Fluid-driven Reactions

Infiltration of nonequilibrium fluid causes downstream propagation of pronounced shifts in chemistry and mineralogy that originate at the upstream end of the flow system. These reaction fronts were the focus of numerous studies in metamorphic environments as they provide, potentially, the means to determine rates of fluid flow, fluid composition, and fluid transport mechanisms. The "tracers" used to identify fronts include changes in modal mineralogy resulting from progress of fluid-driven net-transfer reactions, changes in elemental concentrations resulting from fluid-rock exchange reactions, and shifts in stable and radiogenic isotope ratios resulting from fluid-rock isotope exchange reactions.

Displacements of chemical fronts allow estimates of one-dimensional fluid fluxes with relations of the form [see Blattner and Lassey, 1989]:

\[ z_{\text{front}} = \psi ut \]

where \( z_{\text{front}} \) is the tracer front displacement, \( \psi \) is a "carrier porosity" equivalent to \( \phi / (\phi + (1 - \phi)k) \) in terms of interconnected porosity \( \phi \) and equilibrium distribution coefficient \( k \), \( u \) is fluid pore velocity, and \( t \) is time. It is now becoming clear, however, that critical application of the above equation to field relations is warranted. The proviso that \( k \) refers only to exchangeable quantities of the species of interest means that \( \psi \) depends on the mechanism of mass transfer; processes that operate within system REVs must be known in detail if continuum mechanics is to yield useful information. Recognition of such complexities is driving researchers to examine more closely the factors that govern formation of reaction fronts.

The duration of flow is also of interest if metamorphic hydrodynamics is to be quantified, yet deconvolution of \( \psi \), \( u \), and \( t \) requires additional independent information. Shapes of reaction fronts (in terms of distance versus tracer quantity space), controlled by dispersive forces that act to distend the fronts, are providing such information. Dispersive forces that have been considered include diffusion in the fluid and solid phases, hydrodynamic dispersion, and the kinetics of fluid-mineral reaction [Bowman and Willett, 1991].

Lasaga and Rye [1993] analyzed the effects of kinetics that can be propagated downstream during fluid-driven metamorphic reactions. They presented simple analytical equations showing that fluid-rock reaction fronts defined by the exhaustion of a reactant mineral propagating in the direction of fluid flow will likely be associated with a zone of marked nonequilibrium between fluid and rock. The width (in the case of one-dimensional flow) of this zone is determined by the ratio of fluid velocity to reaction rate. Following earlier work by Lasaga, the propagating reaction front and associated zone of nonequilibrium is referred to as a "kinetic isograd."

A central theme in the work of Lasaga and Rye is the concept of "steady state" in reactive rock systems
open to fluid flow. They stated that the persistence of nonequilibrium between fluid and rock over a fixed geometry is a form of steady state. It can be argued that the use of the term ``steady state'' in this context is unfortunate as it obscures the likely pervasiveness of the phenomenon that they describe. This is because for many workers steady state has a very precise meaning: time invariance for the quantity of interest. In their derivations Lasaga and Rye used as their quantity of interest the concentration of a chemical species in a packet of fluid that flows through a rock system. Time invariance of solute concentration \( c \) for a flowing fluid packet implies \( dc/dt = 0 \). Nonequilibrium time-invariance, by this definition, occurs only under certain special circumstances (for example, in the case of nonlinear reaction kinetics presented by Lasaga and Rye) and accordingly is unlikely to be the general case in nature. However, the steady state referred to by Lasaga and Rye is the local time invariance customary in fluid mechanics and other disciplines. In this definition of steady state, the quantity of interest is the concentration in the fluid at a fixed position in the rock column rather than in a flowing packet of fluid. That is, \( \partial c / \partial t \) \( x, y, z \) = 0 (\( x, y, z \) are spatial coordinates) while \( dc/dt \neq 0 \); concentration \( c \) changes by virtue of motion through the rock column only. The quantity used in the derivations is not the same as that used to define steady state. What is more, the relevant equations are derived without imposing even this less restrictive steady state condition \( \partial c / \partial t \) \( x, y, z \) = 0. The latter is simply the consequence of invoking steady rates of fluid flow and reaction. Local concentrations at a fixed point will always achieve time invariance when supply and withdrawal occur at constant rates.

It is worth emphasizing then, that the conclusions reached by Lasaga and Rye [1993] do not depend on fortuitous circumstances leading to time invariance but are, in fact, the inevitable consequences of constant rates of fluid flow and reaction! The question is not whether steady state is viable, but rather whether fluid velocities and reaction rates are likely constant (or nearly so) for geologically long time periods.


Gradient Reactions

Perhaps the most significant change in the field of metamorphic fluid flow over the last quadrennium was the trend toward abandonment of fluid-rock ratios in favor of time-integrated fluid fluxes as the principal measures of "amounts" of fluid that flowed during metamorphism. Although both parameters can serve as relative measures of the degree of fluid-rock interaction, fluid fluxes are preferred over fluid-rock ratios because numerical values for the latter are difficult to interpret in terms of hydrodynamics. For example, a reactive rock column that has experienced steady one-dimensional advection of fluid for an arbitrary time interval can record fluid-rock ratios ranging from 0 to along the flow path while simultaneously recording a single time-integrated flux of fluid. The latter quantity has more physical significance than the former in that it was stipulated that fluid did indeed pass everywhere through the entire length of the column.

The shift away from fluid-rock ratios and toward fluid fluxes was due largely to a paper by Baumgartner and Ferry [1991]. They showed that the time-integrated form of the equation of continuity, or mass balance equation, for a species \(i\) in the fluid phase,

\[
\Delta n_i = \nabla \cdot (\mathcal{z}_i J_t)
\]

can be rearranged to yield a straightforward equation that relates time-integrated molar fluid flux \(J_t\) \(\text{(mol/m}^2\text{)}\) to reaction progress \(\xi\):

\[
J_t = \frac{\xi (\nu_i - \mathcal{z}_i \sum_j \nu_j)}{\nabla \mathcal{z}_i}
\]

where \(n_i\) is the total moles of fluid species \(i\) produced or consumed per unit rock volume, \(\mathcal{z}_i\) is the mole fraction of \(i\) in the fluid phase, and \(\nu_j\) are stoichiometric coefficients for fluid species \(j\) in the reaction. Implicit is a low porosity and predominance of advection of fluid over dispersive transport. In cases of more complicated reactions, \(J_t\) can be written as a sum over each of the component linearly independent reactions that describe the complete reaction history of the rock [Young and Morrison, 1992].

Assuming that equilibrium between fluid and rock is maintained throughout the flow path, Baumgartner and Ferry expanded \(\nabla \mathcal{z}_i\) to yield:

\[
J_t = \frac{\xi (\nu_i - \mathcal{z}_i \sum_j \nu_j)}{(\frac{\partial \mathcal{z}_i}{\partial T})_P \nabla T + (\frac{\partial \mathcal{z}_i}{\partial P})_T \nabla P}
\]

The specified changes in \(\mathcal{z}_i\) with \(T\) and pressure \(P\) are constrained by phase equilibria owing to the assumption of local equilibrium. The expanded equation thus describes gradient reactions where \(\nabla T\) and
\( \nabla P \) are the driving forces. The flux \( J_t \) is a measure of fluid available for reaction, but regardless of its magnitude no reaction is permitted for \( \nabla T = \nabla P = 0 \) because of the assumption of local equilibrium. Usually, \( \nabla T \gg \nabla P \) and so the distribution and extent of fluid-rock reaction is controlled by \( \nabla T \) and \( J_t \).

Phillips [1991] noted that the product \( J_t \cdot \nabla T \) is sometimes referred to as the "rock alteration index" for this reason.

One of the principal uses of the equation presented by Baumgartner and Ferry [1991] has been assessment of the direction of fluid flow relative to thermal gradients in contact and regional metamorphic terranes. For this purpose only the signs of the various terms are decisive. In many common metamorphic terranes phase equilibria dictates positive \( \left( \frac{\partial x}{\partial T} \right)_P \). The sign of the rock alteration index, and hence the polarity of reaction progress, is then determined by the sign of \( \nabla T \) (flux is positive by definition). Baumgartner and Ferry argued that for forward progress of many metamorphic reactions to have occurred, as indicated by field observations, \( \nabla T \) must have been positive, i.e., flow must have been in the direction of increasing temperature.

Dipple and Ferry [1992] presented equations and interpretations similar to those of Baumgartner and Ferry, but formulated explicitly for stable isotope exchange reactions between fluid and rock. Although not expressed in the same fashion, for purposes of illustration one can show that the salient features of the model of Dipple and Ferry are embodied in a time-integrated flux-reaction progress equation analogous to that of Baumgartner and Ferry:

\[
\alpha J_{18O} = - \delta^{18}O_{\text{rock}} - \delta^{18}O_{\text{fluid}} \cdot (\frac{\partial (\delta^{18}O_{\text{fluid}})}{\partial T})_{\nabla T}
\]

where \( \alpha \) is the equilibrium rock/fluid isotope ratio fractionation factor (essentially 1), \( J_{18O} \) is a time-integrated flux of fluid oxygen (as traced by \( ^{18}O \), parameter \( B_t \) of Dipple and Ferry), and \( \delta^{18}O_{\text{rock}} (\delta^{18}O_{\text{fluid}}) \) is the per mil deviation of \( ^{18}O / ^{16}O \) from a standard) signifies the initial \( \delta^{18}O \) for the rock at a particular position along the flow path. Dipple and Ferry presented detailed \( \delta^{18}O \) distance profiles for a variety of circumstances. The principal implications of these profiles are gleaned from the equation above. The equation is seen immediately to apply to gradient-controlled exchange of \( ^{18}O \) and \( ^{16}O \) between fluid and rock; in the absence of a temperature gradient \( \nabla T \), no shift in rock \( \delta^{18}O \) occurs and the extent of isotopic alteration is a function of the rock alteration index \( J_{18O} \cdot \nabla T \). For the typical case of flow of \( H_2O \) through carbonate or quartz-feldspathic lithologies, \( (\partial \delta^{18}O_{\text{fluid}} / \partial T)_{\nabla T} \) is positive so that flow up temperature, or positive \( \nabla T \), results in a decrease in rock \( \delta^{18}O \) at any location on the flow path, while flow down temperature, or negative \( \nabla T \), results in an increase in rock \( \delta^{18}O \).

In their analysis of isotope exchange Dipple and Ferry gave a cogent illustration of the effects of exhaustion of a reactant during progress of a gradient reaction in a continuum. In this case it is the \( ^{18}O / ^{16}O - 1 \) exchange capacity of the rock that is depleted. An isotopic front then develops. Unlike fluid-driven fronts, the shape of the gradient reaction fronts are strongly influenced by the rock alteration index. Because the infiltrated fluid enters the system in equilibrium with the rock there is no step in \( \delta^{18}O \) to be propagated downstream, as there is in a fluid-driven front. The gradient front is therefore defined by a discontinuity in \( \delta^{18}O \) rather than a step. The difference between fluid-driven and gradient exchange \( \delta^{18}O \) fronts is topologically reminiscent of the dissemblance between first-order and second-order reaction enthalpies, respectively (for the thermodynamically inclined reader). Upstream of the

http://www.agu.org/revgeophys/young01/node7.html
Gradient isotope exchange front $\delta^{18}O_{\text{fluid}}$ is constant and equal to the initial value at the inlet of the flow system. Rock $\delta^{18}O$ values are controlled by this constant initial fluid $\delta^{18}O$ and temperature. Downstream the system exhibits the gradual changes typical of gradient reactions.

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The Sign of : A Question of Fluid Source?

Debates over directions of fluid flow in the presence of temperature gradients revolve around implications for contact metamorphic terranes. Studies of the Notch Peak contact-metamorphic aureole by Ferry and Dipple [1992] and Nabelek and Labotka [1993] focused the deliberations.

Ferry and Dipple [1992] proposed that H2O-rich fluids that drove decarbonation reactions in the aureole flowed up temperature from low-grade rocks toward the igneous pluton that was the source of heat during metamorphism. Nabelek and Labotka [1993], building on their previous studies and those of their co-workers, presented evidence intended to controvert the model of Ferry and Dipple. They argued that the flow of aqueous fluid was down temperature away from the pluton.

Both proposed flow regimes are adequate to explain the major features of the aureole: a sequence of diopside and wollastonite isograds in calcareous argillites up temperature toward the pluton, and a general decrease in whole-rock argillite carbonate δ18O values toward the pluton. Although the distinction between the proposed models is usually cast in terms of direction of flow relative to temperature, the essence of the debate has as much to do with gradient versus fluid-driven reactions and, by corollary, the origin of the infiltrated fluid. Ferry and Dipple propose flow coupled with gradient reactions while Nabelek and Labotka propose flow coupled with fluid-driven reactions.

Ferry and Dipple based their model on the assumption that fluid entered the aureole in chemical and isotopic equilibrium with the distal country rock. The reactions that ensued were thus envisaged to have been gradient reactions. Reactant and product minerals are predicted to coexist over a distance prescribed by the rock alteration index J · ∇T, and consumption of reactant phases, comprising gradient reaction fronts, should not coincide with isograds if this model is correct (isograd is used here to refer to the first appearance of product minerals up temperature). Accordingly, Ferry and Dipple focused on field relations in the zones between the diopside and wollastonite isograds in which the relative positions of lines that apparently demarcate loss of reactant minerals (gradient fronts) relative to isograds serve to constrain their model. Flow up-temperature toward the pluton reproduces these relations. They interpreted the isotope data as being indicative of a gradual change in δ18O with distance as is expected for gradient isotopic exchange. Up-temperature flow was invoked to explain the decrease in argillite δ18O toward the pluton.

Nabelek and Labotka presented trace element evidence that indicate fluid that infiltrated the aureole came from the pluton and was not in equilibrium with the country rock. Fluid-rock reactions were therefore envisaged to be fluid-driven. Reactant and product minerals are not expected to coexist over finite distances because reaction progress is driven to completion by the difference in composition between infiltrated and equilibrated fluid. Isograds are thus fluid-driven reaction fronts in this model, and their positions are controlled by J · ∇T and the difference in composition between infiltrated and equilibrated fluid. Because fluid compositions at equilibrium are a function of temperature, the positions of the fronts envisaged by Nabelek and Labotka are a function of ∇T. In this circumstance the rock alteration index influences the positions of both gradient and fluid-driven fronts, although in different
ways. Nabelek and Labotka interpreted the isotope data as defining a sharp step-like change in $\delta^{18}O$ with distance, consistent with a fluid-driven exchange front.

The fundamental unknowns are the composition of the fluid relative to rock and the nature of the fluid-rock reaction. Derivation of reactive fluid from the pluton implies down-temperature flow, and derivation from distal country rock implies up-temperature flow assuming simple radial fluid stream lines, but there is little inherent in the direction of flow relative to $\nabla T$ itself that requires one model or the other. The salient features of the isotope data, for example, including the existence of a front like that described by Nabelek and Labotka, could be explained by up-temperature flow of a nonequilibrium fluid (instead of the down-T flow posited by the latter authors) if that fluid had $\delta^{18}O$ values several per mil greater than indicated by equilibration with distal country rock [figure 2 of Dipple and Ferry, 1992].

One concludes that the oxygen isotope data can be explained by flow either up or down temperature given suitable initial $\delta^{18}O$ for the infiltrated fluid. The most conspicuous mineralogical features of the aureole are also explained by either up or down-temperature flow, but only where the degree of equilibration between fluid and rock is specified expressly. For example, no one has suggested that fluid in equilibrium with the country rock flowed down temperature in the aureole because such a flow regime would have caused mineralogical reactions to progress in directions opposite to those observed [e.g., Dipple and Ferry, 1992; Ferry, 1991]. Down-temperature flow is permitted for fluid-driven reactions but gradient reactions coupled with down-temperature flow are precluded by first-order observations.

Both models for development of the Notch Peak aureole are based on continuum mechanics and were acknowledged by the protagonists to be at least partly schematic. In the future, the assumptions inherent in the continuum models can be tested at sub-REV scales. Such investigations should help sharpen our picture of aureole formation. Nabelek and Labotka alluded to this fact in their discussion of enhanced fracture flow in the wollastonite zone relative to the outer aureole.

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