for the total concentration of silicic acid of the form:

\[
\frac{\partial}{\partial t} [\phi U] + \nabla \cdot [q U - \phi D^* \nabla U] = R^\text{min}
\]  

which is for dilute solutions under the assumption of equal diffusivities of each species. Here, U is the “total” concentration of silicic acid (in units of molarity). For these simulations U is nearly the same as c$_{\text{H}_4\text{SiO}_4}$ = c$_{\text{Si}}$. The small difference (of ~0.2 percent) arises from the definition of total concentration and the slight dissociation of silicic acid. t is time in seconds (s), \(\phi\) is the porosity fraction (volume of void/bulk volume), D* is the diffusion/dispersion coefficient (in units of m$^2$/s, where m is meters), and q is the Darcy velocity (in m/s). The Darcy velocity \(q\) is related to the local volume averaged Eulerian velocity in the pores, \(u\), by \(q = \phi u\). The
gradient operator is $\nabla$, and the bold dot represents the dot product between vectors. As suggested above, we also track the concentrations of $H^+$, $H_2SiO_4^-$, and $OH^-$. For cases with more species in solution or with a multimineralic solid matrix there is more than one type of total concentration. Such cases require an index representation for both $U$ and $R$ (compare Soler and Lasaga, 1996b). The term $R^{\text{eq}}$ is the production of silicic acid from the solid quartz phase [in units of moles/(bulk volume in liters)/s], for which we used the kinetic data on quartz dissolution from Rimstidt and Barnes (1980), which for dilute solutions may be rewritten as

$$R^{\text{eq}} = \frac{A_t}{V_t} k_R s \left( \frac{1 \text{ m}^3 \text{ bulk}}{10^3 \text{ L bulk}} \right).$$

where the unit conversion is necessary as the reference volume for concentration is liters, while area reference $m^2$. Also

$$k_R = k_R^{mb} \left( 1 - \frac{c_{Si}}{c_{Si:eq}} \right).$$

In the expressions above, $c_{Si}$ is the concentration of silicic acid (that is, $c_{H_4SiO_4}$ in molarity), $k_R^{mb}$ and $k_R$ have units of mol $m^{-2}$ $s^{-1}$, $A_t$ is the surface area between the solid and fluid phases (with units of $m^2$), $c_{Si:eq}$ is the temperature-dependent concentration of silicic acid in equilibrium with quartz, and $V_t$ is the fluid volume in units of $m^3$. The actual silicic acid concentration is found from the “total” concentration of silicic acid by inverting a nonlinear system at each computational node and time step via a Newton-Raphson procedure.

For a partially occluded spherical close pack of grains, with a close pack radius initialized as $R_0$, we allow overgrowth of the grains in the direction of the holes in the structure to an effective radius $R_N$. We correct the surface area to fluid volume ratio for the volumes and areas occluded during growth. The porosity may also be calculated analytically. The change of particle radii with time is

$$\frac{\partial R_N}{\partial t} = -\nabla q_A k_s A,$$

where $k_s$ is defined above, $\nabla q_A$ is the molar volume [in $m^3$ of quartz/mol], and $A_s$ is unity. After a statistically stationary state was achieved, the term $A_s$ on the right-hand side of this equation was increased to typically 1000, as further discussed in app. B (A_s is an “acceleration” factor to move forward in time more rapidly). We used the Kozeny-Carman equation (see Bear, 1972, p. 165-166) as the permeability/porosity relation, which for our close pack model becomes

$$k = \frac{(R_0^3)^2}{45} \left( \frac{\phi^2}{(1 - \phi)^2} \right).$$

An alternative grain model is described in app. C.

The heat equation has a form similar to the solute equations, involving advection, diffusion, and sources. We have

$$\frac{\partial}{\partial t} \left[ (\rho c_p)_b T + \nabla \cdot [q T (\rho c_p)_f] \right] = \nabla \cdot [k_b \nabla T] + Q_b,$$

where $T$ is temperature in Kelvin ($K$), $\rho$ is the density [in kg/m$^3$ of the relevant phase], $c_p$ is the heat capacity at constant pressure [in J/kg/K, where $J$ is Joules], $\lambda$ is the thermal conductivity [in (kg m)/s$^3$/K], and $Q_b$ is the bulk rate of heat production in the matrix [in J/s/m$^3$], but the minor heat production was ignored in the present simulations. The bulk averages are calculated from

$$\lambda_b = (1 - \phi) \lambda_s + \phi \lambda_f$$

$$\rho c_p)_b = (1 - \phi) (\rho c_p)_s + \phi (\rho c_p)_f$$

where the subscript $b$ indicates the bulk matrix average, which includes both the fluid and solid phases, the subscript $s$ indicates the solid phase, and the subscript $f$ indicates the fluid phase. Under the assumption that
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\( (pcp)_\alpha, (pcp)_\beta \) and \( \lambda_b \) are constant and that \( Q_b \) is negligible (as assumed in this study), we may write

\[
\frac{\partial T}{\partial t} + \frac{1}{\sigma} \nabla \cdot [qT] = \lambda^* \nabla^2 T
\]

(AA-10)

where \( \sigma = (pcp)_\alpha/(pcp)_\beta \) and the thermal diffusivity \( \lambda^* = \lambda_\alpha/(pcp)_\beta \). An important fact about porous media convection for the parameter values considered in this paper arises from the difference in where \( \phi \) appears in the solute equation and the heat equation. This leads to the fact that the propagation rate of a thermal pulse generally lags the propagation rate of a pulse of solute concentration, owing to the thermal inertia of the medium and to the fact that the solute only travels in the pores.

For an immobile, constant density solid phase, conservation of mass is represented by

\[
\frac{\partial}{\partial t} [\rho s \phi] + \nabla \cdot [\rho s \mathbf{q}] = \Gamma = \rho_s \frac{\partial \phi}{\partial t}
\]

(AA-11)

where \( \rho_s \) is the density of the solid phase, and \( \Gamma \) is the rate of mass transfer from the solid to the fluid. For nearly incompressible fluids, the long-term changes in relative porosity may be larger than the long-term changes in fluid density. This implies that

\[
\nabla \cdot \mathbf{q} = \frac{\rho_s}{\rho_s} - 1 \frac{\partial \phi}{\partial t}
\]

(AA-12)

The fluid flow for a fluid-saturated porous media can be represented by Darcy’s law:

\[
\mathbf{q} = \frac{1}{\mu} \mathbf{k} \cdot (\nabla P + \rho \mathbf{g} \hat{k})
\]

(AA-13)

where the gravitational acceleration \( g \) is downward (in m/s\(^2\)), \( \hat{k} \) is the vertical unit vector (upward and non-dimensional), \( \mathbf{k} \) is the intrinsic permeability tensor (in m\(^2\)), \( \mu \) is the dynamic viscosity of the fluid (in kg/m/s), and \( P \) is pressure (in kg/m/s\(^2\)). In this study we assume that \( \mathbf{k} \) is isotropic, yet heterogeneous. We may then replace \( \mathbf{k} \) by \( \hat{k} \) and still have spatially and temporally dependent permeability. For flow in two dimensions (in the x–z plane), with mass exchange between the solid and fluid phases, we may decompose the Darcy velocity into two components: \( \psi \) the stream function, and \( \psi_\beta \) a velocity potential. Thus

\[
\mathbf{q} = \mathbf{q}_s + \mathbf{q}_\beta
\]

(AA-14)

with \( \mathbf{q}_s = \nabla \times (\hat{j} \psi) \) and \( \mathbf{q}_\beta = \nabla \psi \), yielding

\[
\mathbf{q} = \{\psi_\beta - \psi_s, 0, \psi_\beta + \psi_s\}
\]

(AA-15)

where \( \hat{j} \) is the unit vector perpendicular to the plane of fluid flow, \( \times \) denotes a cross product, and the subscripts \( x \) and \( z \) represent partial derivatives. The part of the flow dependent upon the stream function \( \mathbf{q}_s = \nabla \times (\hat{j} \psi) \) accounts for the solenoidal (divergence free) part of the velocity field. This part also naturally accounts for any vorticity production in the flow induced by buoyancy or heterogeneous permeability. The remaining part \( \mathbf{q}_\beta = \nabla \psi \) accounts for mass exchange between the solid and fluid phases. Conservation of mass then implies (by AA-12)

\[
\nabla \psi = \left[\frac{\rho_s}{\rho_s} - 1\right] \frac{\partial \phi}{\partial t}
\]

(AA-16)

Given \( \partial \phi/\partial t \) (from the kinetic and porosity/grain-size formulations), this equation may be solved for \( \psi \). Darcy’s law also implies

\[
\nabla \psi + \frac{\gamma_\beta}{\gamma} (\psi - \psi_s) + \frac{\gamma_\beta}{\gamma} (\psi_\beta + \psi_s) = -\frac{g}{\gamma} \frac{\partial \psi_\beta}{\partial x}
\]

(AA-17)

with \( \gamma = \mu/k \), and \( \psi \) is known from the decoupled mass conservation equation. For slow changes in porosity (for these simulations solid mass changes contributed less that 0.005 percent to the imposed injection
velocities), the above equation may be further simplified by neglecting $\partial//$, which we have done for the simulations presented in this paper. In this limit we have

$$\nabla^2 \psi + \frac{\gamma_r}{\gamma} \psi_s + \frac{\gamma_s}{\gamma} \psi_u = -\frac{\sigma \delta\ell_s}{\gamma \partial x}$$  \hspace{1cm} \text{(AA-18)}$$

In the plots of the streamlines (constant values of the stream function) the velocities are tangents to the streamlines at any instant (this is strictly true in the plots with no vertical exaggeration and of course we assume here that the velocity field is solenoidal).

In our calculations we use a simple linear equation of state for water:

$$\rho_l = \rho_0 (1 - \alpha (T - T_0) + \beta (S - S_0))$$  \hspace{1cm} \text{(AA-19)}$$

where $\alpha$ is the thermal expansion coefficient, $\beta$ represents the effect of solutes on the density, $S$ is the sum of the concentrations of $\text{H}_2\text{SiO}_4$ and $\text{H}_3\text{SiO}_4$, and the "o" subscript denotes a reference state. The reference states are $\rho_0 = 1000 \text{ kg/m}^3$, $T_0 = 298 \text{ K}$, and $S_0 = 0$. In this paper we used the temperature-dependent viscosity [from Bruges, Latto, and Ray, 1966]. The pressure dependence of material properties has been ignored in this study.

The stream function equation has the general form of a Poisson equation, which we solved with a spectral-transform method [compare Christensen and Harder, 1991]. The momentum equation was solved only each 5 or 10 time steps, depending on the flow regime and the size of the Courant number for solute advection. The solute and heat equations have similar forms, for which we found a third-order upwinding scheme to behave satisfactorily, and only moderate overshoots are apparent in the front propagation tests. The results presented here have been computed with third-order upwinding [from Leonard, 1984], adapted to two dimensions. No advection scheme is without disadvantages. Aside from inaccuracies associated with sharp front propagation, all schemes have some degree of anisotropy in that pulses are propagated differently when flow is parallel with the grid direction as opposed to when the flow is at a diagonal angle with respect to the grid. We have recently developed a particle tracking (Lagrangian) method with curvature corrections that nicely solves the anisotropy problem, but this scheme is not sufficiently optimized for efficient use in large-scale simulations. The source term (from the kinetics) in the solute equation is treated implicitly, with the integrals of the source contribution estimated from values at the beginning and end of each time step. The implicit nature of this formulation adds another layer of nonlinear equations to solve at every node and time step (using a secant method), but an overall speedup of about a factor of 5 was achieved.

### APPENDIX B

**On the use of accelerated porosity changes**

If the rate of change of the porosity is slow in some appropriate sense, the long-term changes of the porosity field can be calculated approximately by using an "acceleration factor" $A_r > 1$ [compare eq AA-5]. Extreme care must be taken when using such a procedure, and the results must be thoroughly tested. Lichtner (1988, 1991) described the quasi-stationary state (QSS) approximation in detail. Our use of an acceleration factor is similar to but distinct from this approximation. The partial time derivative of the solute concentration is dropped from the solute equation in the QSS approximation, whereas we instead simply accelerate the rate of change of porosity. The QSS approximation requires that reaction zone boundaries, surface areas, porosities, and permeabilities change slowly compared to the time required to establish a stationary state. Lichtner analyzed this approximation for dilute solutions in isothermal porosities, and permeabilities change slowly compared to the time required to establish a stationary state. Near zone (A), there are regions of saturation state reversals during the cycle where the net change in porosity is smaller than the total variation over a cycle. Throughout the domain, the net porosity change over ten cycles is extremely close to ten times the net change over one cycle. We exploit this fact by using $A_r > 1$. 

...
feedback in a porous medium with heterogeneous permeability

We must test the use of large acceleration factors (\(A_c \gg 1\)) by comparing to some standard which had smaller \(A_c\) or a standard with \(A_c = 1\) (that is, full integration of the system without acceleration). We applied various norms that compared the porosity change of a test case (with large \(A_c\)) to that of a standard case. Norms can be based on pointwise comparisons, spatial averages, or some combination of these. We also wish to utilize a norm that is relatively insensitive to the length of time of the integration. This is accomplished by norms formed by a ratio of the form:

\[
 f_1 \left( \frac{\Delta \phi_{\text{test}}}{\Delta \phi_{\text{std}}} \right)
\]

where \(f_1\) and \(f_2\) are functional operators to be chosen, \(\Delta \phi_{\text{test}} = \phi_{\text{test}} - \phi_{\text{init}}\), \(\Delta \phi_{\text{std}} = \phi_{\text{std}} - \phi_{\text{init}}\), \(\phi_{\text{init}}\) is the porosity of the test case at the end of an integration, \(\phi_{\text{std}}\) is the porosity of the standard case at the end of an integration, and \(\phi_{\text{init}}\) is the initial porosity at the beginning of an integration. Given some time step \(\Delta t\), equal for both the standard and test cases, and by starting both cases with the same initial conditions, equivalent final times of the test and standard runs are achieved by adjusting the number of time steps. The effective elapsed time of a simulation is \(t_{\text{final}} - t_{\text{initial}} = N(\Delta t)A_c\), where \(N\) is the number of time steps. Equivalent final times require \(N_{\text{test}}A_c: test = N_{\text{std}}A_c: std\).

We examined several choices for \(f_1(\Delta \phi_{\text{test}})\), including \(\text{avg}(\text{abs}(\Delta \phi_{\text{test}}))\), \(\text{max}(\text{abs}(\Delta \phi_{\text{test}}))\), and \(\Delta \phi_{\text{test}}\) itself. The latter choice has the disadvantage of taking small values near saturation state reversals (\(\Delta \phi_{\text{test}}\) is a function of space) and leads to divergent norms. In the above, \(\text{avg}\) denotes a spatial average, \(\text{abs}\) denotes a local absolute value, and \(\text{max}\) denotes the maximum value over the domain. The norm with \(f_2(\Delta \phi_{\text{test}})\) as \(\text{avg}(\text{abs}(\Delta \phi_{\text{test}}))\) is much more conservative than the max-abs norm, typically by a factor of 10. The choice of \(f_1\) can be made in a similar way. We let

\[
 P_1 = \frac{100 \times \Delta \phi_{\text{test}}}{\text{avg}(\text{abs}(\Delta \phi_{\text{test}}))}
\]

and

\[
 P_2 = \frac{100 \times \text{avg}(\text{abs}(\Delta \phi_{\text{test}}))}{\text{avg}(\text{abs}(\Delta \phi_{\text{std}}))}
\]

These norms have units of percent difference of the test versus the standard, compared to the change in the standard from the initial state. \(P_1\) is spatially dependent and very conservative. \(P_2\) reduces the spatial distribution to a single average value. For relatively small changes in \(A_c\), the norms scale as \(P \propto A_c^k\), where \(P\) is \(P_2\) or max (\(P_1\)). For very large \(A_c\) (>10000), the exponent \(k\) ranges from 0.5 to 1. As \(A_c\) drops below 5000, \(k\) ranges from 1 to 2, implying a more rapid drop in the norm as \(A_c\) is reduced.

All simulations indicated that it was very important to integrate in time well past the transient phase before using acceleration. For example, in simulation L2, use of \(A_c = 10000\) produced \(P_2 = 920\) percent for tests using acceleration during the transient phase. The same acceleration, applied after the transient phase, produced \(P_2 = 1.9\) percent. Use of \(A_c = 1000\) after the transient phase yielded \(P_2 = 0.1\) percent and max (\(P_1\)) = 0.7 percent.

Figure AB-1-A shows \(P_1\) for simulation L1, where the test case used \(A_c = 5000\) compared to a standard using \(A_c = 1000\). Certainly \(A_c = 5000\) is still too large. Most of the error is confined to the zone of lateral stalk migration near the lower boundary. The effective time span of each case was 630,000 yrs. Further testing must be done to elucidate the time scale of stalk migration. Such migration did not really begin until long into the simulation, after significant precipitation had occurred in zone (C).

Figure AB-1-B shows \(P_1\) for simulation L2, comparing an \(A_c = 1000\) test with a standard of \(A_c = 500\). This test covered an effective time of 80000 yrs. We feel that the max (\(P_1\)) = 0.7 percent with \(P_2 = 0.1\) percent implies that \(A_c = 1000\) is very acceptable everywhere. Figure AB-1-C shows \(P_1\) for simulation L3, comparing an \(A_c = 5000\) test with a standard of \(A_c = 1000\). This test covered an effective time of 400000 yrs, all after the transient phase. For this case, max (\(P_1\)) = 26 percent with \(P_2 = 2.4\) percent. The \(A_c = 5000\) factor was too large, but other results for \(A_c = 1000\) have been calculated to have max (\(P_1\)) < 2 percent.

Use of \(A_c > 1\) must be done with care. The transient phase must be avoided for such acceleration. Although the term “transient phase” should be made more precise, we simply waited long enough for the system to settle to a statistically stationary state. For simulation L1, we waited until after the end of the time encompassed by figure 4 before applying \(A_c > 1\). Acceptable levels of error are obtained with \(A_c = 1000\), even
Fig. AB-1. The spatial distribution of the norm $P_1$ as defined in app. B, for testing of the acceleration parameter $A_\alpha$. See app. B for details. (A) For simulation L1; (B) for simulation L2; (C) for simulation L3.
for the oscillatory zone (A) of simulation L1. With due caution, acceleration can significantly reduce the computational time necessary for long-term simulation of slowly evolving systems.

**APPENDIX C**

*Tube-edged cubic grain model*

The partially-occluded spherical close pack, used as the subgrid-scale grain model for simulations L1 to L6, is not valid for porosities lower than 0.036 (3.6 percent). In order to investigate lower porosities we chose tube-edged cubes as the “unit-cell” shape for “grains.” The basic shape is shown in figure AC-1. For a monomineralic matrix, a periodic extension of this shape (without space between “grains”) results in an array of square cross-section tubes in all three orthogonal directions. We call the basic unit of center to center grain separation $l$ and use $l = w$ for this formulation, where $w$ is the width of each “grain” (the distinction between $l$ and $w$ is retained here for comparison to a multimineralic grain model to be discussed in a future publication). The tube width is $\delta$ which results in $d = w - \delta$. To be usable as a grain model, we must have analytical representations for the factors important for modeling flow and kinetically controlled reactions, namely the porosity, the surface area per fluid volume, and the permeability.

It is convenient to choose a reference volume for the bulk (the bulk is the total volume occupied by both pores and solid) for which we use 1 m$^3$ and represent this by $V_b$, where the b subscript stands for the bulk. The number of grains in the reference volume is $\overline{N}$, where the overbar indicates that the quantity is normalized to the reference volume $V_b$. For a monomineralic system with $l$ being the distance between the grains (in meters), we have $\overline{N} = 1/l^3$. As mentioned above, we assume $w = l$. The volume per grain for this shape is

$$V_G = d^3 + 3d^2\delta$$  \hspace{1cm} (AC-1)
Note that our choice of the unit cell as shown in figure AC-1 is periodically continued in all three dimensions, and the protruding squares are on only three of the cubic faces rather than six. The fraction of the bulk occupied by solid is then \( \phi_s = \frac{\mathbf{N}}{V_f} \), while the porosity fraction is \( \phi = \phi_s = 1 - \phi_c \), where we have assumed a fluid saturated medium (the subscripts s and f stand for the solid and the fluid, respectively). This results in

\[
\phi = \frac{\phi_c^2}{(3/\gamma - 2d)} \tag{AC-2}
\]

which in the limit of low porosity tends toward \( 3\phi_c^2/\gamma^2 \). (Note that \( 3/\gamma - 2d = 3d + \delta \) and \( 3/\gamma - 2d = 3h + d \). As input to our code we specified \( \gamma \) and the initial \( \phi_c \) and solved eq AC-2 using Newton-Raphson iteration to calculate the initial \( d \) and \( \delta \). We assumed that \( \mathbf{N} \) and \( \gamma \) remain constant throughout the simulation, but \( \delta \) and \( d \) are allowed to vary via growth and dissolution. In order to preserve the basic shape of the “grain” in figure AC-1, we allowed dissolution or growth only on the reactive surfaces (shaded) affecting \( \phi \) and \( d \) (as opposed to allowing the flat portions of adjoining grains to change shape). Under this assumption, the area of mineral available for exchange with the fluid per fluid volume is

\[
A_c = \frac{6d}{\delta(3d + \delta)} \tag{AC-3}
\]

which in the low porosity limit tends toward \( 2/\delta \). Given these assumptions, the evolution of grain size can be calculated from

\[
\frac{d\phi_c}{dt} = -\nabla_k A_c \tag{AC-4}
\]

(compare to eq AA-5 for the spherical close pack). If all surfaces were allowed to dissolve, the basic unit grain shape would be different from what is shown in figure AC-1 (eroding into the flat surfaces of adjoining “grains”), and the above expression (eq AC-4) would need a factor of 2 on the right-hand side.

For tube-edged cubes, we calculated the permeability using

\[
k = \frac{\phi \delta^2}{36} \tag{AC-5}
\]

We also estimated what the actual permeability would be for square-section tubes and randomized orientations which yielded \( \sim 19 \) for the denominator rather than 36. Irregularities associated with variable throat apertures and increasing tortuosity tend to yield lower porosities, so the use of the larger denominator can be qualitatively justified for this grain model based on square-section throats. The factor of 36 has often been quoted for plane fractures. For this square cross-section case we simply used the more conservative value of 36. We have not incorporated a finite pinch-off porosity.

REFERENCES


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