

Chapter 11

Geochemical Kinetics and Transport

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11.1 Introduction

The kinetics of geochemical and biogeochemical processes can be studied in isolation in the laboratory, but only rarely is it possible to separate these processes from those of transport when considering their importance in natural systems at the field scale. This is because the driving force for most reactions of interest in water–rock interaction is transport. The most intense geochemical and biogeochemical activity occurs at the interface between global compartments like the oceans, the atmosphere, and the Earth’s crust where elemental and nutrient fluxes provide the maximum driving force for reactions to take place. The important role of transport in these settings makes it critical to consider these time-dependent processes in conjunction with those processes we think of as more purely biogeochemical. In other words, these global interfaces are *open systems*, where both mass and energy transfers must be accounted for.

For the sake of convenience, geochemical and biogeochemical kinetics are often studied in closed systems in the laboratory, but it is important to keep in mind how different the closed systems can be from open systems. In a closed system, the best analogue of which is the batch reactor in the laboratory (in its simplest form, just a laboratory beaker, Fig. 11.1a), the solution begins out of equilibrium initially and evolves over time towards either thermodynamic equilibrium, or to some other end point beyond which the reaction cannot proceed. Either equilibrium is achieved (where net reaction rates are, by definition, = 0), or rates become so slow that the system effectively no longer changes. In an open system, a good laboratory analogue of which is the continuously stirred tank reactor (CSTR) or well-mixed flowthrough reactor (Fig. 11.1b), the continuous injection of solution that is out of equilibrium (either with itself, or with a solid phase inside the reactor) causes the solution composition coming out of the reactor to reach a

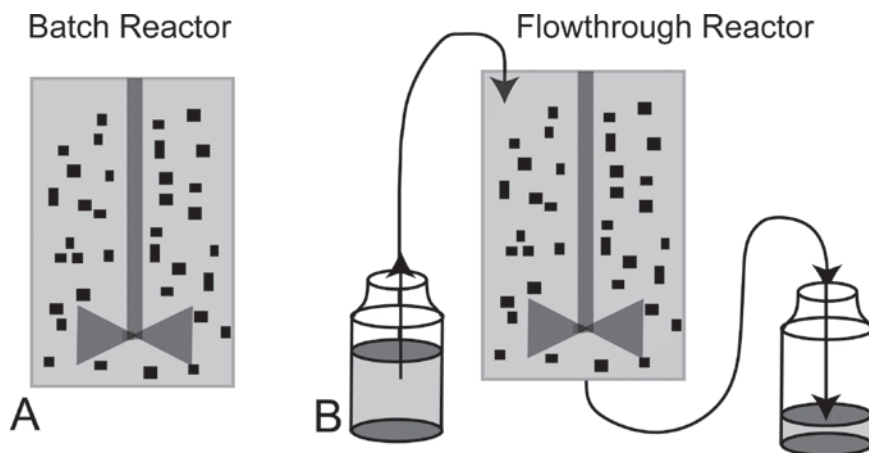


Fig. 11.1 Contrast between closed and open system behavior: **a.** In a laboratory batch reactor, the solution evolves from some initial state to a final equilibrium state, or one where the driving force for reaction disappears. **b.** In a continuously stirred tank reactor, the continuous injection of solution out of equilibrium with respect to the solid phases in the reactor results in steady-state conditions where solution and solids may remain out of equilibrium

steady state (Fig. 11.1b). If the residence time in the CSTR is long enough, equilibrium between the solution and solid phase may be achieved—otherwise, the solution and solid phase may remain some distance from equilibrium at steady state.

The characteristic residence and reaction times can be more formally compared in the case of a CSTR with a set of simple equations. Considering a dissolved species, we can define:

- t = time (s)
- M = mass of solute (g)
- Q = volumetric flow rate (cm^3/s)
- V = volume of reactor (cm^3)
- C = concentration of solute (g/cm^3)
- R = reaction rate (g/s),

where the concentration, volumetric flow rate, and reaction rate are defined respectively by

$$C = \frac{M}{V}, Q = \frac{V}{t}, \quad \text{and} \quad R = \frac{M}{t}. \quad (11.1)$$

The volumetric flow rate Q , therefore, can be thought of simply as the volume of fluid flowing through the reactor for a given time t . A mass balance equation for this system must account for the accumulation or loss of mass of the solute inside the reactor, the flux of the solute into and out of the reactor, and the loss or gain of the solute in the aqueous phase as a result of reaction (e.g., precipitation or dissolution).

The flux (mass per unit time) into the reactor is given by

$$J_{in} = \left[\frac{M}{V} \right]_{in} \left[\frac{V}{t} \right]_{in} = C_{in} Q_{in}, \quad (11.2)$$

while the flux out is given similarly by

$$J_{out} = \left[\frac{M}{V} \right]_{out} \left[\frac{V}{t} \right]_{out} = C_{out} Q_{out}, \quad (11.3)$$

leading to an overall mass balance for the aqueous phase in the reactor of

$$\frac{dM}{dt} = J_{in} - J_{out} - R = C_{in} Q_{in} - C_{out} Q_{out} - R, \quad (11.4)$$

where by convention R is taken as positive for precipitation, negative for dissolution. If the reaction rate is written as a first-order reaction with a rate k in units of s^{-1}

$$R = kCV, \quad (11.5)$$

then at steady state ($dM/dt = 0$) the reaction rate is equal to the difference between the flux in and the flux out of the reactor (i.e., the divergence of the flux)

$$R = kC_{out}V = C_{in}Q_{in} - C_{out}Q_{out}. \quad (11.6)$$

Assuming the flow in the reactor is steady (so $Q_{in} = Q_{out}$) and defining the residence time (or characteristic transport time) as

$$\tau_{res} = \frac{V}{Q}. \quad (11.7)$$

The characteristic time for reaction, τ_{react} , is given by

$$\tau_{react} = \frac{1}{k}. \quad (11.8)$$

The ratio of the characteristic residence and reaction times, then, is given by

$$\frac{\tau_{res}}{\tau_{react}} = \frac{kV}{Q} = \frac{(C_{in} - C_{out})}{C_{out}}. \quad (11.9)$$

In the case where the reactions drive the system towards some equilibrium state, it is clear that the approach to equilibrium has nothing to do with geologic time, but is controlled by the ratio of the characteristic residence (or transport) time and reaction time in the reactor.

11.2 Transport Processes

The continuously stirred tank reactor provides perhaps the simplest example where rates of transport can be compared to rates of reaction. But in porous and/or fractured media, reactions can be driven by a variety of transport processes. The most important of these transport processes are advection, molecular diffusion, and mechanical dispersion. Although widely neglected, electrochemical migration is a flux created by the diffusion of charged species at differing rates which may be important in some cases. Below, these transport processes are defined mathematically in terms of fluxes, that is, the amount of solute passing through a unit area per unit time.

11.2.1 Advection

Advection is the most straightforward of the transport processes, since it involves the translation in space of dissolved or suspended material at the rate of movement of the bulk fluid phase. No modification of the shape of a front and no dilution occurs when transport is purely via advection—a sharp front remains so when undergoing purely advective transport. The advective flux of a dissolved species in porous media can be described mathematically as

$$J_{adv} = \phi v C_i, \quad (11.10)$$

where ϕ is the porosity, v is the average linear velocity in the media, and C_i is the concentration of the i th species. In most (but not all) examples of water–rock interaction, flow is through a porous medium and is described with Darcy’s Law.

11.2.1.1 Darcy’s Law

The fluid velocity in porous and fractured media is usually calculated from Darcy’s Law, which states that the volumetric flux of water ($\text{m}^3_{\text{fluid}}/\text{m}^2_{\text{medium}}/\text{s}$), $\mathbf{q}$, is a vector proportional to the gradient in the hydraulic head, h

$$\mathbf{q} = \phi \mathbf{v} = -\mathbf{K} \nabla h = -K_x \frac{\partial h}{\partial x} - K_y \frac{\partial h}{\partial y} - K_z \frac{\partial h}{\partial z}, \quad (11.11)$$

where $\mathbf{K}$ is the hydraulic conductivity (here a second-order tensor) in units of m/s (Darcy, 1856). One can also write Darcy’s Law in terms of fluid pressure by defining the hydraulic head as

$$h = z + \frac{P}{\rho g}, \quad (11.12)$$

Table 11.1 Range of values of hydraulic conductivity and permeability (Modified from Bear, 1972. Additional information from Wikipedia, 2006)

K (cm/s)	10 ²	10 ¹	10 ⁰	10 ⁻¹	10 ⁻²	10 ⁻³	10 ⁻⁴	10 ⁻⁵	10 ⁻⁶	10 ⁻⁷	10 ⁻⁸	10 ⁻⁹	10 ⁻¹⁰
K (cm ²)	10 ⁻³	10 ⁻⁴	10 ⁻⁵	10 ⁻⁶	10 ⁻⁷	10 ⁻⁸	10 ⁻⁹	10 ⁻¹⁰	10 ⁻¹¹	10 ⁻¹²	10 ⁻¹³	10 ⁻¹⁴	10 ⁻¹⁵
Unconsolidated sand gravel	Clean gravel		Clean sand or sand and gravel			Very fine sand, silt, loess, loam							
Unconsolidated clay and organic					Peat		Stratified clay			Unweathered clay			
Consolidated rocks	Highly fractured rocks				Oil reservoir rocks			Sandstone		Limestone			Granite

where z is the depth, P is the fluid pressure, ρ is the fluid density, and g is the acceleration due to gravity. The hydraulic conductivity is defined as

$$\mathbf{K} = \frac{\kappa \rho g}{\mu}, \quad (11.13)$$

where κ is the permeability and μ is the dynamic viscosity. One can also write Darcy's law explicitly in terms of the fluid pressure, permeability, and the viscosity

$$\mathbf{q} = \phi \mathbf{v} = -\frac{\kappa_r \kappa}{\mu} [\nabla P - \rho \mathbf{g}]. \quad (11.14)$$

In this case, we have also added the relative permeability, κ_r , which is equal to 1 under fully saturated conditions and is less than 1 under partially saturated conditions. Darcy's Law is applied where the porous medium can be treated as a continuum in which a representative elementary volume (REV) is significantly larger than the average grain size. In the case of flow at the pore-scale, the averaging does not apply and Darcy's Law cannot be used. Representative values of the hydraulic conductivity (or permeability) are given in Table 11.1 for various subsurface materials.

11.2.2 Molecular Diffusion

Molecular diffusion as a transport process in water-rock interaction has been relatively neglected. This may be partly due to the fact that much of the transport theory has been brought over from hydrogeology, where the medium of interest is often relatively permeable aquifers in which advection is much more important than diffusion. In water-rock interaction, however, we are often concerned with transport through low porosity and permeability material, in which case molecular diffusion needs to be considered carefully. The treatment of molecular diffusion has also suffered to some extent from the assumption that Fick's First Law (described below) is sufficient, but as shown below, this is *true only in the case of diffusion of uncharged species in dilute solutions*. A more general formulation relates the diffusive flux linearly to gradients in the *chemical potential rather than concentration*, but we

begin with the simpler Fickian description of diffusion so as to follow its historical presentation.

11.2.2.1 Fick’s First Law

Molecular diffusion is usually described in terms of Fick’s First Law, which states that the diffusive flux (here shown for only a single coordinate direction x) is proportional to the concentration gradient

$$J_i = -D_i \frac{\partial C_i}{\partial x}.$$

(11.15)

D_i is referred to as the diffusion coefficient and is specific to the chemical component considered as indicated by the subscript i . Fick’s First Law is a phenomenological theory for diffusion that relates diffusion to the “driving force” provided by the concentration gradient, although it can also be derived atomistically (Lasaga, 1998). In the case of diffusion in porous media, it is normally necessary to include a tortuosity correction as well (see Sect. 9.2.2.5). Values of diffusion coefficients for selected ion at infinite dilution in water at 25°C are given in Table 11.2.

Table 11.2 Tracer diffusion coefficients of ions at infinite dilution in water at 25°C. (Modified from Lasaga, 1998)

Cation	$D_i \times 10^5 \text{ cm}^2/\text{s}$	Anion	$D_i \times 10^5 \text{ cm}^2/\text{s}$
H ⁺	9.31	OH [−]	5.27
Li ⁺	1.03	F [−]	1.46
Na ⁺	1.33	Cl [−]	2.03
K ⁺	1.96	Br [−]	2.01
Rb ⁺	2.06	I [−]	2.00
Cs ⁺	2.07	IO ₃ [−]	1.06
NH ₄ ⁺	1.98	HS [−]	1.73
Ag ⁺	1.66	HSO ₄ [−]	1.33
Mg ²⁺	0.705	NO ₂ [−]	1.91
Ca ²⁺	0.793	NO ₃ [−]	1.90
Sr ²⁺	0.794	HCO ₃ [−]	1.18
Ba ²⁺	0.848	H ₂ PO ₄ [−]	0.846
Mn ²⁺	0.688	H ₂ AsO ₄ [−]	0.905
Fe ²⁺	0.719	H ₂ SbO ₄ [−]	0.825
Co ²⁺	0.699	SO ₄ ^{2−}	1.07
Ni ²⁺	0.679	SeO ₄ ^{2−}	0.946
Cu ²⁺	0.733	CO ₃ ^{2−}	0.955
Zn ²⁺	0.715	HPO ₄ ^{2−}	0.734
Cd ²⁺	0.717	CrO ₄ ^{2−}	1.12
Pb ²⁺	0.945	MoO ₄ ^{2−}	0.991
UO ₂ ²⁺	0.426	PO ₄ ^{3−}	0.612
Cr ³⁺	0.594		
Fe ³⁺	0.607		
Al ³⁺	0.559		

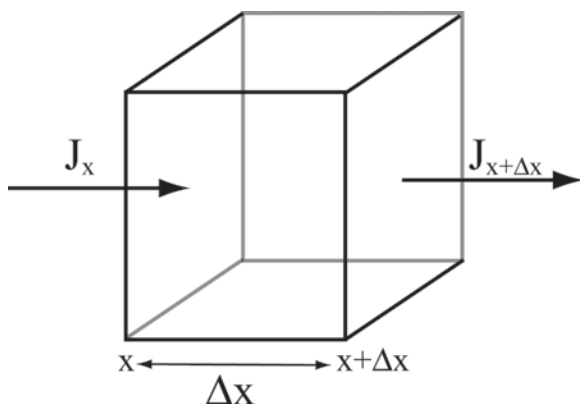


Fig. 11.2 Derivation of a continuity equation (Fick's Second Law)

11.2.2.2 Fick's Second Law

Integrating the diffusive fluxes over a control volume leads to Fick's Second Law, which is just one of many continuity equations in use (Bear, 1972; Lasaga, 1998). By defining the fluxes at the faces of an elemental volume as in Fig. 11.2 (here shown for only a single coordinate direction x) a general form of the continuity equation can be derived by considering the change in concentration inside an elemental volume for a given time increment (analogous to the flowthrough reactor described in Eq. (11.4)):

$$\frac{dC}{dt} = \frac{1}{\Delta x} [J_x - J_{x+\Delta x}] = -\frac{1}{\Delta x} [J_{x+\Delta x} - J_x]. \quad (11.16)$$

Written as a partial derivative as Δx and $\Delta t \rightarrow 0$, and substituting Fick's First Law (Eq. (11.15)), Eq. (11.16) becomes

$$\frac{\partial C_i}{\partial t} = -\frac{\partial}{\partial x} [J_i] = \frac{\partial}{\partial x} \left[D_i \frac{\partial C_i}{\partial x} \right], \quad (11.17)$$

which provides an expression for the change in concentration in terms of the divergence of the diffusive flux.

Integration of Eq. (11.17) provides a solution for the time and space evolution of the concentration field. This equation is quite straightforward to integrate numerically, but analytical solutions are also available, with the general form

$$C(x, t) = A + B \operatorname{erf} \left[\frac{x}{2\sqrt{Dt}} \right], \quad (11.18)$$

where A and B are constants that depend on the initial and boundary conditions. For the case where the initial mass is located between $-h$ and h , with concentrations

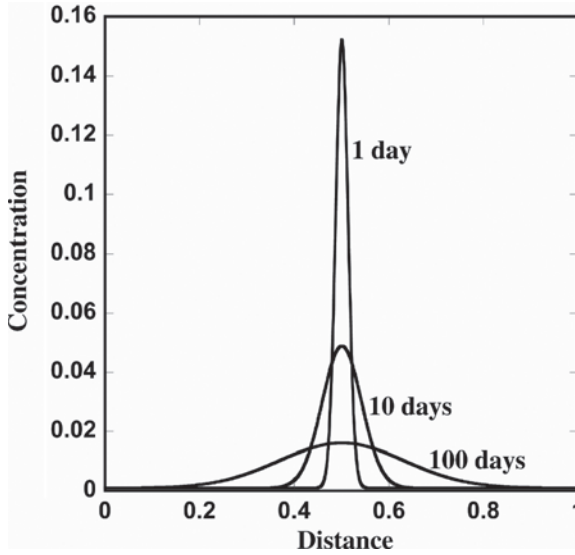


Fig. 11.3 Spreading of an initially sharp solute plume as a result of molecular diffusion

equal to zero elsewhere, the analytical solution is given by

$$C(x,t) = \frac{1}{2}C_0 \left[\operatorname{erf} \left(\frac{x+h}{2\sqrt{Dt}} \right) - \operatorname{erf} \left(\frac{x-h}{2\sqrt{Dt}} \right) \right], \quad (11.19)$$

where erf is the error function and C_0 is the initial concentration between $-h$ and h (Lasaga, 1998). Figure 11.3 shows the evolution of such an initially narrow and sharp zone with time as a result of molecular diffusion.

11.2.2.3 Electrochemical Migration

Fick's First Law is strictly applicable only in the case of an infinitely dilute solution with uncharged chemical species. In electrochemical systems or systems containing charged species, it is also necessary to consider the process of electrochemical migration. Strictly speaking, this should be considered as a separate flux on the same level as advection and diffusion, but in most systems of interest in the Earth sciences, this effect is related to diffusion of charged species. The full expression for the migration of a charged species in an electric field (written again in terms of a single coordinate direction, x , for the sake of simplicity) is given by (Newman, 1991)

$$J_i^{migr} = -z_i u_i F C_i \frac{\partial \Phi}{\partial x}, \quad (11.20)$$

where z_i is the charge of the species, u_i is its mobility, F is Faraday's constant ($= 96,487$ C/equivalent), and Φ is the electrical potential. The mobility refers to the

average velocity of a species in solution acted upon by a unit force, independent of the origin of the force. The flux of charged species in an electric field gives rise to a current, which can be expressed as

$$i = F \sum_i z_i J_i, \quad (11.21)$$

where i is the current density in units of amperes per m^2 . Expanding Eq. (11.21) in terms of the migration term (Eq. (11.20)) and the diffusive flux (Eq. (11.15)), the current density can be written as

$$i = -F^2 \frac{\partial \Phi}{\partial x} \sum_i z_i^2 u_i C_i - F \sum_i z_i D_i \frac{\partial C_i}{\partial x}. \quad (11.22)$$

Where no concentration gradients are present, the current is given by the first term on the right hand side

$$i = -\kappa_e \frac{\partial \Phi}{\partial x} \quad (11.23)$$

where

$$\kappa_e = F^2 \sum_i z_i^2 u_i C_i \quad (11.24)$$

is the conductivity of the solution. Note that using Eq. (11.24), it is possible to determine the mobility of an ion by measuring the conductivity of a solution. The mobility in turn can be used to determine the diffusion coefficient for an ion from the Nernst-Einstein equation (Lasaga, 1998; Newman, 1991)

$$D_i = RT u_i, \quad (11.25)$$

where R is the gas constant and T is the temperature on the Kelvin scale. Rearranging Eq. (11.22) to obtain an expression for the gradient in the electrical potential

$$\frac{\partial \Phi}{\partial x} = -\frac{i}{\kappa_e} - \frac{F}{\kappa_e} \sum_i z_i D_i \frac{\partial C_i}{\partial x}, \quad (11.26)$$

it is apparent that even in the absence of an electrical current, i , it is possible to have a gradient in the electrical potential as a result of concentration gradients of charged species. The second term on the right hand side of Eq. (11.26) is known as the diffusion potential, which vanishes when all of the diffusion coefficients for the charged species are the same. To proceed further, it is useful to define the fraction of the current carried by a species j (or the transference number)

$$t_j = \frac{z_j^2 u_j C_j}{\sum_i z_i^2 u_i C_i}, \quad (11.27)$$

which can be used along with the substitution of Eqs. (11.26) and (11.24) into Eq. (11.20) to obtain an expression for the migration flux

$$J_j^{migr} = \frac{t_j i}{z_j F} + \frac{t_j}{z_j} \sum z_i D_i \frac{\partial C_i}{\partial x}. \quad (11.28)$$

This equation (still only strictly applicable to relatively dilute solutions) can be used to describe the case where an electrical current is present (e.g., an electrochemical cell), although more commonly in water–rock interaction one encounters only the second term. It should be noted that even in the absence of a current, the diffusion of charged species are coupled through the diffusion potential in the case where diffusion coefficients differ (Newman, 1991).

In the absence of a current and advection, the total flux (combining Fickian diffusion and electrochemical migration) is then given by

$$J_i = -D_i \frac{\partial C_i}{\partial x} + \frac{t_j}{z_j} \sum z_i D_i \frac{\partial C_i}{\partial x}. \quad (11.29)$$

As noted above, the second term vanishes when all of the diffusion coefficients for the charged species are the same, but since this is in general not the case, this term should normally be retained along with the first term. Note also that the effect of electrochemical migration may be important (and perhaps even more important, as discussed below) in dilute systems.

Although widely neglected in quantitative studies of water–rock interaction, electrochemical migration has several important consequences. Inclusion of electrochemical migration prevents the unrealistic build up of charge in calculations using differing diffusivities for charged species. The typical way to avoid this problem in transport calculations is to use the same diffusion coefficient for all of the charged species, in which case the diffusion potential driving electrochemical migration disappears. However, this approach does not provide the same results as would a full treatment of electrochemical migration. An example illustrating some of the potential effects is shown in Fig. 11.4, where a fixed boundary condition on the left side is separated by 20 mm of 10% porosity material from a reacting feldspar (albite) grain. At 25°C, the dissolution rate of feldspar is sufficiently slow that concentration gradients will not develop (Murphy et al., 1989). At higher temperatures where the rate of surface reaction is more rapid, however, it is possible to develop diffusion-limited dissolution (the rate of surface reactions is significantly faster than the rate at which ions can diffuse across the 20 mm distance, and thus a gradient develops). Comparison of the full multicomponent diffusion and electrochemical migration calculation with one based on identical diffusion coefficients (no electrochemical migration) for all species indicates that conservative quantities like alkalinity need not have linear profiles where electrochemical migration is important. Comparing the two cases with identical albite dissolution rates, the concentrations of dissolved species next to the albite grain are not even the same. This is primarily due to the rapid diffusion of hydrogen ion, which results in a more nearly linear profile for pH

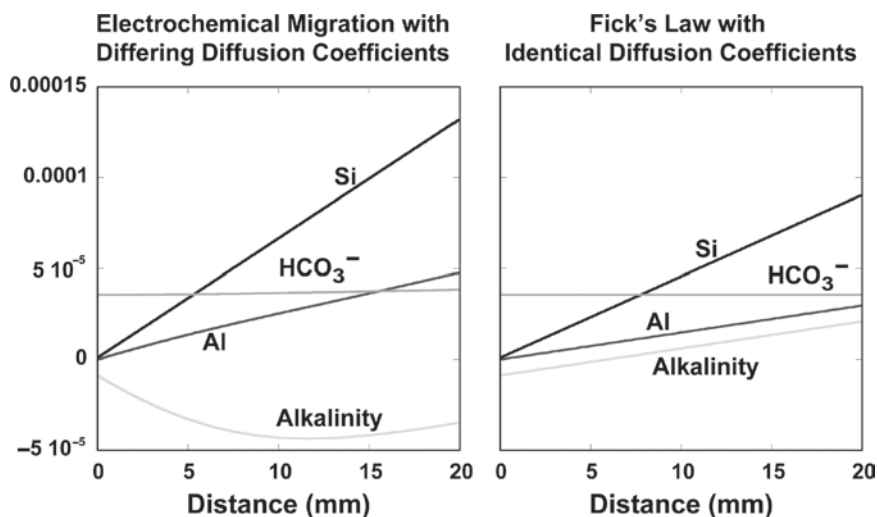


Fig. 11.4 Comparison of diffusion profiles in the case of a dilute, mildly acidic solution (pH 4) on the left reacting with an albite grain located 2 cm to the right. The left panel shows a calculation using differing diffusion coefficients for the ions (see Table 11.2) and includes electrochemical migration. The right panel shows a calculation in which identical diffusion coefficients for all species are used – in this case, electrochemical migration vanishes and diffusion occurs according to Fick's Law. Note the curvature of the alkalinity profile in the case where electrochemical migration and differing diffusion coefficients are used and the difference in concentrations of the various species immediately adjacent to the albite grain in the two cases

in the multicomponent diffusion/electrochemical migration case as compared to the identical diffusion coefficient case.

11.2.2.4 Diffusion in Concentrated Solutions

Fick's First Law runs into additional difficulties in concentrated aqueous solutions. A more rigorous and general expression is given by

$$J_j^{diff} = -L_{ji} \frac{\partial \mu_j}{\partial x}, \quad (11.30)$$

where the L_{ij} are the phenomenological coefficients introduced in the theory of irreversible thermodynamics (Lasaga, 1998; Onsager, 1931; Prigogine, 1967) and μ_j is the chemical potential of the j th species. Here, the fluxes are linearly related to gradients in the chemical potentials of the solutes rather than to their concentrations as in Fick's Law. The phenomenological coefficients, L_{ij} , can be linked back to measurable quantities by making use of the mobility again as the "velocity" of a particle acted upon by a force, with the force in this case provided by the chemical

potential rather than the concentration

$$J_j^{diff} = -u_j C_j \frac{\partial \mu_j}{\partial x}. \quad (11.31)$$

In the case where a gradient in chemical potential rather than concentration is used, the migration flux (compare to Eq. (11.28) in the absence of a current) becomes

$$J_j^{migr} = \frac{t_j}{z_j} \sum_i z_i D_i \frac{\partial \mu_i}{\partial x}. \quad (11.32)$$

By writing the chemical potential as (Denbigh, 1981)

$$\mu_j = \mu_j^0 + RT \ln(\gamma_j C_j), \quad (11.33)$$

where γ_j is the activity coefficient for the species, and differentiating with respect to x , we obtain the following combined expression for the pure diffusive flux and electrochemical migration by making use again of the definition of the ion mobility (Eq. (11.25))

$$J_j = -D_j \frac{\partial C_j}{\partial x} - D_j C_j \frac{\partial \ln \gamma_j}{\partial x} + \frac{t_j}{z_j} \sum_i z_i D_i \frac{\partial C_i}{\partial x} + \frac{t_j}{z_j} \sum_i z_i D_i \frac{\partial \gamma_i}{\partial x}. \quad (11.34)$$

This more general expression, which reduces to Eq. (11.29) where gradients in activity coefficients are negligible (for example, for diffusion of a trace species in a strong electrolyte), makes clear that both the diffusive and electrochemical migration fluxes can depend on the activity coefficients for the species. If gradients in one or more activity coefficients are negative, it is possible for “uphill diffusion”, in which a species diffuses up its own concentration gradient, to occur (Lasaga, 1998).

11.2.2.5 Tortuosity

Since water–rock interaction commonly takes place in porous materials, it is important to account for the effect of tortuosity (Fig. 11.5), which is defined as the ratio of the path length the solute would follow in water alone, L , relative to the tortuous path length it would follow in porous media, L_e (Bear, 1972)

$$T_L = (L/L_e)^2. \quad (11.35)$$

In this definition of tortuosity (sometimes the inverse of Eq. (11.35) is used), its value is always < 1 and the effective diffusion coefficient in porous media is obtained by multiplying the tortuosity by the diffusion coefficient for the solute in pure water. With this formulation, the diffusion coefficient in porous media is given by

$$D_i^* = T_L D_i. \quad (11.36)$$

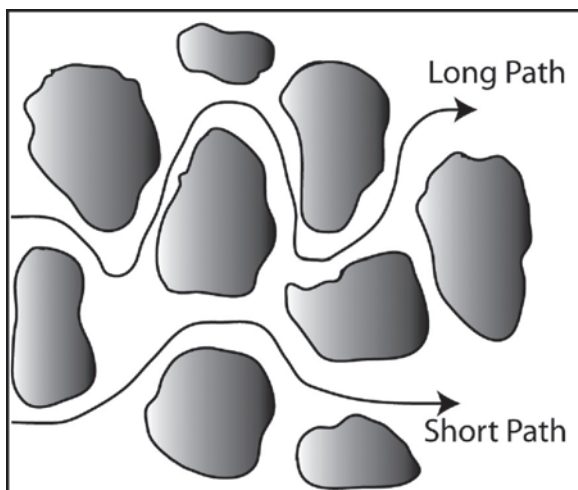


Fig. 11.5 Tortuous diffusion paths in porous material

The diffusive flux, then, is given by

$$J_i^{diff} = -\phi D_i T_L \frac{\partial C_i}{\partial x} = -\phi D_i^* \frac{\partial C_i}{\partial x}. \quad (11.37)$$

An alternative formulation for the coefficient for molecular diffusion in porous media is given by the formation factor, F , defined as (Bear, 1972)

$$F = (L_e/L)^2 / \phi = 1/\phi T_L, \quad (11.38)$$

in which case the diffusive flux in porous media becomes

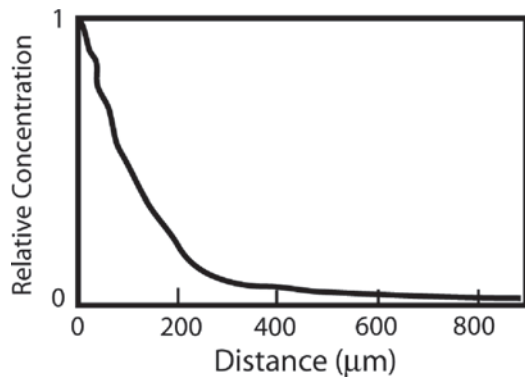
$$J_i^{diff} = -\frac{D_i}{F} \frac{\partial C_i}{\partial x}. \quad (11.39)$$

Various approaches for calculating formation factors (and thus, the diffusion coefficient in porous medium) are in use, with a formulation based on Archie's Law being the most common

$$F = \frac{1}{a\phi^m}, \quad (11.40)$$

where a is a fitted constant and m is the cementation exponent. Values of $a = 0.71$ and $m = 1.57$ have been suggested for unfractured granite (Pharmamenko, 1967), although values of $m = 2$ have been reported for many more porous and permeable subsurface materials (Oelkers, 1996). Values for the formation factor in igneous intrusive rock in Sweden range from 10^3 to 10^7 (Skagius and Neretnieks, 1986). In the case of low porosity materials, especially those with poor pore connectivity, the formation factor may be quite large (and thus, the diffusion coefficient in porous

Fig. 11.6 Profile of bromide front in low porosity (3%–5%) basalt after 35 days as imaged with μ -X-ray fluorescence at the Advanced Light Source at the Lawrence Berkeley National Laboratory. Numerical modeling to match the diffusion profile indicated a formation factor of approximately 2×10^6 . Sample courtesy of Alexis Navarre-Sitchler



media quite small). Values as high as 2×10^6 were determined using μ -X-ray fluorescence mapping of bromide tracer fronts in low porosity (3%–5%) basalt from Costa Rica at the Advanced Light Source at the Lawrence Berkeley National Laboratory (Fig. 11.6). Such an extremely low formation factor, combined with an only moderately low porosity, suggests the use of a percolation/diffusion threshold model in place of Archie's Law.

11.2.3 Hydrodynamic Dispersion

The phenomenon of hydrodynamic dispersion was noted as early as 1905 when Slichter reported that the concentration of an electrolyte monitored in an aquifer downstream of an injection point increased only gradually, with the plume shape becoming longer and wider as it advanced (Slichter, 1905). The spreading of the solute mass as a result of dispersion is a diffusion-like process that has led to the use of Fick's First Law to describe the process in one dimension as

$$J_i^{disp} = -D_h \frac{\partial C_i}{\partial x}, \quad (11.41)$$

where D_h is the hydrodynamic dispersion coefficient. The coefficient of hydrodynamic dispersion is defined as the sum of molecular diffusion and mechanical dispersion, since these effects are not separable where flow is involved (Bear, 1972)

$$D_h = D^* + D. \quad (11.42)$$

11.2.3.1 Mechanical Dispersion

Mechanical dispersion is a result of the fact that variations in the flow velocities exist, even where an average flow rate (as in Darcy's Law) can be defined for a particular representative elementary volume (REV). If all the detailed flow paths could

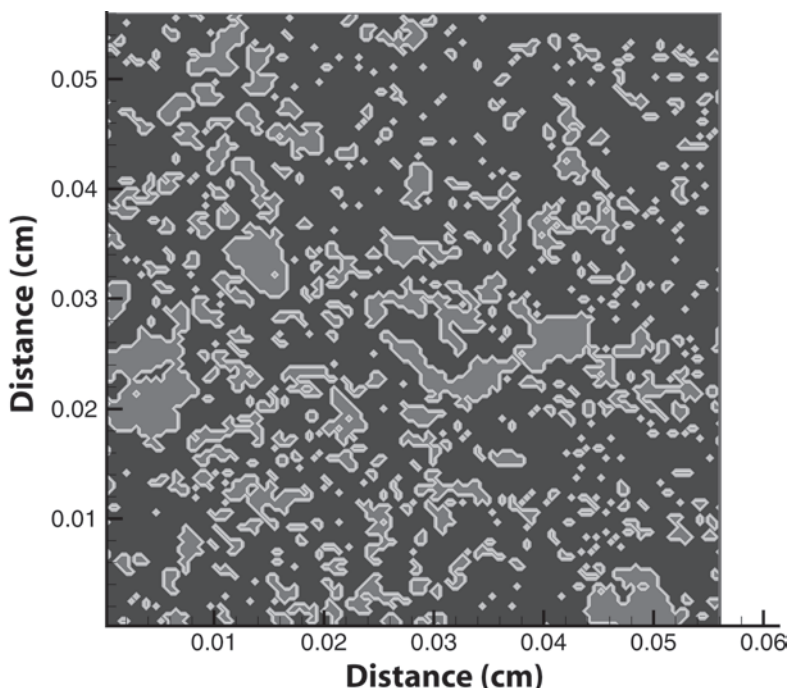


Fig. 11.7 Microtomographic image of micron-scale pores (red in color, gray in grayscale) and basaltic rock matrix (blue in color, dark gray in grayscale) based on X-ray synchrotron imaging at the Advanced Light Source

be captured (implying a resolution of microns or less), then there would be no need for inclusion of a dispersion coefficient. Even if such high resolution calculations were possible, however, a detailed knowledge of the actual pore structure (and thus the flow paths) is typically lacking. Although microscopic information on the pore structure of subsurface materials may never be routine, the increasing availability of X-ray synchrotron mapping has now made it possible to image the microscopic pore structure down to the micron scale. Figure 11.7 shows a 2D section through a 3D X-ray microtomographic image of a basalt specimen subjected to chemical weathering over tens of thousands of years. The mineral dissolution resulting from the weathering process has created new porosity or “micro-wormholes” that are clearly visible as red zones (in color) or gray (in grayscale image) in the skeletonized sections of the weathered rock (blue in color or dark gray in grayscale is the relatively unweathered rock matrix with pore sizes below the resolution of the synchrotron microtomography). Such heterogeneities will give rise to variations in flow velocity at the micron to centimeter scale, and thus to mechanical dispersion.

Mechanical dispersion was first clearly discussed for the case of laminar flow and transport within a cylindrical tube (Taylor, 1953). In the case where a non-reactive tracer is instantaneously released at the inlet of the tube and complete mixing does not occur, the tracer pulse will arrive first where the flow is fastest, later where the flow is slower. At any one time, the bulk concentration of the fluid leaving the

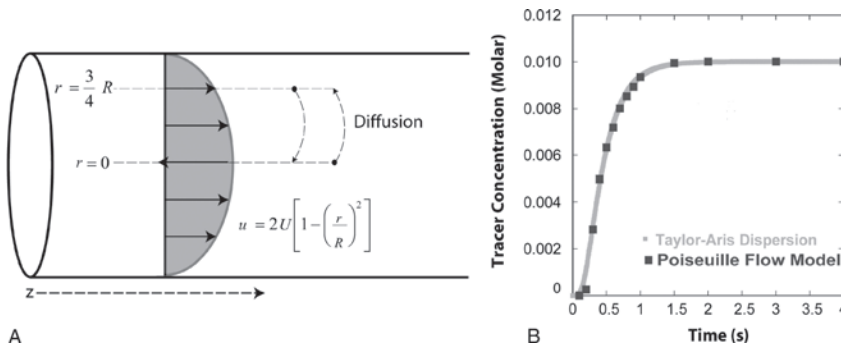


Fig. 11.8 a. Schematic representation of the parabolic velocity distribution that develops in the case of Poiseuille flow. **b.** Comparison of non-reactive tracer breakthrough profile using a Taylor-Aris dispersion coefficient (Taylor, 1953) and a full two-dimensional calculation of transport in a cylindrical tube using the analytical solution for Poiseuille flow (Eq. (11.43))

tube represents a flux-weighted average of the concentration in the fast and slow moving flow paths, so the breakthrough of the tracer will appear as disperse or gradual rather than sharp. This effect is referred to as Taylor dispersion (Aris, 1956; Taylor, 1953). Assuming Poiseuille's equation for flow in a cylinder holds, the steady-state parabolic velocity distribution as a function of radius r can be calculated from (Daugherty and Franzini, 1965)

$$u(r) = \frac{2Q}{\pi R^2} \left[1 - \left(\frac{r}{R} \right)^2 \right] = 2U \left[1 - \left(\frac{r}{R} \right)^2 \right], \quad (11.43)$$

where $u(r)$ is the local fluid velocity within the cylinder, Q is the volumetric flow rate, R is the radius of the cylinder, and U is the average velocity (Fig. 11.8a). Using Eq. (11.43), Taylor derived an analytical expression for the dispersion in the case of Poiseuille flow

$$D_h = D + \frac{UR^2}{D}, \quad (11.44)$$

where D_h is the dispersion coefficient, and D is the molecular diffusion coefficient. Note that the dispersion coefficient depends on the molecular diffusion coefficient for its contribution to longitudinal spreading (the first term on the right hand side of Eq. (11.44)), but also inversely on the molecular diffusion coefficient in the second term on the right hand side because radial diffusion acts to eliminate the gradients in concentration developed by the non-uniform velocity profile (Fig. 11.8a). A comparison of the breakthrough curve for a non-reactive tracer calculated with the Taylor-Aris dispersion coefficient given in Eq. (11.44) and a full two-dimensional axisymmetric cylindrical Poiseuille flow calculation in which dispersion is represented only through the variation in flow velocities and through molecular diffusion (i.e., no explicit dispersion coefficient is included) is given in Fig. 11.8b.

A similar effect occurs within porous media (which are often conceptualized as bundles of capillary tubes), since the velocity adjacent to a solid grain is slower than

the velocities in the center of the pore. Even in the case of a perfectly homogeneous porous medium (e.g., glass beads all of the same size), therefore, spreading of a solute plume will occur. Additional effects in porous media are related to the tortuosity of flow paths (Fig. 11.5) and to differences in pore size, since velocities will be higher in those pores with wider apertures (Bear, 1972).

Dispersion needs to be quantified at much larger scales in porous media, however, so some averaging of these dispersion mechanisms is usually required. Dispersion in porous media is typically defined as the product of the fluid velocity and a dispersivity, α , with longitudinal and transverse components

$$\begin{aligned} D_L &= \alpha_L V_i \\ D_T &= \alpha_T V_i' \end{aligned} \quad (11.45)$$

where V_i refers to the average velocity in the principal direction of flow, and the subscripts L (longitudinal) and T (transverse) refer to the dispersion coefficient parallel and perpendicular to the principal direction of flow respectively (Bear, 1972).

11.2.3.2 Macrodispersion

The treatment of hydrodynamic dispersion as a Fickian process (that is, one in which the flux is linearly proportional to the concentration gradient) has been widely criticized (Dagan, 1988; Gelhar, 1986; Gelhar and Axness, 1983; Gelhar et al., 1992). As pointed out by a number of investigators, dispersion is scale-dependent, with larger dispersivities observed for larger observation scales. At the column scale, a typical dispersivity may be on the order of a centimeter, but at the field scale, apparent dispersivities from 10 to 100 m or more are common. Gelhar (1986) showed that the dispersivity increased with scale of observation, although even at a single observation scale, dispersivities could range over 2–3 orders of magnitude due to differing degrees of aquifer heterogeneity at the different sites (Gelhar, 1986; Gelhar et al., 1992). The increase with dispersivity as a function of the scale of measurement is related to the hierarchical nature of natural porous medium and is often referred to as macrodispersion. At the pore-scale, variations in flow velocity and direction are related to pore-scale heterogeneities like the variation in grain size and pore apertures, but at the field scale, additional heterogeneity features (sedimentary features, fractures, faults) are encountered which add to the spreading of the solute plume. As in the case of Taylor dispersion, the spreading of a solute plume is fundamentally related to the variations in flow velocity, with fast-flowing pathways leading to earlier breakthrough than slow flow pathways. In the case of Poiseuille flow in a tube, the effect is predictable and rigorously quantifiable because of the well-defined physics of the system, but in natural porous media where multi-scale heterogeneities typically occur, the problem of determining dispersivities is much more difficult and usually requires a stochastic treatment.

The effect of macrodispersion can be illustrated with a simple example. Consider a permeability field with approximately 8 orders of magnitude variability in permeability (Fig. 11.9a). The heterogeneous distribution of and strong contrast in

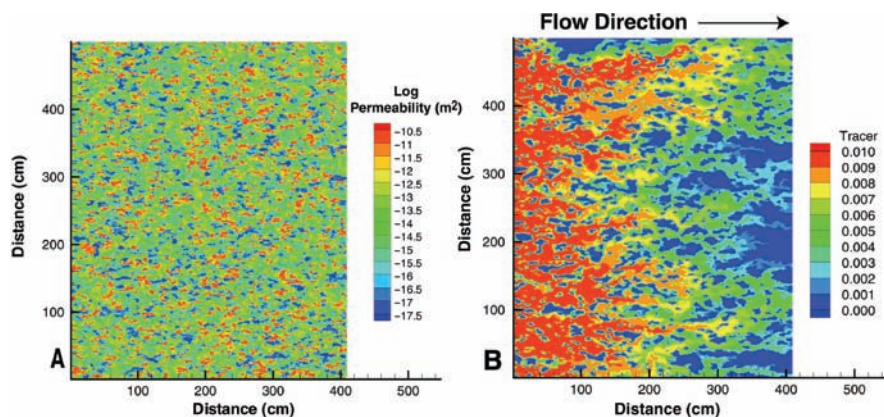


Fig. 11.9 **a.** Heterogeneous permeability (m^2) field for 2D problem. **b.** Concentration field at 0.5 years as a result of flow from left to right across the heterogeneous domain.

permeability results in preferred flow paths that lead to fingering of a non-reactive tracer plume as it moves with the flow from left to right (Fig. 11.9b). The two-dimensional numerical simulation was conducted without including a Fickian treatment of hydrodynamic dispersion and using an accurate Total Variation Diminishing (TVD) scheme that minimizes numerical dispersion (Steefel and MacQuarrie, 1996). When a flux-weighted average of the solute concentration is calculated over the entire length of the capture plane on the right hand side, perpendicular to the flow direction (similar conceptually to what occurs where flow converges into a pumping well), one observes a gradual, disperse breakthrough as a result of the mixing of the early and late arriving fluid packets (Fig. 11.10). To match the disperse breakthrough curve in the heterogeneous flow field with a one-dimensional simulation of flow in a homogeneous permeability field, it is necessary to use a dispersivity, α , of about 50 cm (Fig. 11.10).

11.2.3.3 Stochastic Descriptions of Dispersion

There is much interest now in more rigorous descriptions of macrodispersion in particular. One approach has been to treat the parameters controlling transport (primarily the hydraulic conductivity or permeability, but also potentially such parameters as mineral volume fractions and/or reactive surface area) as stochastic rather than deterministic parameters, since the exact distribution of these parameters in the subsurface is typically poorly known (Dagan, 1989; Gelhar, 1986, 1993). This is a particularly useful approach when the primary data available are breakthrough curves for tracers at an observation point. The shape of the curve can be used to deconvolve a stochastic distribution of hydraulic conductivities in the aquifer, implying that while we do not know the exact path a particular solute particle followed, we do have a statistical representation of the ensemble of solute travel times that could have produced the observed tracer concentrations at the observation point.

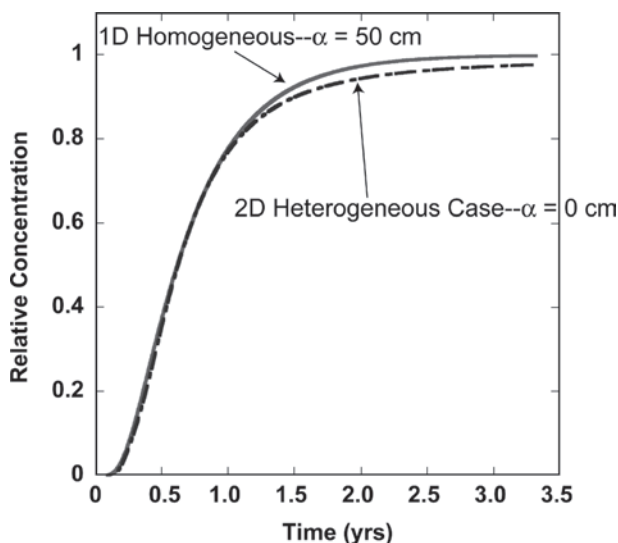


Fig. 11.10 Comparison of solute breakthrough curves for the case of the heterogeneous permeability field shown in Fig. 11.9a, calculated with a dispersivity, α , = 0, and a 1D homogeneous permeability field calculated with α = 50 cm.

Tracer breakthrough data, therefore, is often used to generate probability density functions for hydraulic conductivities and travel times, although this concept need not be strictly stochastic.

11.3 Advection-Dispersion-Reaction Equation

We are now ready to combine the transport processes outlined above with expressions for kinetically controlled geochemical and biogeochemical reaction. A comprehensive and modern treatment would require the use of a sophisticated numerical simulator capable of handling variations in system properties (hydraulic conductivity, porosity, tortuosity, etc.) in both space and time, along with rigorous treatments of multicomponent diffusion and advection. Our interest here, however, is in exploring the first-order dynamics when reaction and transport are coupled, and for this purpose a simplified version of the advection-dispersion-reaction equation is adequate. For a system with transport of a non-reactive tracer, an expression for the conservation of solute mass can be derived by accounting for the flux of solute across the faces of a volume element. For a one-dimensional system (fluxes in the Y and Z directions = 0), the net flux is obtained from

$$\frac{\partial J_i}{\partial x} = \lim_{\Delta x \rightarrow 0} \frac{J_i|_{x+\Delta x} - J_i|_x}{\Delta x}. \quad (11.46)$$

In a multidimensional system involving porous media, the accumulation of solute mass is given by the difference (that is, the divergence) of the fluxes summed over all of the faces of the element

$$\frac{\partial(\phi C_i)}{\partial t} = -\nabla \cdot \mathbf{J}_i = -\left(\frac{\partial J_i}{\partial x} + \frac{\partial J_i}{\partial y} + \frac{\partial J_i}{\partial z}\right), \quad (11.47)$$

where $\mathbf{J}_i$ is the flux vector. Substitution of Eqs. (11.10) and (11.15) into Eq. (11.47) (neglecting electrochemical migration for simplicity) yields

$$\frac{\partial(\phi C_i)}{\partial t} = -\nabla \bullet (\phi \mathbf{v} C_i) + \nabla \bullet (\phi D_i^* \nabla C_i). \quad (11.48)$$

To include reactions, however, it is more instructive to use the one-dimensional version of the advection-dispersion equation, particularly since non-dimensionalization of the equation is more straightforward in this case. For a constant porosity, tortuosity, and flow system characterized by a first-order precipitation and dissolution reaction that can be described in terms of a single chemical component (e.g., $\text{SiO}_{2[\text{aq}]}$ reacting with the single mineral quartz), the advection-dispersion-reaction equation becomes

$$\phi \frac{\partial C}{\partial t} = -\phi v \frac{\partial C}{\partial x} + \phi D^* \frac{\partial^2 C}{\partial x^2} + Ak \left(1 - \frac{C}{C_{eq}}\right), \quad (11.49)$$

where k is the rate constant in units of moles $\text{m}^{-2} \text{s}^{-1}$, A is the reactive surface area of the mineral in units of $\text{m}^2 \text{m}^{-3}$, and C_{eq} is the solubility of the mineral in moles m^{-3} .

11.3.1 Non-Dimensional Form of the Advection-Dispersion-Reaction Equation

The advantage of converting a partial differential equation to its non-dimensional form is that the relative importance of dynamic processes like chemical reaction, advection, and hydrodynamic dispersion are readily apparent. The first step is to define a length scale, l , which may be a characteristic length scale defined by the geology or hydrology (e.g., the flow length through an aquifer or weathering profile), or more commonly a length scale which reflects the spatial distribution of observations. Using this length scale, a non-dimensional or fractional distance can be defined as

$$x' = \frac{x}{l}. \quad (11.50)$$

In addition, this allows us to define a characteristic time for dispersive transport

$$t_D = \frac{l^2}{D^*}, \quad (11.51)$$

and advective transport

$$t_A = \frac{l}{v}. \quad (11.52)$$

When combined with a characteristic time for reaction

$$t_R = \frac{\phi C_{eq}}{Ak}, \quad (11.53)$$

it is possible to define a series of non-dimensional parameters that control the behavior of a water–rock interaction system involving transport: the Damköhler number for advective, Da_I , and diffusive (or dispersive), Da_{II} , systems respectively

$$Da_I = \frac{t_A}{t_R} = \frac{Akl}{\phi v C_{eq}} \quad (11.54)$$

$$Da_{II} = \frac{t_D}{t_R} = \frac{Akl^2}{\phi D^* C_{eq}}. \quad (11.55)$$

In addition, the relative importance of advective versus diffusive (or dispersive) transport is compared in the Péclet number

$$Pe = \frac{t_D}{t_A} = \frac{vl}{D^*}. \quad (11.56)$$

Note that each of these numbers depends on the characteristic length scale considered.

To develop a fully non-dimensional form of the advection-dispersion-reaction equation, it is convenient to introduce a non-dimensional form of the concentration

$$C' = \frac{C - C_{eq}}{C_0 - C_{eq}}, \quad (11.57)$$

where C_0 is the concentration of the fluid injected into the system (Lichtner, 1998). Introducing a dimensionless time

$$t'_D = \frac{D^* t}{l^2}, \quad (11.58)$$

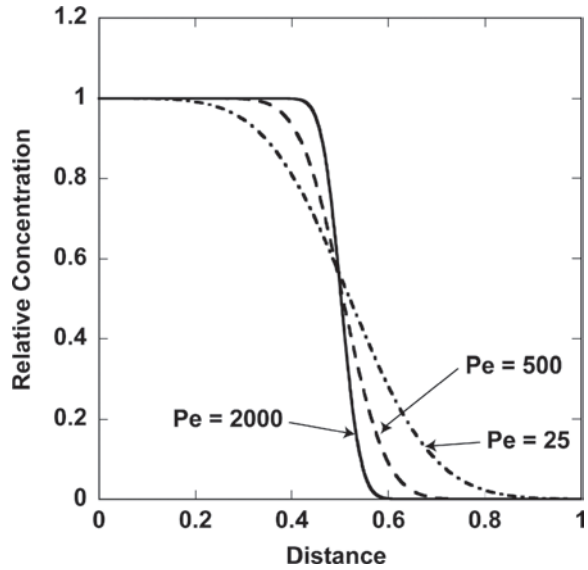
Eq. (11.49) becomes

$$\frac{\partial C'}{\partial t'_D} = \frac{\partial^2 C'}{\partial x'^2} - Pe \frac{\partial C'}{\partial x'} - Da_{II} C', \quad (11.59)$$

which makes clear how the Péclet and Damköhler numbers control the behavior of the advection-dispersion-reaction equation.

At high Péclet numbers ($Pe \gg 1$), advective transport dominates and dispersive and diffusive transport are negligible, with the result that the concentration front is relatively sharp (Fig. 11.11). Similarly, for Damköhler numbers $\gg 1$, reaction times are much faster than transport times for a given length scale. Where this is the case,

Fig. 11.11 Effect of the non-dimensional Péclet number on the shape of a concentration profile. The length scale is given by the flow distance, with flow from left to right



local equilibrium is achieved for a reaction of the form given in Eq. (11.49) over a length scale, l (Bahr and Rubin, 1987). In addition, reaction fronts are relatively sharp where the Damköhler number is large, since the approach to equilibrium requires a small amount of time relative to the time needed for a solute to traverse a distance l (Fig. 11.12). This has been shown more formally by Lichtner (Lichtner, 1988, 1998), who presented a pedagogically valuable solution to the stationary-state advection-dispersion-reaction equation

$$\frac{d^2 C'_i}{dx'^2} - Pe \frac{dC'_i}{dx'} - Da_{II} C'_i = 0. \quad (11.60)$$

or

$$\frac{1}{Pe} \frac{d^2 C'_i}{dx'^2} - \frac{dC'_i}{dx'} - Da_I C'_i = 0, \quad (11.61)$$

by noting that

$$Da_{II} = Da_I Pe. \quad (11.62)$$

Earlier solutions were presented by Ogata and Banks and by Bear (Bear, 1972; Ogata and Banks, 1961). To fully specify the system, boundary conditions are needed

$$C(0) = C_0, \quad (11.63)$$

$$C(\infty) = C_{eq}, \quad (11.64)$$

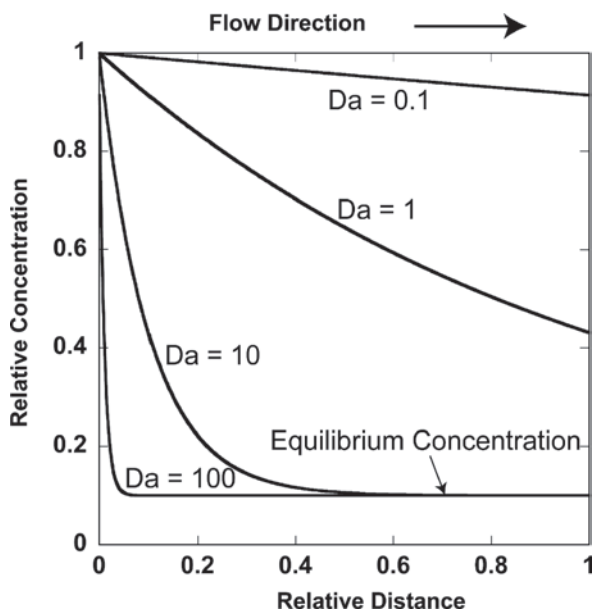


Fig. 11.12 Effect of the non-dimensional Damköhler number on the shape of a concentration profile at steady state. A large Damköhler number indicates that the reaction kinetics are rapid compared to transport rates over the length scale considered, or equivalently, that the characteristic time for transport is significantly more than the characteristic time for reaction. The local equilibrium approximation is justified in such cases

which in the non-dimensional system become

$$C'(0) = 1 \quad (11.65)$$

$$C'(\infty) = 0. \quad (11.66)$$

For the case of pure advective flow (infinite Péclet number) and the boundary condition in Eq. (11.65), the solution to Eq. (11.61) is given by an exponential function (Boyce and DiPrima, 1986; Lichtner, 1998)

$$C' = e^{-\beta' x'}, \quad (11.67)$$

where

$$\beta' = Da_I = \frac{Akl}{C_{eq}\phi v}. \quad (11.68)$$

For the case of pure diffusive transport ($v = 0$) and mixed dispersive-advective transport, the solution of the second-order differential equation in 11.60 can also be written in the form of Eq. (11.67), with the characteristic equation for β' given by (Boyce and DiPrima, 1986; Lichtner, 1998)

$$\beta'^2 - Pe \cdot \beta' - Pe \cdot Da_I = \beta'^2 - Pe \cdot \beta' - Da_{II} = 0. \quad (11.69)$$

The solution in the case of pure diffusive transport ($Pe = 0$) is

$$\beta' = Da_{II} = \frac{Akl^2}{\phi D^* C_{eq}}, \quad (11.70)$$

while for mixed dispersive (diffusive) and advective transport, the solution is given by

$$\beta' = \frac{1}{2} \left[-Pe + \sqrt{Pe^2 + 4Da_I \cdot Pe} \right] = \frac{1}{2} \left[-Pe + \sqrt{Pe^2 + 4Da_{II}} \right]. \quad (11.71)$$

11.3.2 Equilibration Length Scales

As pointed out by Lichtner, these solutions can be used to determine the length scale over which equilibration between the fluid and solid phase occurs. To express the stationary state Eq. (11.67) in terms of actual distance and the boundary conditions given in Eqs. (11.63) and (11.64), we define

$$\beta = \frac{\beta'}{l}, \quad (11.72)$$

which yields

$$C(x) = (C_0 - C_{eq})e^{-\beta(Pe, Da)x} + C_{eq}. \quad (11.73)$$

The fractional distance required to approach equilibrium (referred to as the *equilibration length scale*) is given by the inverse of the parameter β (Lichtner, 1998)

$$\lambda' = \frac{\lambda}{l} = \frac{1}{\beta'}, \quad (11.74)$$

where λ is the equilibration length scale and λ' is the fractional length scale (Fig. 11.13). Where $\beta' > 1$ (implying $\lambda' < 1$), local equilibrium is attained for a given length scale l , while values of $\beta' < 1$ ($\lambda' > 1$) correspond to dominantly surface reaction or kinetic control. Note that it is quite possible that the system is characterized by a mixed equilibrium (solubility) and kinetic control where $\beta' \sim 1$ ($\lambda \sim l$). The overlap between a strict surface reaction and thermodynamic control can become larger when nonlinear rate laws are considered. The equilibration length scale corresponds to the width of the reaction front in a natural (real) system. In general, the width of the reaction front can depend on advection, dispersion, and the rates of surface reactions.

The theory outlined above provides an approach to estimating natural, *in situ* reaction rates if transport rates are independently known. Lacking an independent determination of transport rates, it is evident from Eqs. (11.68) through (11.71) that the width of a reaction front constrains only the *ratio of the transport to reaction rates*. In general, wide reaction fronts are characteristic of low Damköhler number systems. Sharp reaction fronts, which result from equilibration of the fluid phase

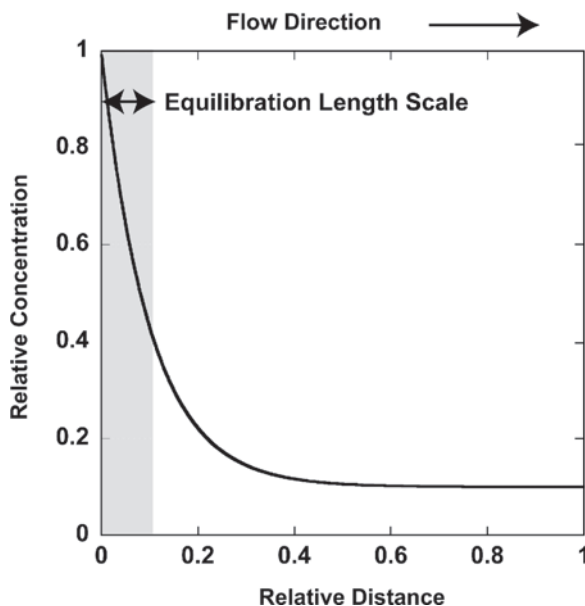


Fig. 11.13 Equilibration length scale given by $1/\lambda$

with the rock over a relatively short distance, indicate a local equilibrium system. Diffusion-reaction systems are particularly useful for assessing natural *in situ* reaction rates, since the range in values of the effective diffusion coefficient is generally less than the range of flow velocities in more permeable media. However, since relatively few determinations of tortuosities (or formation factors) have been carried out in low permeability materials, even the diffusion-reaction problem may be unconstrained.

11.3.3 Reaction Fronts in Natural Systems

While the non-dimensional analysis presented above has a real pedagogical value, the rather stringent assumptions used to derive it should be noted clearly. Perhaps most importantly, it assumes constant transport coefficients over the spatial domain considered. Significant changes in flow velocity over the flow path would have the effect of changing the local Péclet and Damköhler numbers, thus changing the width of the reaction front. Similarly, large changes in porosity can change the local effective diffusivity through the tortuosity effect, making the interpretation of reaction front widths considerably more difficult. A good example is provided by weathering rinds developed in basaltic clasts as reported by (Sak et al., 2004). In the highly weathered material, which is dominated by gibbsite and Fe-hydroxide, the porosity averages about 30%–50%, while in the unaltered basaltic rock, the average porosity

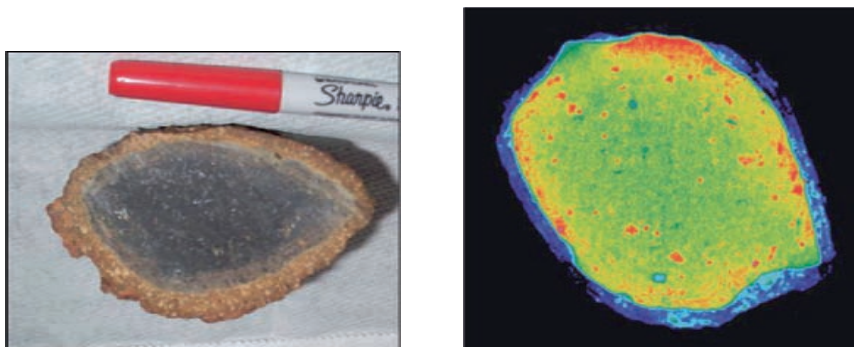


Fig. 11.14 **a.** Photograph of a weathering rind developed in basaltic rock from Costa Rica. **b.** CAT scan of a similar sample showing the sharp density contrast between unaltered (yellow and orange in color, light gray in grayscale) and weathered material (blue in color, mottled gray in grayscale). The interface between unweathered and weathered rock is associated with a large change in such physical properties as the porosity and tortuosity. Samples courtesy of Alexis Navarre-Sitchler.

is on the order of 3%–5% (Fig. 11.14). This discontinuity in porosity, and thus in transport parameters, can cause a sharpening of the reaction front that might be misinterpreted as a strict Damköhler number effect. In such a system characterized by transport rates that vary spatially, the principal control on rates may change depending on the portion of the system considered.

Another point that needs to be considered carefully is whether the width of a reaction front is not due in part to heterogeneous flow paths through the reacting material. The analysis presented above strictly applies only to a homogeneous system. If flow is not uniform through a reactive rock, then the extent of reaction will depend on the local flux. Integrated over long times, the extent of reaction will vary, with the result that a sampling transect carried out perpendicular to the principal flow direction (parallel to the reaction front in the homogeneous case) will result in a gradual or disperse reaction front if the results are averaged. This is another example of macrodispersion, in this case integrated over long periods of time to produce a disperse reaction front. Again, a simple Damköhler number analysis could underestimate the rates of reaction in this case by interpreting the broadness of the front as due solely to slow reaction kinetics. These cases, however, can be analyzed with numerical reactive transport software.

A third point to keep in mind is that the reaction kinetics presented above involved linear kinetics. In the case of important Earth-forming minerals like the feldspars, the rate laws may be considerably more complicated, with catalysis of the dissolution reaction (e.g., by H^+) and inhibition of the dissolution reaction (e.g., by Al^{3+}) contributing to a much more complicated behavior. In addition, a nonlinear dependence of the dissolution rate on the extent of undersaturation (or the reaction affinity) can also result in more complex behavior, with a much wider range of transport and kinetic parameters within which a mixed transport and surface reaction

control could be observed. Fortunately, these more complicated behaviors can be analyzed with modern reactive transport numerical software, even if it is not possible with a relatively simple analytical solution.

A fourth point is that gradual reaction fronts may be due to other factors such as a temperature gradient or local sources of reactive constituents. “Gradient reactions,” where reactions are driven by transport across a temperature gradient, are contrasted with isothermal “reaction front” case discussed above (Phillips, 1991; Steefel and Lasaga, 1994). When a temperature gradient is present, it is likely that a gradient in reaction products will develop even in the absence of any kinetic effects. Similarly, where local sources of reactive constituents are present along a flow path, as in the case of decaying organic matter producing the weak acid CO_2 , then gradients in reaction products are likely to develop that can be unrelated to the equilibration length scale of the primary mineral of interest (e.g., feldspar dissolution). Care must be taken not to interpret either of these as a simple Damköhler number effect. In addition, it stresses the importance of including all relevant physical, chemical, and microbiological processes into the analysis of reaction rates (Maher et al., 2006).

11.3.4 *Transport versus Surface Reaction Control*

Under the steady-state conditions considered here, there is always some theoretical length scale over which local equilibrium could be attained (assuming such an equilibrium state exists), although this length scale may not be realized in a particular geological environment. Where the concentration in the aqueous phase increases or decreases to the point where equilibrium or near-equilibrium is achieved, the overall rate of reaction within the spatial domain defined by the length scale l becomes *transport-controlled*. This implies that the rate-limiting process in the overall reaction evaluated over the length scale l is transport, rather than the rate of attachment and detachment of ions from the mineral. Transport control has often been discussed in the geochemical literature, but usually with regard to experimental studies where transport involved diffusion across a boundary layer next to a reacting mineral (Berner, 1980). For example, numerous studies have shown that the dissolution of calcite is diffusion rather than surface reaction-controlled at pH values < 4 . This can be verified in rotating disk reactors by increasing the speed of rotation—in the case of a diffusion control on the rate of dissolution, the faster rate of spinning reduces the size of the diffusion boundary layer adjacent to the crystal, thus increasing the overall rate of dissolution (Pokrovsky et al., 2005).

While the rotating disk experiment involving calcite is a particularly good example of a transport-controlled system, the concept is much more general and may be applied at any scale. Consider a flow path through a granite undergoing weathering. If a fluid percolating through the granite approaches equilibrium over a flow distance of about 25 m, but we collect water samples issuing from the profile 50 m from the start of flow path, then we are collecting waters close to or at equilibrium

that will express a transport control on the overall rate. Operationally, this means that the flow rate through the weathering profile (due, for example, to an increase in rainfall) controls the weathering flux, $J_{weather}$, in the advection-dominant case over the 50 m according to

$$J_{weather} = qC_{eq}, \quad (11.75)$$

where q is the flow rate and C_{eq} is the equilibrium concentration. If the scale of observation, l , is $\gg$ than the equilibration length scale λ , then the weathering rate will not depend on the reaction kinetics. This is a general result that applies to all water–rock interaction systems (Lichtner, 1993). A comparison of laboratory-determined rates of reaction, which are carried out in most cases under far from equilibrium conditions and thus under surface reaction control, and natural weathering rates evaluated at length scales greater than the equilibration length scale, will be meaningless in this case, since the rate control is not the same. By definition, the field rate when transport controlled will be slower than the surface reaction-controlled rate. But, as stressed above, the control on rates is scale-dependent, so data collected at a length scale $\ll$ than the equilibration length scale may show evidence for a surface reaction control on rates and far from equilibrium conditions. Thus, observations of etch pitting in primary minerals, generally taken as good evidence of far from equilibrium conditions (White and Brantley, 2003), may be fully compatible with an overall transport control on weathering rates, depending on how the scales of observations compare to the equilibration length scale.

11.3.5 Propagation of Reaction Fronts

The expressions presented above assume a reaction front present at $x = 0$, but the equations can be generalized easily to consider the case of a reaction front that propagates through space over time. For example, it is possible to define a new spatial coordinate in terms of distance from the reaction front, x_f , according to

$$x_f = x - l_f, \quad (11.76)$$

where l_f is the position of the reaction front, and to use this in the expressions discussed above.

The velocity at which fronts propagate as a function of transport and kinetic rates can also be determined. Lichtner has shown that the velocity of the reaction front, v_l , can be calculated from the expression (Lichtner, 1988)

$$v_l = \frac{dl_f}{dt} = \frac{1}{\tau_0\beta} \left(\frac{C_{eq} - C_l}{C_{eq} - C_0} \right), \quad (11.77)$$

where C_l is the concentration at the reaction front, β is defined in Eqs. (11.68) through (11.72) and τ_0 , the time required for a mineral to dissolve completely at the

inlet of a porous column, is given by

$$\tau_0 = \frac{\phi_m}{\bar{V}_m Ak (C_{eq} - C_o)}, \quad (11.78)$$

where ϕ_m is the initial volume fraction of the mineral and $\bar{V}_m$ is its molar volume. In Eq. (11.77), the last term represents the jump in concentration across the reaction front and is given by

$$\frac{C_{eq} - C_l}{C_{eq} - C_0} = 1; \text{Pure Advection} \quad (11.79)$$

$$\frac{C_{eq} - C_l}{C_{eq} - C_0} = \frac{1}{\beta l + 1}; \text{Pure Diffusion} \quad (11.80)$$

$$\frac{C_{eq} - C_l}{C_{eq} - C_0} = \frac{\frac{v}{\beta D^*} \frac{1}{1 - e^{-vl/D^*}}}{\left(\frac{v}{\beta D^*} \frac{1}{1 - e^{-vl/D^*}} + 1 \right)}; \text{General Case.} \quad (11.81)$$

The pure advective case can also be derived through the use of the traveling wave approximation (Ortoleva et al., 1986).

According to Lichtner, the formation of a reaction front can be divided into three periods: (1) a transient, surface reaction-controlled regime where the mineral in question is dissolved at the inlet to the system, (2) a transitional regime, and (3) an asymptotic regime which is at local equilibrium except within the reaction front (Lichtner, 1996). In the asymptotic regime, the rate of front propagation is independent of the kinetic rate constants. This was shown more formally in 1993 via a scaling analysis of the reactive transport equations in the case where boundary and initial conditions are scale-invariant and no inherent length scale exists for the system (Lichtner, 1993). In this case, the field variables of interest, F , obey the scaling relationship

$$\lim_{\sigma \rightarrow \infty} F(\sigma x, \sigma t; v, D_h, Ak) = \lim_{\sigma \rightarrow \infty} F(x, t; v, \sigma^{-1} D_h, \sigma Ak), \quad (11.82)$$

where σ is the scale factor. Eq. (11.82) states that in the limit of infinite space and time, the reactive transport equations approach the pure advective local equilibrium limit as diffusion and dispersion vanish and the reaction rate constant and surface area become infinitely large.

11.4 Rates of Water–Rock Interaction in Heterogeneous Systems

Most studies of the kinetics of water–rock interaction carried out to date have assumed flow and reaction through a homogeneous, well-mixed system, as would be the case with a single continuously stirred flowthrough reactor (Haggerty et al., 1998; Snodgrass and Kitanidis, 1998; White and Brantley, 2003; Zhu, 2005). This

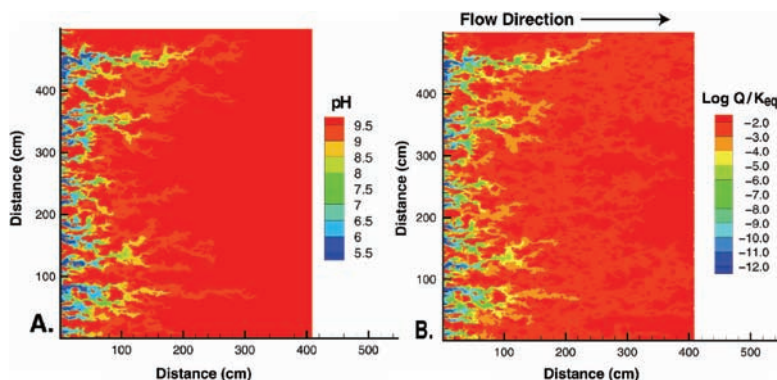


Fig. 11.15 **a.** pH distribution for the 2D heterogeneous flow field shown in Fig. 11.9. pH at the left side of the flow domain is fixed at 5. The principal reaction is the dissolution of plagioclase with a rate law that includes dissolved aluminum inhibition (from Oelkers et al., 1994). **b.** The saturation state of the pore fluid with respect to plagioclase ($\log Q/K_{eq}$) varies spatially, resulting in a heterogeneous distribution of surface reaction versus transport control of the rate.

is perhaps somewhat strange given the enormous number of studies on macrodispersion in the hydrologic literature indicating that travel times, and thus residence times, in the subsurface are not all the same. Fortunately, the effects of both physical and chemical heterogeneities and their role in water–rock interaction are now beginning to be discussed (Li et al., 2006; Malmström et al., 2000; Meile and Tuncay, 2006). The role of physical heterogeneities can be clarified by returning to the heterogeneous permeability field shown in Fig. 11.9. If we now include reactions along with the flow and transport, in this case the dissolution of plagioclase according to the kinetic scheme proposed by Oelkers and co-workers (Oelkers et al., 1994), we see that the numerical modeling of the reactive transport predicts a steady-state fingering of the pore water pH that follows the high permeability zones (Fig. 11.15a). Similarly, a contour plot of the logarithm of the mineral saturation states (the distance the pore water is from equilibrium with respect to plagioclase) shows a similar strong spatial variability—a transect in the Y direction at $X = 10\text{ cm}$ would encounter up to 10 orders of magnitude variability, ranging from far from equilibrium to relatively close to equilibrium pore waters (Fig. 11.15b). Therefore, a single transect could encounter both surface reaction and at least partly transport-controlled rates. While this is a model result, it should be broadly representative of what would be expected for any reactive system with 7 orders of magnitude variation in the local permeability.

11.4.1 Residence Time Distributions

The concept of macrodispersion has important implications for the kinetics of water–rock interaction. One can also think of these variations in flow velocity and/or

flow length as leading to a distribution of residence times for aqueous species migrating through reactive material. A sample collected from a stream draining a catchment, for example, typically includes waters that have moved through a myriad of flow paths and distances. Some water may have moved through relatively shallow portions of the soil profile—these flow paths would typically involve relatively short residence times, with less exposure to primary reactive phases forming the bedrock. In contrast, other water may have moved along deeper, slower flow paths, encountering a greater abundance of reactive primary minerals along the way. The residence time of reactive water in contact with rock, therefore, can vary substantially in a natural system. Locally, the system may be far from equilibrium, elsewhere close to equilibrium. Conceptually, one might think of the overall system as an ensemble of flowthrough reactors, some with short residence times and/or small amounts of reactive material, others with much longer residence times. In some cases, the residence time will have been long enough that the fluid actually equilibrates within the reactor, leading to a rate that is transport rather than surface reaction-controlled. If the effluent of this ensemble of flowthrough reactors were to converge into a single sampling tube (the experimental analogue of a stream gauging station at the catchment scale or a pumping well drawing water from a heterogeneous aquifer), then the total extent of reaction (i.e., the upscaled, volume-averaged reaction rate) would reflect the full distribution of residence times and reactive mineral mass.

Many examples of reactive flow through permeable rocks or sediment exist where strong contrasts in porosity and permeability result in regions characterized by very different transport regimes. This is often referred to as multi-region transport (Harvey and Gorelick, 2000). The most common example is a dual permeability (or porosity) system, where a portion of the system is sufficiently permeable that macroscopic flow occurs within it, another portion is so impermeable that flow is negligible and transport is by molecular diffusion. Perhaps the best example of a dual permeability system is provided by fractured rock, where the permeability of the fractures is typically many orders of magnitude higher than the permeability of the rock matrix (Steefel and Lichtner, 1998).

Much of the evidence that multi-region transport systems exist in the subsurface comes from measurements of hydraulic conductivities on small laboratory-scale samples. Another source of evidence is provided by groundwater ages determined with various methods (Plummer et al., 2001). Although these groundwater ages are often interpreted as the result of mixing between two end members (old and young water), what we have learned about the distribution of hydraulic conductivities, and thus residence times, in heterogeneous 3D subsurface media argues against this (Bethke and Johnson, 2002; Tompson et al., 1999; Varni and Carrera, 1998; Weissmann et al., 2002). For example, Fig. 11.16 shows groundwater ages determined using the chlorofluorocarbon (CFC) technique compared to simulated CFC ages based on high resolution groundwater flow simulation of a heterogeneous alluvial fan aquifer in California (Weissmann et al., 2002). The high resolution flow modeling argues that the individual CFC ages are real, and not simply the result of mixing of old and young waters.

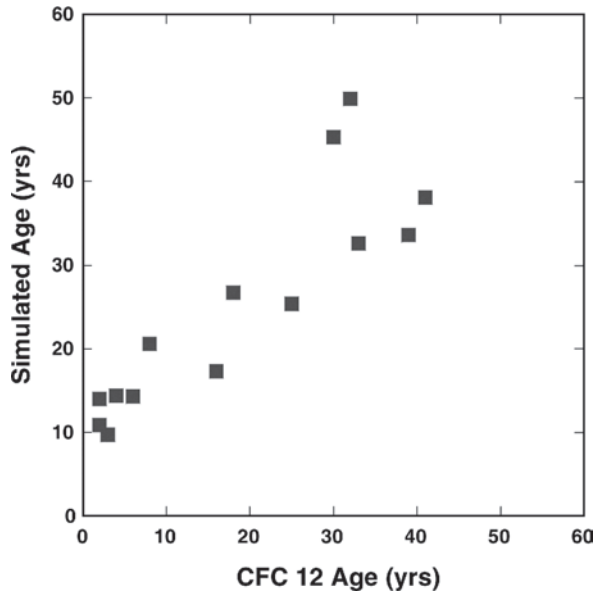


Fig. 11.16 Chlorofluorocarbon (CFC) ages compared to simulated CFC ages based on high resolution groundwater flow modeling from a heterogeneous alluvial fan aquifer in California (From Weissmann et al., 2002)

Evidence also comes from non-reactive tracer concentration profiles (or “break-through curves”) determined in subsurface wells. Tracer concentration profiles at an observation well (or at the end of a laboratory column) characterized by multi-region effects typically show an early, usually sharp breakthrough, followed by a long gradual approach to a maximum value in the case of a constant injection. In the case of a transient pulse of a tracer followed by another fluid (a common case in contaminant hydrology), the tracer is eluted only very slowly from the column or aquifer. This behavior occurs because it requires some time for the tracer to be transported into the low permeability material, and once elution begins, then to be flushed from this zone.

Tracer breakthrough curves can be used to estimate a residence time distribution. With release of a non-reactive tracer pulse, fast pathways will deliver tracer first. Lower permeability regions within the flow domain will flush the tracer more slowly, providing information on the longer residence times. Using the first derivative of the concentration in the breakthrough curve in Fig. 11.10, the formal probability density function for residence times can be determined (Fig. 11.17).

11.4.2 Upscaling Reaction Rates in Heterogeneous Media

Mineral reaction rates are typically measured in well-stirred laboratory systems where the intent is to eliminate gradients in concentration within the solution.

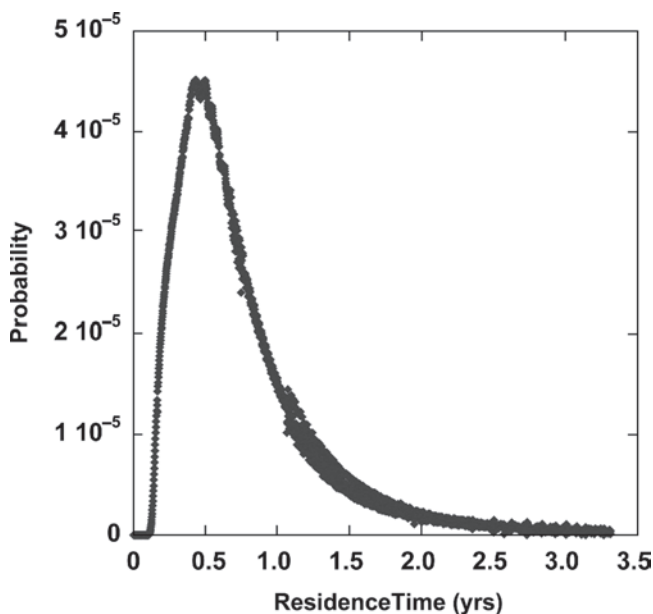


Fig. 11.17 Residence time distribution for the two-dimensional flow case presented in Fig. 11.9. Residence times are presented in terms of probabilities and are calculated recursively based on the breakthrough curve shown in Fig. 11.10

An individual crystal is expected experience the same chemical environment as its neighbor. To the extent that a diffusion boundary layer can be eliminated via stirring, potentially a problem with a rapidly reacting mineral like calcite at low pH (Pokrovsky et al., 2005), the rate of the mineral reaction is surface reaction-controlled. In porous media where water-rock interaction takes place, however, physical, chemical, and microbiological heterogeneities can lead to the development of gradients in concentration, and thus to a spatially variable reaction rates. Perhaps the clearest example is provided by the case where a reacting phase is distributed heterogeneously—obviously, in this case the reaction rate in the microenvironment next to the mineral is greater than what is determined over a larger volume average. If the system is well-mixed via either molecular diffusion or dispersion, however, then the rate should be scale-independent if correction is made for the distribution of reactive surface area. In the case where incomplete mixing at the individual pore or pore network scale occurs, however, significant spatial variations in concentration, mineral saturation state, and reaction rates can occur and lead to a scale dependence to the rate (Li et al., 2006). As shown by Li and co-workers in their study of plagioclase dissolution and kaolinite precipitation at the pore network scale, it is even possible for both precipitation and dissolution of kaolinite to occur simultaneously within the same pore network. A similar effect may occur at larger scale where slow transfer between low permeability zones (often referred to as “immobile”) and higher permeability (“mobile”) zones occurs—large scale

non-equilibrium between these zones may occur, creating gradients in concentration and thus a spatial variability in reaction rates (Harvey and Gorelick, 2000). From the preceding discussion, it should be clear that upscaling reaction rates is not as simple as normalizing the rates to the total reactive surface area in the water–rock system. Rates in natural heterogeneous porous media will always be scale-dependent where incomplete mixing occurs. Future research in water–rock interaction will doubtless focus on methods for upscaling reaction rates in such heterogeneous systems.

11.5 Determining Rates of Water–Rock Interaction Affected by Transport

Rates of reaction can be determined in water–rock interaction systems affected by transport using several approaches. In general, however, intrinsic rates of reaction (e.g., $\text{moles m}^{-2} \text{s}^{-1}$) cannot be determined uniquely without independently determining transport rates. An exception is the case where one process or the other (surface reaction or transport) is clearly the slowest and therefore rate-limiting step in the overall process. Unfortunately, a surface reaction or transport control is often assumed to apply in advance of a rigorous analysis that demonstrates this control. So, for example, it has been common to compare rates of weathering at the field scale to rates of reaction determined in laboratory experiments conducted under far from equilibrium conditions. Such a direct comparison, without the use of an appropriate process model for weathering based on reactive transport, assumes *a priori* that surface reactions control the overall rate (Steefel et al., 2005). Whether this is in fact true, or whether rates are transport or mixed transport–surface reaction-controlled, needs to be established on a case by case basis (Maher et al., 2006).

11.5.1 Rates from Aqueous Concentration Profiles

From Eq. (11.49), it is clear that rates of reaction can be determined from a concentration profile if the rates of transport are known. One can determine rates of water–rock interaction even where non-steady state conditions prevail, but the steady state case is much simpler to deal with. In the case of a steady state system, the rates of reaction in a pure diffusion system will be given by the curvature or second derivative of the concentration

$$R = \phi D^* \frac{\partial^2 C}{\partial X^2}, \quad (11.83)$$

while in a pure advective system, the rate is given by the first derivative or slope of the concentration

$$R = -\phi v \frac{\partial C}{\partial X}. \quad (11.84)$$

Eqs. (11.83) and (11.84) can be used with finite differencing of discrete data to determine local reaction rates, respectively

$$R_j = \left[(\phi D^*)_{j+1/2} \frac{C_{j+1} - C_j}{x_{j+1} - x_j} - (\phi D^*)_{j-1/2} \frac{C_j - C_{j-1}}{x_j - x_{j-1}} \right] \quad (11.85)$$

$$R_{j-1/2} = -(\phi v)_{j-1/2} \left[\frac{C_j - C_{j-1}}{x_j - x_{j-1}} \right], \quad (11.86)$$

where j refers to the discrete data points and x_j is the location of the data in space. In this form, the finite difference equations are written without assuming equally spaced data (implicitly assumed in Eqs. (11.83) and (11.84)). Alternatively, the rates can be fit using the analytical or numerical solution to the governing reactive transport equation, taking into account the appropriate boundary and initial conditions as necessary. If a species is affected by more than one reaction, then all of the relevant reactions need to be factored into the analysis and this is generally best accomplished with modern numerical reactive transport software.

An example of matching a single reaction rate to a concentration profile is shown in Fig. 11.18a. In this example from Site 984 in the north Atlantic (Maher et al., 2006), sulfate reduction under conditions of diffusive transport in unlithified sediments (the only advection term is from burial) results in a decrease in sulfate concentrations and a stoichiometric increase in ammonia. The sulfate reduction rate can be determined to the accuracy of the species diffusivities. Since diffusion coefficients and formation factors for marine sediments are reasonably well known (Boudreau, 1997), the rate determined in this fashion is quite reliable. More difficult is to make use of concentration profiles affected by more than a single reaction. The calcium profile at the same site is affected by the dissolution of plagioclase and by the precipitation of calcite. Fortunately, the alkalinity profile can be used to constrain the rates of both the plagioclase and calcite. Additional support for the reaction rates determined in this fashion are provided by the uranium isotope profiles from the site (Maher et al., 2006). In natural systems, reaction networks composed of multiple sequential or parallel reactions are more common than not and extracting rates from these systems requires fitting multiple concentration profiles simultaneously. Modern numerical reactive transport software is again essential here.

An additional advantage of using modern reactive transport software is that various rate law formulations can be tested relatively easily, including Michaelis-Menten kinetics in the case of microbially mediated systems, or mineral dissolution and precipitation laws based on linear or nonlinear dependences on solution saturation state.

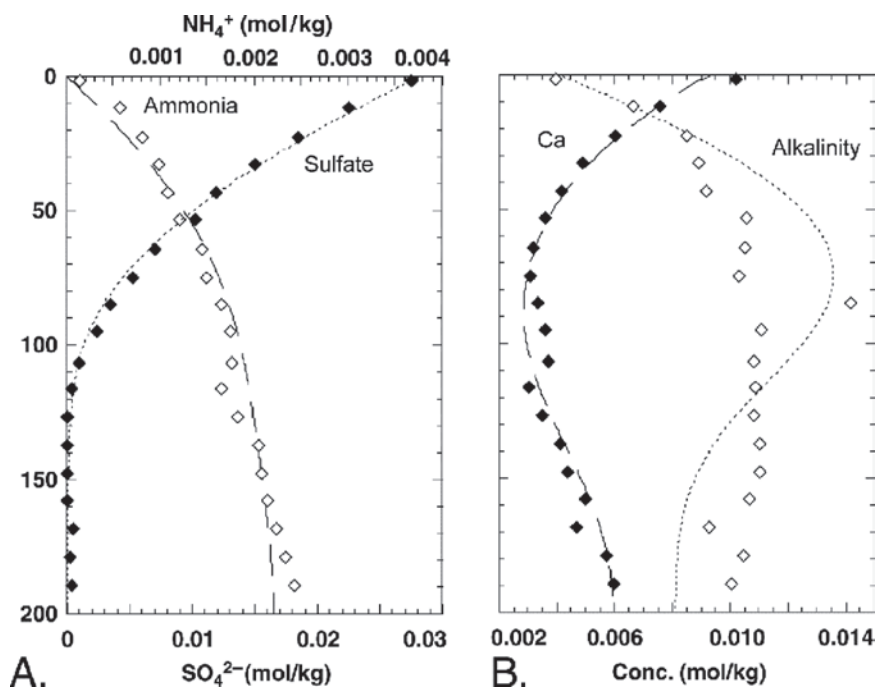


Fig. 11.18 a. Fit of the sulfate and ammonia profiles at Site 984 in the North Atlantic with the reactive transport code CrunchFlow allows the determination of the rate of microbially mediated sulfate reduction. b. Fit of the calcium and alkalinity profiles provides the rates of both plagioclase dissolution and calcite precipitation

11.5.2 Rates from Mineral Profiles

Determining rates from mineral profiles is generally more difficult, both because the mineral profiles reflect integrated rates, but also because the movement of the reaction fronts can introduce additional difficulties of interpretation. From the discussion of equilibration length scales in Sect. 11.3.2, it is clear that rates can be determined from the width of a reaction front in the case where transport rates are independently known. Determining intrinsic rates (per unit surface area mineral), however, is more difficult because the spatial variation of reactive surface area across the reaction front needs to be factored in. The simplest case involves a one-dimensional flow system with constant transport rates over time, an example of which is the chronosequence developed on granitic sand near Santa Cruz, California (White et al., 2006). Downward flow rates through the profile have been determined through tracer studies and the penetration distance of isotopes like ^{36}Cl . Potassium feldspar and plagioclase fronts show distinct penetration depths after 226,000 years of weathering, presumably reflecting the different solubilities and/or rates of the two minerals (Fig. 11.19). Interestingly, the plagioclase profile can be fit reasonably well

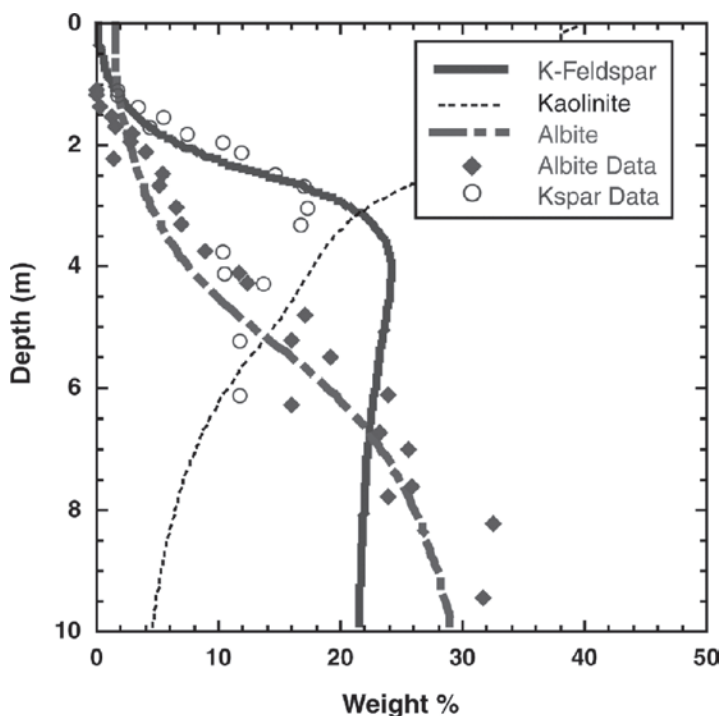


Fig. 11.19 Fitting of the profiles of plagioclase and potassium feldspar from Terrace 5 (226,000 years) at the Santa Cruz chronosequence (White et al., 2006) using the reactive transport code CrunchFlow. Simulations provided by Kate Maher

by allowing its reactive surface area to evolve with a $2/3$ dependence on its volume fraction.

11.6 Feedback between Transport and Kinetics

Feedback between flow, transport, and biogeochemical kinetics can lead to an extraordinarily rich set of behaviors in water–rock systems, but the full range of phenomena associated with these effects is largely beyond the scope of this chapter. Positive feedbacks between these processes can lead to highly complex nonlinear behavior, and in some cases, to pattern formation or self-organization. Interested readers are referred to recent volumes on the topic (Jamtveit and Meakin, 1999; Ortoleva, 1994), but two important and widely discussed examples are treated briefly here. The field promises to be extremely fruitful in the future, with progress made as investigations of a mathematical nature are linked to experimentally and/or field-determined kinetic and transport parameters.

11.6.1 Reactive-Infiltration Instability

Mineral dissolution and precipitation, as well as biomass growth and decay, can modify the permeability and tortuosity of porous media, thus providing a nonlinear feedback between the biogeochemical and flow/transport processes. Perhaps the best known example involves the enhancement of the porosity and permeability via mineral dissolution, a positive feedback that can lead to unstable growth of “reaction fingers” or “wormholes”, or in the extreme case, to karstification. This process is referred to as the “reactive-infiltration instability” (Ortoleva et al., 1987). It is important in the oil-field process of matrix acidizing, where the injection of acid is intended to reverse the damage to permeability caused by drilling. In carbonate rocks, the injected acid results in a dissolution front that propagates as “wormholes” rather than as a planar front. The instability develops as a result of even very minor variability in the permeability (at the macroscopic scale, the material may appear homogeneous). Regions with slightly higher permeability capture more reactive flow than adjacent regions with lower permeability, thus enhancing the propagation rate of the reaction front in the higher permeability regions. As more and more reactive flow is captured due to the enhancement of the local permeability, the reaction fingers accelerate their growth up to the point where diffusion homogenizes the concentration gradients within the reaction finger, or the flow rates outrun the rates of reaction. In fact, the reactive-infiltration instability requires a transport control within the growing fingers, with flow at low Damköhler number (surface reaction control) resulting in slower channel growth and more highly ramified dissolution patterns (Steefel and Lasaga, 1990).

Figure 11.20 shows a simulation illustrating the effect of reaction kinetics on reaction fingering. The simulation uses the heterogeneous permeability field shown in Fig. 11.9a, but in this case with a total initial permeability range of 4 orders of magnitude (10^{-16} – 10^{-12} m², with an average of 10^{-14} m²) and with 10% reactive calcite in a rock with an initially uniform porosity of 2%. The complete dissolution of the calcite leads to an increase in porosity up to 12% and to an increase in permeability by a factor of about 300 according to

$$\kappa = \kappa_0 \left(\frac{\phi}{\phi_0} \right)^3, \quad (11.87)$$

where κ_0 and ϕ_0 are the initial permeability and porosity, respectively. Figure 11.20a shows the results of a simulation in which the rate constant for the calcite is taken as $10^{-6.5}$ mol m⁻² s⁻¹ and an initial reactive surface area of 100 m²/m³—in this case, the pore fluid at the tip of the propagating “wormholes” is close to equilibrium, with the result that the rate of advance of the fingers is transport controlled. Very fine, tortuous wormholes form as a gradual shift to a smaller number of more rapidly propagating fingers occurs at the expense of nearby, more slowly propagating fingers. In contrast, when the rate constant is taken as $10^{-10.5}$ mol m⁻² s⁻¹ (or 4 orders of magnitude slower), the contrast between the rate of growth of individual

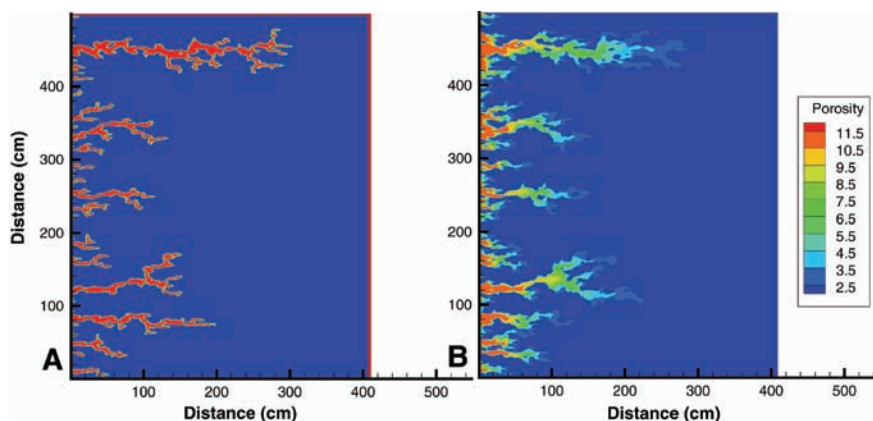


Fig. 11.20 The reactive-infiltration instability results in “wormholing”, as regions experiencing an increase in porosity and permeability as a result of mineral dissolution accelerate their growth at the expense of adjacent regions. The wormholing rate is at a maximum under transport-controlled conditions (Panel A) – at lower Damköhler numbers (Panel B), fingers are more diffuse and the difference between the growth rates of individual fingers is less.

reaction fingers is less, and the pattern of dissolution is more highly ramified and diffuse.

11.6.2 Liesegang Banding

Liesegang banding or rings are often noted in subsurface materials, although the phenomenon has received more discussion in the chemical literature (Liesegang, 1896). In the classic theory, the phenomenon occurs in the absence of convection and involves the interdiffusion of reacting species (e.g., O_2 and ferrous iron) that precipitate in discrete bands separated in many cases by geometrically increasing spacing. The earliest explanation for the phenomenon was provided apparently by Ostwald, who suggested that the process involved local nucleation of crystal seeds where the necessary level of supersaturation was achieved. Once nucleation of crystal seeds occurs, crystal growth is assumed to become the dominant form of mass transfer, thus lowering the supersaturation of the local pore fluid (and adjacent regions influenced by molecular diffusion) below the nucleation threshold. The result is that secondary mineralization only develops in discrete zones or bands. This theory has been disputed based on experimental studies in which colloidal seed material was initially dispersed uniformly in the reacting material and yet banding still developed. Other models in which nucleation is coupled to Ostwald ripening have been suggested (Ortoleva et al., 1986). The nucleation/crystal growth hypothesis may be reasonable for water–rock systems, however, as in the case of discrete bands of iron hydroxide developed in sandstone (Fig. 11.21). Similar patterns may develop in

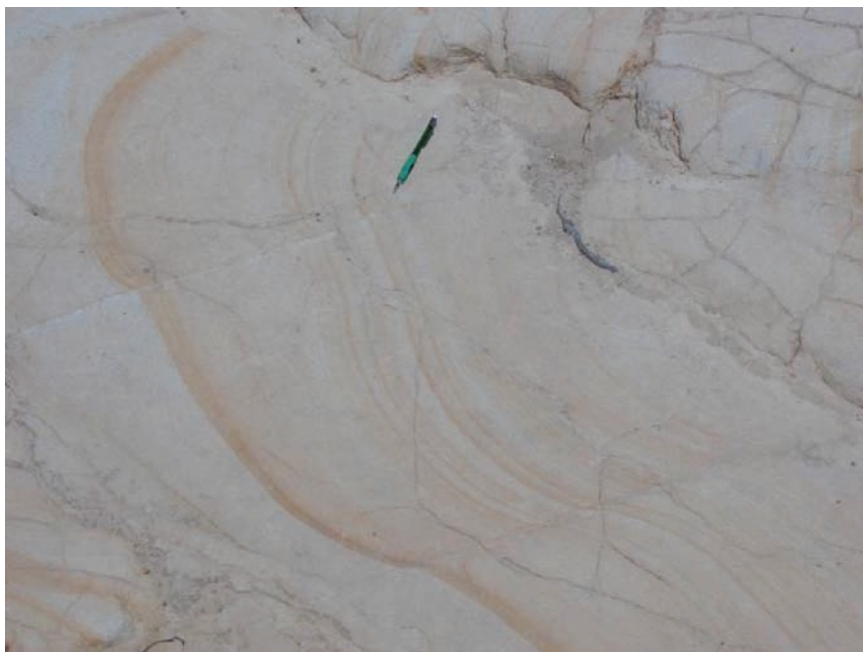


Fig. 11.21 Liesegang bands of ferric hydroxide in sandstone from Mount Diablo, California.

advection-dominant systems as a result of a nucleation/crystal growth mechanism, as shown by (Steefel and Van Cappellen, 1990).

11.7 Concluding Remarks

A good understanding of the coupling between transport and biogeochemical kinetics is essential in the study of water–rock interaction. In this chapter, we have shown that in open systems characterized by transport, the characteristic time scales of reaction need to be compared with the characteristic time scales for transport—geologic time is often irrelevant. The transport processes that are relevant for the study of water–rock interaction include advection, due in most cases to Darcy flow through porous media, molecular diffusion modified by electrochemical migration where charged species are present, and hydrodynamic dispersion. An idealized version of the reactive transport (or advection-dispersion-reaction) equation was presented and the important non-dimensional quantities were derived and discussed in terms of their control of water–rock interaction. Most significant of these for the discussion of the kinetics of water–rock interaction is the Damköhler number, which provides a measure of the importance of reaction kinetics relative to the transport rates in a particular system. The same quantity can be used to determine

approximately the length scale over which equilibrium can be reached and thus provides a useful metric for the validity of the local equilibrium assumption.

The treatment of water–rock interaction systems as well-mixed reactors is challenged and it was shown how an analysis of macrodispersion, which has been widely discussed in the hydrologic literature, can be used to produce a residence time probability density function that predicts the ensemble of reaction times for flow paths through heterogeneous media. Real water–rock systems are typically characterized by physical, chemical, and microbiological heterogeneities that can give rise to concentration gradients, and thus to spatially variable reaction rates. Upscaling reaction rates in water–rock systems that are not perfectly mixed is a new research challenge and will require a careful consideration of the interplay between transport and reactions at multiple scales. Methods for determining *in situ* reaction rates using concentration profiles and mineral volume profiles combined with reactive transport modeling were briefly presented. It was shown that it is necessary to independently determine transport rates in a particular water–rock system in order to uniquely determine *in situ* reaction rates. Finally, two examples of water–rock interaction were given where the feedback between transport and reaction results in pattern formation.

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