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Flow-controlled reactions in rock fabrics

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The percolation of fluids through rock fabrics or through fracture networks, continued over millions of years, is associated with selective dissolution, cementation, fabric alteration in metamorphosis and the formation of certain massive ore deposits in specific locations. The degree of mineral alteration and its spatial distribution are both controlled by the patterns of interstitial flow and three distinct types of flow-controlled reactions are reviewed and analyzed. Isothermal reaction fronts propagate from mineralogical boundaries in the direction of flow at a speed proportional to but less than the fluid transport velocity; their occurrence can be recognized in banded or bimodal mineralogical patterns. Gradient reactions occurs pervasively throughout a fabric at rates proportional to the temperature and pressure gradients and the fluid velocity; they produce gradually changing mineral assemblages throughout, though their rates of reaction are greatest in high permeability lenses and in thermal boundary layers. Mixing zone reactions occur when two fluid masses intermingle and are usually highly localized. In each case, simple but general analytical expressions are given that express the rates of reaction in terms of the flow and geochemical variables.

1. Introduction

The development of geochemistry in the past fifty years has led to the clarification of many aspects of metamorphism, the transformation of minerals from one form to another at depth under conditions of high temperature and pressure. Yet a number of mysteries have remained. Natural processes are, in the large, dispersive as the second law of thermodynamics insists. How is it that local concentrations of minerals aggregate deep inside the Earth, leading to economically valuable resources? The Mississippi Valley lead-zinc deposits were clearly formed subsequently to the lithification of the host rock, its conversion from a sediment to a sedimentary rock, but where did they come from, how did they get there, why did they deposit where they did and not somewhere else? The formation of dolomite from limestone requires the importation of large quantities of magnesium; in these and other geochemical processes there is the evident need to account for the transport of minerals, presumably dissolved, through existing assemblages in quantities much larger than can be associated with compaction of a fluid-saturated matrix and at rates much faster than can be produced by diffusion. It is only fairly recently that the idea has gained acceptance that these chemical transports must be associated with fluid flow through rocks that a hydrologist may consider as hardly permeable, over time intervals of millions or hundreds of millions of years. If non-hydrostatic pressure gradients or bouyancy forces are present, the latter usually associated with horizontal temperature gradients, interstitial fluid may flow through the matrix if it is reasonably permeable or along cracks and micro-fractures if it is less so. The patterns of dissolution, precipitation and fabric alteration depend on the reaction kinetics and the influence on them of temperature, pressure or other dissolved constituents. In many geological situations, however, the controlling factor is the rate at which reactants in solution can be delivered to the reaction site by advection and diffusion in the flow. In these flow-controlled reactions, then there are two sets of balances to be considered – the chemical balances that specify the nature of the reactions and the physical balances that specify the transports, sources and sinks.

For example, the replacement of calcium ions by magnesium in a calcite bed to form dolomite can be represented by the chemical balance

$$\underset{\text{Calcite}}{2\mathrm{CaCO_3}} + \mathrm{Mg^{2+}} \Leftrightarrow \underset{\text{Dolomite}}{\mathrm{CaMg(CO_3)_2}} + \mathrm{Ca^{2+}}; \tag{1.1}$$

but the extent to which the reaction proceeds depends on the delivery of magnesium ions to the reaction site and the removal from it of calcium ions by dissolved interstitial fluid. If c represents the concentration of dissolved magnesium ions in the interstitial fluid (moles per unit fluid volume), the corresponding physical balance for the dissolved magnesium in unit volume of the *fabric* can be represented as

$$\phi \frac{\partial c}{\partial t} + \nabla \cdot (\boldsymbol{u}c) - \phi D \nabla^2 c = \phi Q_c, \tag{1.2}$$

where ϕ is the porosity, the fraction (assumed here to be constant) of the fabric volume occupied by moving fluid, $\boldsymbol{u}$ the transport velocity, the fluid volume flux across unit area of the *fabric*, D the appropriate diffusivity in the fluid, which may be molecular or what is termed 'macroscopic', the result of fluid meandering and dispersing along different pathways (which occurs only in the fluid-filled fraction ϕ) and Q_c is the rate of addition by chemical reaction of the species per unit volume of the fluid (here negative if the reaction (1.1) moves to the right). Alternatively,

$$\frac{\partial c}{\partial t} + \phi^{-1} \nabla \cdot (\boldsymbol{u}c) - D \nabla^2 c = Q_c. \tag{1.3}$$

In this form, it is evident that fluctuations in concentration are advected through the fabric with the interstitial fluid velocity $\phi^{-1}\boldsymbol{u}$, which is considerably larger than the transport velocity $\boldsymbol{u}$ in rocks whose porosity is characteristically small.

The source term Q_c is determined as a function of the interstitial fluid concentration, temperature, pressure and concentrations $c_1, c_2, \ldots$ of other ions etc. by the detailed chemical kinetics, and may generally be represented as

$$Q_c = \gamma c_e f\left(r, \frac{c_e - c}{c_e}\right) = \gamma c_e f(r, b), \tag{1.4}$$

where $c_e = c_e(T, p, c_1, c_2, \ldots)$ is the equilibrium concentration in the fluid, r the mass fraction of mineral undergoing reaction, $b = (c_e - c)/c_e$ can be called the degree of disequilibrium and γ is the reaction rate. Clearly $f = 0$ when $c = c_e$ and $b = 0$. Without loss of generality, we can take $\partial f/\partial b = 1$ when $b = 0$; this merely fixes the numerical value of γ which is otherwise arbitrary. In many mineralogical reactions, the form of the function f and even the reaction rate γ is known poorly if at all, but fortunately, as we shall see, its detailed nature is almost irrelevant in flow-controlled reactions. As magnesium ions in the reaction (1.1) are consumed at the rate $-\phi Q_c$ moles per unit volume of the fabric, the same number of moles of dolomite per unit volume is produced, so that if s is the number of moles of dolomite present, since it is immobile,

$$\frac{\partial s}{\partial t} = -\phi Q_c. \tag{1.5}$$

It will be seen below that there are three distinct types of flow-controlled reactions that have associated with them distinct patterns of fabric alteration, whether dissolution, cementation or mineralization. The first, described by Lichtner (1985, 1988) and others with varying degrees of clarity, involves the propagation of reaction fronts through the matrix at speeds proportional to the transport velocity, in which the reaction goes essentially to completion. In a fabric of variable permeability, this leads to a banded or layered pattern of mineral alteration or a veining in minerals such as marble. These fronts arise at mineralogical boundaries and progress inwards as long as the flow continues. Quite different are what might be called gradient reactions identified by Wood & Hewett (1982) which occur throughout the fabric as interstitial fluid, always close to local equilibrium with its mineralogical surroundings, moves across isotherms or isopycnals. As $c_e(T, p, \ldots)$ changes along the streamlines, reactions occur to maintain the interstitial fluid concentration close to equilibrium; the proportion of solid minerals undergoing reaction gradually changes in response. The signature of this kind of reaction is a more diffuse distribution of mineral assemblages in varying proportions rather than the more bimodal product of essentially isothermal reaction fronts. Different again are mixing-zone reactions, which occur when interstitial fluids of two different compositions intermingle as in a coastal salt wedge along a permeable shoreline that lies underneath a fresh water aquifer. A specific instance of this has been modelled numerically by Sandford (1987); a simple and general analytical description is given in §5 below.

These reaction types may of course occur simultaneously in different parts of the same geological fabric and the distributions of fabric alteration, mineral dissolution and ore deposition depend on the distributions of flow (and its time history over the millennia or eons involved) and, in the case of gradient reactions, on the direction of flow relative to the internal temperature and pressure gradients. The aim of this paper is not to provide solutions for any particular basin or structure, but to give simple quantitative insights that can guide geological interpretation in a variety of contexts. Some preliminary applications of this approach are outlined in §6.

2. The approach to equilibrium at mineralogical boundaries

When interstitial fluid enters a matrix from an adjacent water body or moves across a mineralogical boundary, the concentration of dissolved species moves towards a local equilibrium with the solid phase, but the extent of the region of disequilibrium and the spatial distribution of the mineralogical changes that can result, depend on the speed of flow, the reaction rates and the solute diffusivity. The relationships among these quantities can, in fact, be used in field situations to constrain possible values of the least certain of them (frequently the reaction rate) as well as to provide criteria under which local equilibrium between the fluid and the matrix would or would not be expected.

Let us first consider the dissolution or reaction of a major constituent of a rock fabric (say calcite in a limestone bed) when water, unsaturated with respect to the dissolving species, enters the fabric across a sharp interface. We shall assume here that the time over which the reaction has continued is not so large that the cumulative effect has caused substantial changes in either the porosity or mass per unit volume of the solid undergoing reaction, so that the influence of the mass fraction r in the equations of §1 can be ignored. Quantitative upper limits for this timescale are given later.

In a frame of reference with the x-direction normal to the mineralogical boundary and directed into the matrix, the concentration c of ions in the interstitial fluid generated by reaction is specified by (1.3), or in terms of $b = (c_e - c)/c_e$ by

$$\frac{\partial b}{\partial t} + \phi^{-1} u \frac{\partial b}{\partial x} - D \frac{\partial^2 b}{\partial x^2} = -\gamma f(b), \tag{2.1}$$

where u is the velocity component normal to the interface. A steady distribution of concentration of the interstitial fluid is reached in a time of order γ^{-1} (short on a geological timescale if the reactions are to be of interest) so that the first term in (2.1) can be ignored and the distribution $b = b(x)$ is specified by

$$\phi^{-1} u \frac{\partial b}{\partial x} - D \frac{\partial^2 b}{\partial x^2} = -\gamma f(b). \tag{2.2}$$

At the interface $x = 0$, $b = b_0$, say, determined by the ionic concentration of the incoming fluid; if this is zero, $b_0 = 1$. Far from the interface, the interstitial fluid eventually attains equilibrium so that $b \to 0$ as $x \to \infty$. In general, $1 \geqslant b_0 \geqslant b \geqslant 0$.

Now, the rate of generation of ions in the reaction is in (2.2) balanced by the rate at which they are swept away by advection (represented by the first term) or by the rate of diffusion (the second) or by both at comparable rates. Note that $f(b)$ is not generally equal to but is of the order of b, so that relative to the dissolution term, the respective orders of magnitude of the other terms are

$$\frac{u}{\phi \gamma l_e}, \quad \frac{D}{\gamma l_e^2}, \quad 1; \tag{2.3}$$

where l_e is the differential lengthscale in the equation, or the lengthscale over which equilibrium is approached. Now, if

$$\frac{u}{\phi \gamma l_e} \gg \frac{D}{\gamma l_e^2} \quad \text{or} \quad u \gg \frac{\phi D}{l_e}, \tag{2.4}$$

the diffusion term is minor and the balance must be found between dissolution and advection, so that $u/\phi\gamma l_e \sim 1$ and

$$l_e \sim u/\phi\gamma. \tag{2.5}$$

The equilibration length l_e is then the distance that the solute moves at the interstitial fluid velocity u/ϕ through the matrix in the reaction time γ^{-1}. The condition under which this interpretation is valid is found by substitution of (2.5) in (2.4), namely

$$u \gg \phi (D\gamma)^{\frac{1}{2}}. \tag{2.6}$$

On the other hand, if $u \ll \phi D/l_e$, the balance in (2.2) is between the last two terms, and in (2.3) $D/\gamma l_e^2 \sim 1$; advection is negligible and the dissolving ions are removed by diffusion. The equilibration length is then

$$l_e \sim (D/\gamma)^{\frac{1}{2}}. \tag{2.7}$$

In this circumstance, the equilibration length can be interpreted as the diffusion distance $(Dt)^{\frac{1}{2}}$ in the reaction time $t = \gamma^{-1}$. Finally, when $u \approx \phi(D\gamma)^{\frac{1}{2}}$, advection and diffusion are both important and the expressions (2.5) and (2.7) become identical in order of magnitude.

This length also of course expresses the distance from the interface over which the mineral alterations have occurred as a result of the reaction. As long as the reacting mineral remains a major constituent of the fabric, the rate of increase of any solid product of the reaction is given by

$$\frac{\partial s}{\partial t} = \phi\gamma c_e f(b), \tag{2.8}$$

where s represents the number of moles of the immobile mineral per unit volume of matrix. This is greatest at the interface where $f(b)$ is of order unity and decreases to zero beyond the equilibration distance since $b \to 0$ and $f(b) \to 0$. After a time t_r the molar concentration of reaction product near the interface is of order $\phi\gamma c_e t_r$. If r represents the number of moles per unit fabric volume of the initial mineral undergoing reaction, the condition that r has not changed much is that $\phi\gamma c_e t_r \ll r$ or that the time of reaction

$$t_r \ll (\phi\gamma)^{-1}\left(\frac{r}{c_e}\right). \tag{2.9}$$

When the original mineral constitutes a substantial fraction of the matrix, the solid molar fraction r is generally larger than the molar interstitial fluid concentration c_e by many powers of ten, so that these distributions persist for times enormously longer than the reaction time γ^{-1}. When, finally, the original mineral approaches depletion, a reaction front develops as described in the next section.

Numerical values of the equilibration length can vary widely as a result of the wide range of reaction and flow rates encountered in different situations. For example, suppose that the fluid velocity $u \sim 10^{-6}$ cm s^{-1} = 30 cm/yr and the diffusivity $D = 10^{-5}$ cm^2 s^{-1} in a rock with porosity $\phi = 0.2$. For a fairly slow reaction, $\gamma \sim 10^{-10}$ s^{-1}, the equilibration length is advectively determined and is of order 500 m. For a faster reaction, $\gamma \sim 10^{-6}$ s^{-1}, say, it is only a few centimetres.

These considerations have required only very general information on the form of the source function f in (2.1), so that the concept of equilibration length and the relations defining it are independent of the detailed kinetics. In the particular case of a first-order reaction in which $f = b$, the distribution of b is simply exponential:

$$b = b_0 \exp(-x/l_e),$$

where

$$l_e = \left\{\frac{u}{2\phi D} - \left[\left(\frac{u}{2\phi D}\right)^2 + \frac{\gamma}{\phi D}\right]^{\frac{1}{2}}\right\}^{-1}, \tag{2.10}$$

which reduces to (2.5) and (2.7) in the appropriate limits.

3. Isothermal reaction fronts

If the flow and reaction continue for a time interval of order $(\phi\gamma)^{-1}(r/c_e)$ or larger, the original mineral undergoing reaction becomes depleted near the interface. When it is depleted entirely, the reaction cannot of course continue and the fluid concentration of dissolved solute remains at its entering value until it reaches a position further downstream where unaltered mineral is present and reaction occurs. As a result, the zone of reaction gradually moves downstream, leaving behind the solid product. The solute resulting from the reaction is carried away downstream so that, if the flow ceases, the reaction does not reverse and the pattern remains.

Although, as we shall see, many important aspects of these reaction fronts are independent of the detailed reaction kinetics, their initial formation and propagation can be illustrated by a numerical calculation in which the reaction kinetics is (necessarily) prescribed. Suppose for the purpose of this illustration that no water is produced by the reaction itself, and that the source of solute per unit volume is bilinear in the degree of disequilibrium b and the number of moles s per unit volume of the reacting solid at a point as a fraction of the number of moles initially present, s_0, say. Thus

$$Q_c = \gamma(c-c_e)(s/s_0) = \gamma c_e bS,$$

where $S = s/s_0$ and $b = (c_e-c)/c_e$. When the x-direction is chosen normal to the interface at $x = 0$ and u is the component of the transport velocity in this direction, we have, from (2.1),

$$\frac{\partial b}{\partial t}+\phi^{-1}u\frac{\partial b}{\partial x}-D\frac{\partial^2 b}{\partial x^2} = -\gamma bS. \tag{3.1}$$

For the solid reactant, if n_s is the number of moles of solid consumed per mole of solute produced,

$$\frac{\partial S}{\partial t} = -\left(\frac{n_s\phi\gamma c_e}{s_0}\right)bS. \tag{3.2}$$

Imagine that the fluid starts moving through the matrix at time $t = 0$ so that initially $S = 1$ throughout. The incoming fluid has $c = 0$ at $x = 0$ (so that $b = 1$) and far from the interface it is in equilibrium with the matrix so that $c = c_e$ and $b = 0$.

The simultaneous solution of the coupled nonlinear equations (3.1) and (3.2) specifies the evolution of the distribution $s(x,t) = s_0 S(x,t)$ of the solid reactant and that of the concentration $c(x,t)$ or the degree of disequilibrium of the interstitial fluid. The equations can be rewritten in a form suitable for computation by taking as a timescale the quantity $(n_s\phi\gamma)^{-1}(s_0/c_e)$ (cf. (2.9)) and as a lengthscale the advective equilibration length $l_e = u/\phi\gamma$. With

$$t = (n_s\phi\gamma)^{-1}(s_0/c_e)\tau, \quad x = l_e\xi = (u/\phi\gamma)\xi,$$

the equations reduce to

$$\left.\begin{aligned}\left(\frac{n_s\phi c_e}{s_0}\right)\frac{\partial b}{\partial \tau}+\frac{\partial b}{\partial \xi}-\left(\frac{D\phi^2\gamma}{u^2}\right)\frac{\partial^2 b}{\partial \xi^2} &= -bS,\\ \frac{\partial S}{\partial \tau} &= -bS.\end{aligned}\right\} \tag{3.3}$$

In this pair of dimensionless equations, the terms without coefficients are numerically of order unity. The diffusion term is small under the condition (3.6); the quantity $\phi c_e/s_0$, representing the ratio of the number of moles in solution at equilibrium in the interstitial flow to the number of moles of solid reactant initially present, is also tiny. Neither of these terms has any perceptible influence on the numerical solutions.

The evolving patterns, calculated from (3.3) are shown in figure 1; fluid crosses the interface at $x = 0$ from the left and the curves represent the profiles of s/s_0 and c/c_e after equal time intervals $(s_0/n_\phi \gamma c_e)$. Initially, $s = s_0$ throughout and the interstitial fluid concentration c attains its equilibrium value c_e within a distance of order l_e as described in §2. As the solid reactant is depleted near the interface, the distribution of c flattens; by the time $\tau = 3$ or 4, the solid reactant is in essence zero at the interface and both profiles have assumed an elongated S-shape which then moves through the matrix to the right without further change in shape. The thickness of the front is a few times the equilibration length l_e; it moves a distance l_e in the time interval $\tau = 1$ so that its speed

$$U = \frac{u}{\phi\gamma}\frac{n_s\phi\gamma c_e}{s_0} = un_s\left(\frac{c_e}{s_0}\right), \tag{3.4}$$

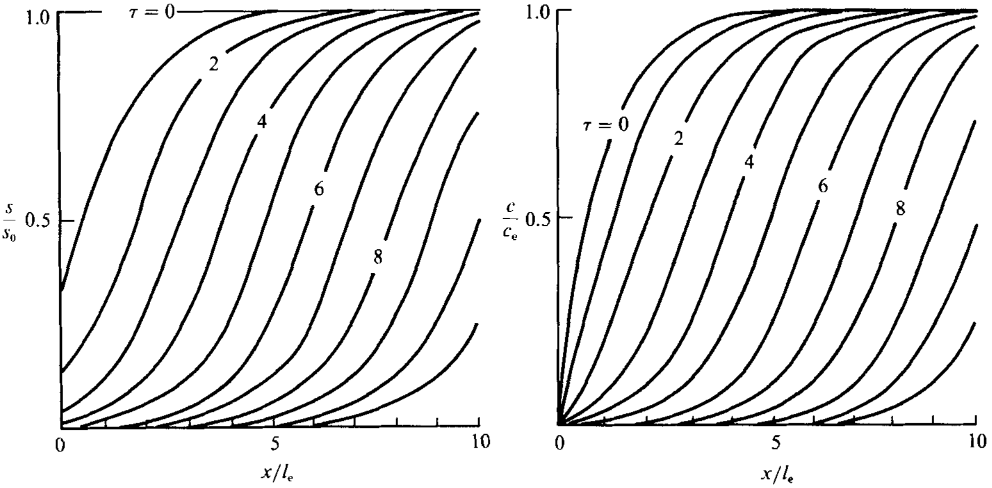

FIGURE 1. The development of an isothermal reaction front. Initially, at time $\tau = 0$ the concentration s of mineral is uniform and the interstitial fluid approaches equilibrium with the mineral over the equilibration length l_e. Profiles are shown for equal time intervals $s_0/n_s \phi \gamma c_e$; by the time $\tau = 2$ the solid mineral is becoming seriously depleted near the interface and by $\tau = 4$ the depletion is virtually complete. The profiles of c/c_e and s/s_0 have become almost identical and they subsequently move away to the right without further change in shape as the reaction front propagates through the fabric.

which is independent of the reaction rate γ. The steadily propagating profiles that develop can be found analytically from (3.3) with the bracketed terms neglected:

$$\frac{c}{c_e} = \frac{s}{s_0} = \left\{1 - \exp\left[\frac{-\phi\gamma(x-Ut)}{u}\right]\right\}^{-1}, \tag{3.5}$$

where U is given by (3.4). These appear in figure 1 when τ is greater than about 4.

The propagation of a reaction zone or front can be described more generally without the specification of the reaction kinetics involved in this numerical example, just as the propagation of a shock wave can be calculated without consideration of its internal structure. In many reactions, water is produced or consumed so that

$$\nabla \cdot \boldsymbol{u} = \frac{\partial u}{\partial x} = \phi n_w V Q_c, \tag{3.6}$$

where n_w is the number of moles of fluid generated per mole of solute and V is the fluid molar volume. Since Q_c is a function only of c and s at any particular temperature and pressure, (1.3), (1.5) and (3.6) allow solutions of the form

$$c = c(x-Ut), \quad s = s(x-Ut), \tag{3.7}$$

representing distributions that move through the matrix with speed U to be determined. Substitution of (3.7) leads to

$$u' = \phi n_w V Q_c, \quad -Uc' + \phi^{-1}(uc)' - Dc'' = Q_c, \quad Us' = n_s \phi Q_c, \tag{3.8}$$

where the primes denote differentiation with respect to the variable $(x-Ut)$. Far upstream of the reaction zone, the concentration c of the dissolved solute is whatever it happened to be in the entering fluid, c_0, and the (less abundant) mineral has already been consumed, so that $c \to c_0$, $s \to 0$, $u \to u_0$ when $\xi = (x-Ut) \to -\infty$. Downstream of the reaction zone, the solute is in equilibrium and the mineral is unconsumed so that $c \to c_e$, $s \to s_0$, its initial value, and $u \to u_1$, the inflow velocity augmented by any fluid generated in the reaction.

The equations (3.8) can be integrated across the reaction zone to obtain overall balances, and with the use of these conditions, it appears that

$$u_1 - u_0 = \phi n_w V \mathscr{Q}, \quad -U(c_e - c_0) + \phi^{-1}(u_1 c_e - u_0 c_0) = \mathscr{Q}, \quad s_0 = \phi(n_s/U)\mathscr{Q}, \tag{3.9}$$

where

$$\mathscr{Q} = \int Q_c \,\mathrm{d}\xi, \tag{3.10}$$

the total rate of production of solute per unit area of the reaction zone normal to the flow. The elimination of $\mathscr{Q}$ and u_1 from the set (3.9) gives for the speed of front propagation

$$\frac{U}{u_0} = \frac{c_e - c_0}{\phi(c_e - c_0) + (s_0/n_s)(1 - n_w V c_e)}, \tag{3.11}$$

or, when $s_0 \gg n_s \phi c_e$,

$$\frac{U}{u_0} = \frac{n_s(c_e - c_0)}{s_0(1 - n_w V c_e)}. \tag{3.12}$$

This simplifies further when the rate of generation of fluid in the reaction is zero or can be neglected. Then $n_w = 0$ and we recover (3.4):

$$\frac{U}{u_0} = \frac{n_s \Delta c}{s_0}; \tag{3.13}$$

the propagation speed of the reaction zone is smaller than the flow velocity by the ratio of the change in molar concentrations of the interstitial fluid to the initial concentration of the reacting mineral, then multiplied by the number of moles of solid consumed per mole of solute produced.

The fluid–rock ratio r in these reactions is defined as the volume of fluid with which unit volume of rock reacts. In a time interval $\mathrm{d}t$ the reaction zone moves ahead a distance $U\,\mathrm{d}t$ and the volume of fluid moving into it is $(u_0 - U)\,\mathrm{d}t$ so that

$$r = \frac{u_0}{U} - 1. \tag{3.14}$$

Equivalently

$$\frac{U}{u_0} = \frac{1}{r+1}.$$

The fluid–rock ratio can be expressed from (3.12) as

$$r = \frac{s_0(1 - n_w V c_e)}{n_s(c_e - c_0)} - 1 = \left(\frac{\phi \mathscr{Q}}{U}\right)\frac{1 - n_w V c_e}{c_e - c_0} - 1.$$

Now $\phi \mathscr{Q}\,\mathrm{d}t$ represents the total production of volatile solute in the zone in the time interval $\mathrm{d}t$ and the volume of reaction is $U\,\mathrm{d}t$ so that $\phi \mathscr{Q}/U$ represents the number of moles n_v of volatile species released per unit volume of rock during metamorphosis and

$$r = \frac{n_v(1 - n_w V c_e)}{c_e - c_0} - 1, \tag{3.15}$$

which is equivalent to the expression given by Ferry (1987). If, during a certain time interval t, the reaction front moves a distance $d = Ut$, the total volume of interstitial fluid that has crossed unit area of the fabric over this time interval is $u_0 t = (r+1)\,d$.

If the time over which the reaction has proceeded can be estimated and the distance of propagation measured, the fluid-to-rock ratio provides a local meter for the interstitial flow.

4. Gradient reactions

As fluid moves into a fabric or from one mineral assemblage to another, beyond the equilibration length l_e it is close to equilibrium with the new assemblage at the ambient pressure and temperature. If, however, these variables change along the flow path, the equilibrium concentration also changes so that, even though the composition of interstitial fluid may remain the same in time at each point, it varies along the flow trajectory so that solute is continually being added to or taken from solution. As a consequence, the mineral composition is gradually altered along the flow path. In general, the equilibrium concentration of the interstitial fluid $c_e = c_e(T, p, c_1, c_2 \ldots)$, where c_1, c_2, etc. express the dissolved concentrations of other species (including hydrogen ions) that may influence the reaction, and is specified by the chemistry, not the flow. It was realized by Wood & Hewitt (1982) that the fluid concentration balance equation then becomes a prescription for the source terms, the rate of addition of species to the solution (number of moles per unit volume of the fabric per unit time) needed to maintain the equilibrium at all points in the moving fluid:

$$\phi Q_c = \boldsymbol{u} \cdot \nabla c_e - \phi D \nabla^2 c_e. \tag{4.1}$$

As was shown earlier, the macroscopic dispersion coefficient is of the order $\phi^{-1} u l_0$ where l_0 is the grain size which is *very* much smaller than the distances l over which the temperature and the pressure vary significantly, so that in these situations, dispersive effects are quite negligible. Accordingly,

$$\begin{aligned} \phi Q_c &= \boldsymbol{u} \cdot \nabla c_e\,(T, p, c_1, c_2 \ldots) \\ &= \boldsymbol{u} \cdot \left\{ \frac{\partial c_e}{\partial T} \nabla T + \frac{\partial c_e}{\partial p} \nabla p + \sum_r \frac{\partial c_e}{\partial c_r} \nabla c_r \right\}, \end{aligned} \tag{4.2}$$

from the chain rule for partial differentiation. The summation is over whatever other species $r = 1, 2 \ldots$ that influence the equilibrium. Even though the total fluid pressure may be close to lithostatic, the local *gradient* in total pressure in a connected region is primarily hydrostatic so that

$$\boldsymbol{u} \cdot \nabla p = -\rho g \boldsymbol{l} \cdot \boldsymbol{u} = -\rho g w,$$

where $\boldsymbol{l}$ is a vertical unit vector and w the vertical component of transport velocity. The last term, involving the concentration gradients of other solutes, can be simplified considerably. If they do not enter the reaction (but may be purely inhibitory), their concentration remains the same along the flow path and this term vanishes. If any of them do, then a species balance can be written for this species with a source term equal to $-\phi Q_c$ times the number of moles consumed per mole of the solute (4.1) generated:

$$\boldsymbol{u} \cdot \nabla c_r = -m_r \phi Q_c$$

and the rate of mineralization $Q_m = -\phi Q_c$ becomes

$$Q_m = -\left\{ 1 + \sum_r m_r \left(\frac{\partial c_e}{\partial c_r} \right) \right\}^{-1} \left\{ \left(\frac{\partial c_e}{\partial T} \right) \boldsymbol{u} \cdot \nabla T - \left(\frac{\partial c_e}{\partial p} \right) \rho g w \right\}. \tag{4.3}$$

Several comments should be made concerning these expressions. At first sight, surprisingly, the rate at which reaction or dissolution or precipitation occurs is independent of the chemical kinetics, provided only that the reaction rate is sufficiently rapid to make the equilibration length small compared with the size of the region. The determining factor is physical – the rate at which fluid moves through the system, the variation in fluxes of species into and out of each volume element of the matrix. In gradient reactions, the interstitial fluid is close to equilibrium with the mineral assemblage, and the chemical kinetics, specifically the reaction rate, only determine *how* close – the small degree of disequilibrium is needed to provide for the reaction. The faster the reaction rate, the closer to equilibrium. Note that Q_c represents the rate of addition of species to the solution so that in dissolution, $Q_c > 0$ and in precipitation $Q_c < 0$.

Many experimental values for the variation of saturation solubilities with temperature and pressure are given in the *International Critical Tables* (Washburn 1929) and by Barnes (1979). For most mineral assemblages $\partial c_e/\partial T > 0$ and the effect of the temperature-gradient term in (4.3) is usually larger than that of the pressure-gradient term, so that, for a given mineralogy, the quantity $\boldsymbol{u}\cdot\nabla T$ can be taken as a useful index of rock alteration. In the case of dissolved silica, for example, both $(\partial c_s/\partial T)$ and $(\partial c_e/\partial p)$ are positive so that in a rising fluid, moving down both the temperature and pressure gradients, $Q_m > 0$ and quartz is precipitated either in the matrix or along microcracks as veinlets. In the calcite dissolution reaction

$$CaCO_3 + CO_2 + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^-,$$

(4.3) specifics the rate of formation of solid mineral (negative in dissolution); CO_2 in solution is produced when calcite is deposited and Ca^{2+} is depleted. The term $\partial c_e/\partial c_1$ represents the variation in equilibrium concentration of Ca^{2+} ions with concentration of dissolved CO_2 and, since the equilibrium concentration is smaller when CO_2 is depleted, $\partial c_e/\partial c_1 > 0$ and the first factor in (4.3) is smaller than unity. Calcite is, however, anomalous in that the equilibrium concentration decreases with increasing temperature – $\partial c_e/\partial T < 0$. With a partial pressure of CO_2 of 1 atmosphere and at 100 °C, $\partial c_s/\partial T \sim -4\times10^{-6}\,°C^{-1}$ (Barnes 1979). The term $\partial c_s/\partial p$ is positive but its magnitude is insufficient to overcome the increase in solubility of a rising fluid moving down the geothermal temperature distribution. Calcite dissolution then occurs in a rising fluid, deposition or cementation in fluids moving downwards. The rate of reaction is in any event proportional to the flow speed so that the rates of fabric alteration are greatest when the flow is concentrated by sloping lenses or layers of relatively high permeability.

A few simplifications to (4.3) are appropriate in particular circumstances. When the multiplicative factor is simply unity and the isotherms are horizontal, $\boldsymbol{u}\cdot\nabla T = -wG$ where w is the vertical component of the transport velocity and $G = -\partial T/\partial z$ the geothermal gradient. Equation (4.3) then becomes

$$Q_m = w\left\{G\left(\frac{\partial c_e}{\partial T}\right) + \rho g\left(\frac{\partial c_e}{\partial p}\right)\right\}. \tag{4.4}$$

Over a given time interval, the total number of moles of mineral deposited by the reaction per unit volume of the matrix is therefore

$$M = V\left\{G\left(\frac{\partial c_e}{\partial T}\right) + \rho g\left(\frac{\partial c_e}{\partial p}\right)\right\}, \tag{4.5}$$

where V is the total volume of fluid per unit area that has moved vertically through the matrix in this time interval. If two different reactions are proceeding simultaneously, the rates of number of moles deposited of each is the ratio of the respective factors on the right of (4.5).

In summary, in gradient reactions the interstitial fluid remains close to equilibrium with the suite of minerals in the surrounding fabric, but as time goes by, the relative abundance of these minerals alters, some increasing and some decreasing as the reaction continues. The process is ubiquitous, occurring throughout those parts of the fabric where the fluid flow crosses isotherms or isobars. As long as all the minerals are present, the interstitial solution is buffered at this equilibrium value for the ambient temperature and pressure. However, if, locally, one of the minerals involved in the reaction, say S_1, disappears entirely, the interstitial fluid there moves to a new equilibrium among the remainder of the minerals present. As this fluid moves into an adjacent region where S_1 is not yet depleted, a reaction front will develop between the now distinct mineralogical regions and start to propagate as described in the previous section.

When the Péclet number of a hydraulically driven flow or the Rayleigh number of a convective flow is large, however, as in an active geothermal area, the isotherm pattern is substantially modified by the flow. In interior regions the temperature becomes almost constant along the streamlines and $\boldsymbol{u}\cdot\boldsymbol{\nabla}T \approx 0$, so that gradient reactions are produced predominantly by the variation of c_e with pressure p as fluid moves across isobars. Reactions associated with the variation of c_e with temperature T then tend to be confined to regions near the boundaries of a permeable domain and particularly near the surface where fluid may rise through the water table down a geothermal gradient that is locally large.

When the reaction rates are so slow or the flow speeds so rapid that the equilibration length l_e is large compared with the lengthscale l of the flow, the concentration of that species does not change much from the initial value (c_0) in the fluid entering the region and will remain either unsaturated or supersaturated throughout. The reaction rate

$$Q_c = \gamma c_e f\left(\frac{c_e - c_0}{c_e}\right) \tag{4.6}$$

is then independent of the flow speed but may vary throughout the matrix as the reaction rate γ and the local equilibrium concentration c_e vary, largely with temperature. Since, however, the temperature fields are characteristically much more diffuse than flow fields (which may be focused by lenses, inclusions or fractures) the patterns of fabric alteration in this case are also much more diffuse. The rates of alteration are independent of the distribution and magnitude of the flow provided only that it is sufficient to ensure that $l_e \gg l$.

5. Mixing zones

Alterations in mineral composition or precipitation or dissolution can also occur by the mixing of different interstitial waters. One common example is afforded by a coastal salt wedge, where seawater infiltrates beneath the freshwater outflow of a coastal aquifer and mixing occurs along its upper edge. Fluid diffusion or dispersion is necessarily involved, and this is greatly augmented by the presence of lenses or more permeable layers. If one is concerned with the structural details of the reaction patterns, it is necessary to resolve the flow details on the scale of the lenses; if one

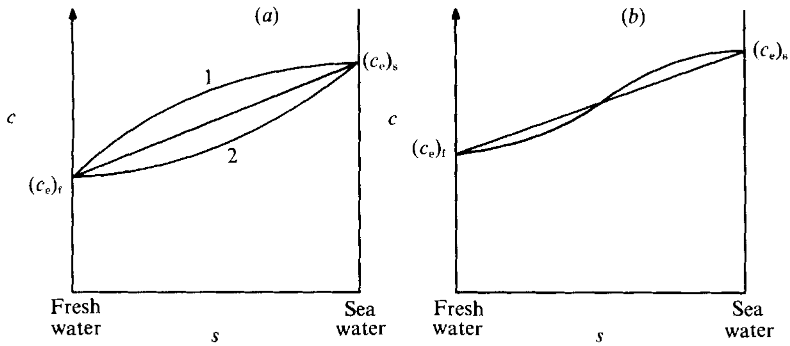

FIGURE 2. When salt water and fresh water, both saturated with respect to $CaCO_3$ (say) are mixed, the resulting concentration lies along the straight line joining $(c_e)_s$ and $(c_e)_f$. If $c_e(s)$ lies above the line, $\partial^2 c_e/\partial s^2 < 0$ (curve 1 in (a) the solution is unsaturated with respect to $CaCO_3$ and dissolution occurs. When it is below, $\partial^2 c_e/\partial s^2 > 0$ as in curve 2, it is then supersaturated and precipitation occurs. If the curvature of $c_e(s)$ changes as in (b), dissolution occurs at high salinities and precipitation at low.

is content with a description of only the general characteristics of the region, it may be adequate to represent the mixing in terms of a megadispersion coefficient

$$D \sim \phi^{-1} ul,$$

where l is the lengthscale of the lenses. It should be remembered, though, that this is a fairly coarse approximation. The overall mixing behaviour can be represented only asymptotically in terms of a dispersion coefficient when the lens scale is small compared with the scale of the overall flow, and this may not be so in many applications. Usually, however, the lens structures or the distributions of permeability inhomogeneities are not known in detail, and this approximation may be the best available.

In any event, when the equilibration length l_e is small, the source term is again specified by (4.1), but now the lengthscale over which the fluid composition varies may be small (the lens thickness when D is the usual macroscopic dispersivity, or the mixing zone thickness with D the megadispersion coefficient when we do not choose to resolve the individual lens flows). The equilibrium concentration c_e of any particular species may depend on the local mixing ratio of the two fluids, and it will be seen that reactions occur when c_e is other than a linear function of this ratio.

For the sake of definiteness, consider the dissolution or precipitation of calcium carbonate in a coastal fresh-water salt-water mixing zone. The equilibrium concentration of dissolved $CaCO_3$ in the fresh water of the aquifer is generally less than that in seawater, and although the concentration of dissolved NaCl may not enter the dissolution process directly, the salinity s is a useful index of the mixing ratio. The equilibrium concentration c_e is therefore a function of s as illustrated in figure 2. When seawater and fresh water, each initially saturated with respect to $CaCO_3$, are mixed, the resulting concentration of $CaCO_3$ lies along the straight line joining $(c_e)_s$ and $(c_e)_f$ in this figure and unless c_e is precisely linear in s, the mixture is unsaturated over a certain range or ranges of the mixing ratio s and supersaturated over others, or possibly undersaturated or supersaturated over the whole range if the curvature of $c_e(s)$ is everywhere concave downwards or upwards as illustrated in figure 2(a). When undersaturated, we would expect local dissolution, when supersaturated, precipitation.

The rate of dissolution of $CaCO_3$ per unit volume of fabric is specific by (4.1),

$$Q_s = \boldsymbol{u}\cdot\nabla c_e - \phi D \nabla^2 c_e, \tag{5.1}$$

where $c_e = c_e(s)$ and D is either the macroscopic or megadispersion coefficient as described earlier. The distribution of salinity s is governed by a similar advection–diffusion balance but without a source term:

$$0 = \boldsymbol{u}\cdot\nabla s - \phi D \nabla^2 s. \tag{5.2}$$

Now, since $c_e = c_e(s)$,

$$\nabla c_e = \left(\frac{\partial c_e}{\partial s}\right)\nabla s,$$

and

$$\nabla^2 c_e = \left(\frac{\partial^2 c_e}{\partial s^2}\right)(\nabla s)^2 + \left(\frac{\partial c_e}{\partial s}\right)\nabla^2 s$$

from the chain rule for partial differentiation. Consequently

$$\begin{aligned} Q_s &= \left(\frac{\partial c_e}{\partial s}\right)\{\boldsymbol{u}\cdot\nabla s - \phi D \nabla^2 s\} - \phi D \left(\frac{\partial^2 c_e}{\partial s^2}\right)(\nabla s)^2 \\ &= -\phi D \left(\frac{\partial^2 c_e}{\partial s^2}\right)(\nabla s)^2, \end{aligned} \tag{5.3}$$

by virtue of (5.2).

This very simple and important result shows clearly (*a*) that the rate of dissolution when $(\partial^2 c_e/\partial s^2) < 0$ or precipitation, $(\partial^2 c_e/\partial s^2) > 0$, is proportional to the curvature of the function $c_e(s)$, which is determined by the solution kinetics; (*b*) that the rates are proportional to the *square* of the salinity gradient and are therefore greatest when this gradient is largest, at the sea-level outflow in the salt wedge situation; and (*c*) that they increase linearly with the flow velocity, through the linear dependence of D on u. The formation of sea-level caverns in the limestone Yucatan aquifer has been interpreted in these terms by Sandford (1987).

More generally, when fluid in an aquifer is drawn into a more permeable lenticular inclusion, any vertical gradient in interstitial fluid concentration is amplified by the focusing ratio G as is the flow speed. The reaction rate is then, from (5.3) increased by the factor G^3 which can be very large. If $\partial^2 c_e/\partial s^2 \neq 0$, then, *mixing zone reactions are especially concentrated* in more permeable layers – the rate of gradient reactions and the speed of advance of isothermal reaction fronts increase only linearly with the flow velocity.

6. Some field examples

There are many difficulties to the establishment of close connections between the results presented here and the present-day distributions of ore deposition or mineral alteration. Tectonic movements, erosion and sedimentation over the ages may have changed the distributions and directions of interstitial flow in a given geological basin, but there are already a few instances in which at least qualitative connections can be made. One concerns the distribution of lead-zinc deposits in the Mississippi Valley. The Paleozoic sediments of the greater Mississippi Valley provide the locale for extensive major and minor deposits of galena, PbS, sphalerite, ZnS, barite, $BaSO_4$ and fluorite, CaF_2, all of which posses such striking geochemical and geological similarities amongst themselves and with similar regions on other continents, that they are all generally known as Mississippi-Valley-type deposits. They have, of course, been studied extensively and are the subject of a fine review by Sverjensky (1986). It appears to be well established that they are formed from hot, saline aqueous solutions some time after the lithification of the host rock, but the detailed geochemistry involved in their formation has been a matter of some dispute (i.e. whether the precipitation reactions involved sulphate reduction or pH changes or dilution etc.); different possibilities are reflected in differences in the chemically determined coefficients in equations such as (4.3).

Nevertheless, the outstanding characteristics of Mississippi-Valley-type deposits, as listed by Sverjensky, include the following:

1. They occur principally in the limestone or dolostone that forms a relatively thin cover over an igneous or highly metamorphosed basement.
2. They consist of bedded replacements and veins, the ore being strongly controlled by individual strata; they are generally not associated with igneous rocks.
3. They always occur in areas of mild deformation, expressed in brittle fractures, broad domes and basins and gentle folds.
4. The ore is never in the basement rocks but its distribution is often spatially related to basement highs with the ore located within sandbanks, ridges and reef structures that surround the basement highs.
5. The ore is generally at shallow depths, generally less than 600 m relative to the present surface and was probably never at depths greater than 1200 m.
6. Fluid inclusions remaining in sphalerite, fluorite, barite and calcite always contains dense, saline aqueous fluids and often oil and/or methane.

These characteristics all seem to be consistent with the dissolution of dispersed minerals, fluid transport and local deposition and concentration, probably by gradient reactions. An important clue is provided by the absence of ore deposits in undeformed regions. Here, any fluid flow is essentially along the isotherms so that the solute transport is constant; in flow through regions of deformation or over basement highs, the flow crosses the isotherms so that on the flanks of these highs, $\boldsymbol{u}\cdot\nabla T$ and w in (4.3) are both non-zero. Local deposition occurs in regions of rising fluid when the chemical coefficients in (4.5) are positive or in regions of sinking fluid when they are negative. The fact that they are associated with more permeable regions near basement highs is again consistent with flow focusing there and more rapid deposition in gradient reactions. It does not appear to be known whether the formation of these shallow deposits was associated with fluid discharge regions, where the near-surface temperature gradient would be anomalously large.

Finally, the close association between the spatial distribution of metamorphism and paleo-flow has been demonstrated in a fine detailed field study by Ferry (1987) on regionally metamorphosed biotite- and garnet-grade rocks of the Vassalboro Formation and the limestone member of the Waterville Formation in south central Maine. The biotite forming reaction involves decarbonation:

$$\underset{\text{Muscovite}}{\mathrm{KAl_3Si_3O_{10}(OH)_2}} + \underset{\text{Ankerite}}{\mathrm{3CaMg(CO_3)_2}} + \underset{\text{Quartz}}{\mathrm{2SiO}}$$

$$\rightleftharpoons \underset{\text{Biotite}}{\mathrm{KMgAlSi_3O_{10}(OH)_2}} + \underset{\text{Plagioclase}}{\mathrm{CaAl_2Si_2O_8}} + \underset{\text{Calcite}}{\mathrm{2CaCO_3}} + \mathrm{4CO_2}.$$

The geometrical distribution of reaction products, with gradual variations through the fabric rather than abrupt transitions suggests that gradient reactions were involved rather than the movement of isothermal reaction fronts. Baumgartner & Ferry (1990), interpreting the metamorphism in terms of gradient reactions and using the appropriate stoichiometric coefficients, showed that the total time-integrated volume transports over the period of formation were in the range 10^4 to 10^6 cm^3/cm^2. Although the variations among different lithologic layers were considerable (reflecting variations in permeability), the calculated fluxes from samples at different points in the same layer are very similar, indicating the channelling of fluid flow along it. By taking 10^7 years as an upper limit for the time interval involved, Baumgartner & Ferry calculated volume fluxes or transport velocities of order 10^{-2} cm/yr at least.

These individual studies, particularly the last, give tantalizing glimpses of the insights that are beginning to be developed through the combination of flow pattern considerations and geochemical analyses. The end is nowhere in sight. There remains the continuing need for much more detailed analyses and many more carefully documented and thoughtfully interpreted field studies if the association is to flower as it can.

Postscript

It was my second day at Cambridge. After the long trip from Sydney on the old *Strathmore* and a few days in London, I was there at last. I cycled up Trumpington Road on my new–old black bicycle looking for the address on Barrow Road to which I had been sent by the college porter. The door was opened by the lean, aquiline figure that I would come to know so well. 'Dr. Batchelor?' I asked, 'I'm Phillips'. 'I was expecting you. Hang on a moment. I'm coming in' he said. We cycled to the Cavendish and entered through the arch off Free School Lane, and in the tiny closet that then served as his office, just big enough for a desk, two chairs and a blackboard, he suggested, 'Why not think about the final period of decay of a turbulent wake?' I must have looked perplexed, having no idea what the final period of decay was and only the vaguest notions about turbulent wakes, but he paused for only a moment before, 'All right, off you go!'

A new direction. One of the diverse things that George's students learned from him as they progressed from apprenticeship to scientific independence is that fluid mechanics reaches far beyond the topics then taught in the classroom, that the world is full of interesting things that await those with the curiosity to explore them. The percolation of fluids through rocks, at rates of perhaps only a few centimeters a year but continuing for thousands of millennia and producing cumulatively massive mineralogical changes, this is a far cry from turbulent wakes, but the new direction that it represents for me is in the spirit of that first meeting, thirty-seven years ago. It is dedicated to George on this happy occasion.

REFERENCES

Barnes, H. L. 1979 (Ed.) *Geochemistry of Hydrothermal Ore Deposits.* Holt, Rinehart and Winston.

Baumgartner, L. P. & Ferry, J. M. 1990 A physical model for infiltration-driven mixed volatile reactions and its applications to regional metamorphism. *Contr. Mineral. Petrol.* (In press.)

Ferry, J. M. 1987 Metamorphic hydrology at 13 km depth and 400–500 °C. *Am. Min.* **72**, 39–58.

Lichtner, P. C. 1985 Continuum model for simultaneous chemical reactions and mass transport in hydrothermal systems. *Geochim. Cosmochim Acta* **49**, 779–800.

Lichtner, P. C. 1988 The quasi-stationary state approximation to coupled mass transport and fluid-rock interaction in a porous medium. *Geochim. Cosmochim. Acta* **51**, 143–65.

SANDFORD, W. R. 1987 Assessing the potential for calcite dissolution in coastal seawater mixing zones. Ph.D. dissertation, Pennsylvania State University, 103 pp.

SVERJENSKI, D. A. 1986 Genesis of Mississippi-Valley-type lead-zinc deposits. *Ann. Rev. Earth Planet. Sci.* **14**, 177–99.

WASHBURN, E. W. 1929 *International Critical Tables.* McGraw-Hill.

WOOD, J. R. & HEWETT, T. A. 1982 Fluid convection and mass transfer in porous limestones – a theoretical model. *Geochim. Cosmochim. Acta* **46**, 1707–13.