

Fluid flow in metamorphic environments

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Introduction

The study of fluid flow in metamorphic environments progressed over the last quadrennium mainly from a focus on the tenets of continuum mechanics, in which rock properties such as porosity and tortuosity that control flow are assumed to be homogeneous over a specified finite volume. Advances have been afforded by these principles not only from their direct application, but also from tests of their veracity. Assumptions inherent in the continuum approach are based on the scale of observation and, in conjunction with the advent of new analytical technologies, have given new impetus for examining mechanisms of material transfer between fluids and metamorphic rocks at smaller and smaller scales. Thus, even as continuum mechanics has laudably come to be widely utilized in the study of metamorphic fluid flow, the "empirical adequacy" [Oreskes *et al.*, 1994] of the methodology is being assessed through access to previously unattainable scales of observation.

These new developments revealed some unexpected results. Among them are indications that fluid movement during regional metamorphism has been, at least in some cases, punctuated, with individual episodes lasting as little as several tens of thousands of years. This observation is particularly important in view of the widespread practice of estimating quantities of fluid on a time-integrated basis. Conventional ideas about the direction of fluid flow in variable temperature fields, the extent of elemental mobility, the scale of hydrothermal circulation during metamorphism, and the depth of infiltration of surface fluids have all been challenged by studies completed in the past four years.

The Role of Continuum Mechanics

Until recently, a majority of studies used purely scalar properties (e.g., equilibrium thermodynamics) to describe metamorphic fluid flow. In the last quadrennium, however, there has been widespread, albeit belated, acknowledgement among metamorphic petrologists and geochemists that fluid flow, being an inherently vectorial phenomenon rather than a scalar phenomenon, must be examined using transport theory; accurate description of fluid-rock interactions requires use of field variables, variables which are functions of both position

and time. Continuum mechanics provides a framework for relating both field and scalar-valued variables using volume-averaged properties of the porous rock system. Averaging is performed over some "representative elementary volume," or REV. The REV size for a particular system depends implicitly on the scale of observation but in any case must be significantly larger than the size of individual fluid pathways (i.e., pore size, grain size, or fracture width).

Micrometers to Kilometers: A Prospectus

New-sprung emphasis on the continuum approach does not mean that processes operating at sub-REV scales have been ignored. Indeed it is these phenomena that determine the properties of the continuums, and there is an emerging need to characterize links between kinetic processes that operate on disparate scales as fluid flows through reactive rock [Torgersen, 1994].

The exchange of energy between reactive metamorphic rock and flowing fluid has generally been accounted for by adjusting heat capacities to accommodate heats of reaction (or some equivalent formalism). While rates of irreversible processes have been included in this approach, the *energetics* of irreversibility have not because rates and coupled heat capacities alone do not provide for irreversible interconvertibility among chemical, mechanical, and thermal energy. Given that real processes are irreversible, is this preterition severe?

Nonequilibrium thermodynamics suggests that entropy might be a useful device for assessing the importance of coupling of small-scale irreversibility (intra-REV or intrasystem phenomena) and larger scale metamorphic fluid flow (inter-REV phenomena).

The time (t) evolution of the entropy (S) of an evolving rock REV is composed of a net flow term $\nabla \cdot \mathbf{J}_s$ and a production term η :

$$\frac{\partial S}{\partial t} = -\nabla \cdot \mathbf{J}_s + \eta.$$

Entropy flow results from temperature-normalized heat and material flows through the system. It depicts the energy associated with larger scale, inter-REV processes such as fluid flow. Entropy production is a positive definite sum of fluxes multiplied by forces that drive them. It includes intra-REV force-flux products arising from reaction kinetics, mass transfer, heat transfer, and viscous flow that occur at small (e.g., microscopic) scales. The time rate of change in REV entropy is thus seen to depend on both macroscopic and microscopic processes.

Recent work by Carlson and Denison [1992] and

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Paper number 95RG00601.
8755-1209/95/95RG-00601\$15.00

Denison and Carlson [1993] underscores the importance of integrating all scales of observation. Using high-resolution X ray tomography to quantify the disposition and size of mineral grains at the millimeter scale, Carlson and Denison showed that porphyroblast growth rates are controlled by intergranular chemical diffusion in a variety of metamorphic rocks, including calcsilicate skarn affected by coeval fluid infiltration. In the case of the skarn, the results imply that rates of intergranular diffusion exceeded fluid pore velocities. Having documented the prevalence of irreversible (i.e., real) diffusive mass transfer in rock during metamorphic fluid flow by virtue of its rate-limiting character, we are now impelled to consider the energetics of the process. Entropy flow and production can be used for this purpose.

Consider the case of entropic steady state where $\partial S/\partial t = 0$. The entropy budget for irreversible diffusion of species i at constant temperature yields the conservation relation

$$\frac{1}{T} \nabla \cdot \left(\mathbf{J}_q - \sum_i \mu_i \mathbf{J}_i \right) = \sum_i \mathbf{J}_i \cdot \nabla \left(\frac{-\mu_i}{T} \right),$$

where $\mathbf{J}_s$ has been written in terms of temperature T and heat flux $\mathbf{J}_q$ ($\mathbf{J}_q$ is corrected for heat contributed by flowing material), μ_i is the chemical potential of diffusing component i , and $\mathbf{J}_i$ is the molar diffusive flux of component i . The equation shows that entropy production by irreversible chemical diffusion (right-hand side) can, in principle, influence net heat flux (left-hand side) during metamorphism. Since local entropy production by diffusion is positive, so is the associated change in heat flux. Some of this thermal energy was advected by flowing fluid in the case of the skarn.

Data needed to evaluate such couplings are scant at present. However, estimates for diffusive flux and chemical potential gradients summarized by *Joesten* [1991] indicate that the amount of thermal energy liberated by diffusion could be substantial (e.g., commensurate with heats of reaction).

How do irreversible processes like diffusive mass transfer influence thermal budgets when integrated over entire fluid flow systems? How does the presence or absence of fluid affect η ? At what scales, from micrometer to kilometer, might we expect to see manifestations of such effects? Answers to these and similar questions should be forthcoming as the mutual influences of hydrodynamics and geochemical reactions are explored over a wide range of scales by workers in the field, in the laboratory, and in the realm of numerical models.

Simulations

Computational simulations of metamorphic fluid flow systems on the scale of kilometers concentrated on the interrelationships among fluid flow, heat transfer, and chemical reaction progress.

Workers have traditionally drawn clear distinctions between metamorphic environments in which reactions were driven by infiltration of disequilibrium fluid, re-

ferred to here as “fluid-driven reactions,” and those in which fluids and rock maintained equilibrium (or nearly so) as reactions proceeded in response to changes in other factors such as temperature or pressure. *Phillips* [1991] refers to the latter as “gradient reactions.” Models by *Steefel and Lasaga* [1992] showed that such distinctions are somewhat artificial.

Steefel and Lasaga constructed a finite-difference model for two-dimensional flow of surface-derived water into zones of active low-temperature metamorphism on the scale of several kilometers. Results show that hydrodynamic dispersion can result in mixing among particles of fluid having different temperature-composition histories along closely spaced stream lines of flow. The scale of dispersive mixing is commensurate with the scale of significant temperature gradients in the fictive system, implying that the driving forces for reactions are likely to include both fluid-driven and gradient components. Hydrodynamic dispersion can now be added to the list of processes that influence metamorphic reaction paths.

Whereas *Steefel and Lasaga* [1992] focused on the effects of hydrodynamic properties on the mineralogical history of rocks, *Hanson* [1992] and *Steefel and Lasaga* [1994] emphasized the influence of metamorphic reactions on kilometer-scale hydrodynamics using two-dimensional explicit and implicit finite difference calculations, respectively. The studies by *Hanson* [1992] and *Steefel and Lasaga* [1994] examined different aspects of the problem. The difference is made evident by summarizing their work in terms of the equation of continuity for fluid flowing through porous rock:

$$\frac{\partial \phi \rho}{\partial t} = -\nabla \cdot \mathbf{J}_m + R.$$

The left-hand term describes the time rate of change of the fluid mass where ϕ is the volumetric porosity, ρ is fluid density, and t is time. The first term on the right describes the change in mass owing to a net change in fluid flux $\mathbf{J}_m$ and the second term R represents the fluid source-sink term.

Hanson [1992] considered the influence of prograde dehydration reactions (reactions that release water from mineral structures in response to increases in temperature) on flow of fluid with constant porosity. Further, the Boussinesq approximation was invoked; fluid expansivity was included in force-balance equations but was deemed sufficiently small that it could be safely neglected in mass-balance equations. In terms of the fluid continuity equation, Hanson concerned himself with situations in which the relation

$$\nabla \cdot \mathbf{J}_m = R$$

obtains. Here, R is attributed to progress of metamorphic reactions.

Steefel and Lasaga [1994], on the other hand, investigated the effects of mineral precipitation and dissolution on patterns of fluid flow by allowing porosity to change. With respect to the fluid continuity equation,

their model describes environments for which the relation

$$\frac{\partial \phi \rho}{\partial t} = -\nabla \cdot \mathbf{J}_m$$

holds. With the Boussinesq approximation the left-hand term reflects changes in porosity only. Dehydration and hydration reactions were excluded in their calculations (i.e., $R = 0$).

Hanson's modeling shows that reactions giving rise to fluid production can strongly influence the pattern of fluid flow during contact and regional metamorphism where permeabilities are on the order of 1×10^{-16} to $1 \times 10^{-18} \text{ m}^2$ or less. Within the stipulations of the model, fluid produced by prograde reactions is expelled as convective flow is diverted around the resulting pressure maximum. Flow is dominantly down temperature gradients when the rate of fluid production is high (i.e., when dehydration reactions are proceeding most vigorously). In as little as 10^5 years production rates adjacent thermal anomalies will decrease to the point where expulsion gives way to up-temperature fluid ingress as density-driven convection is established. Peak fluid-production rates are predicted to occur early in the metamorphic history. Based on these findings, one concludes that moderate-grade hydrous metamorphic rocks may experience drastic changes from expulsion of metamorphic fluid down temperature gradients to up-temperature convective fluid infiltration at near-peak temperatures. Such changes in flow regimes would be accompanied by changes in fluid source and, possibly, fluid composition, and would occur over small time intervals, $\sim 10^5$ years, relative to the total durations of most metamorphic events.

In their modeling, *Steeff and Lasaga* [1994] described chemical reactions between aqueous fluid and rock composed of quartz, albite, K-feldspar, muscovite, and kaolinite with linear rate equations in the system K-Na-Si-Al-Cl-C-H-O. Their results demonstrate that the principal effect of reaction progress on fracture permeability derives from precipitation and dissolution of quartz along fracture walls in the model system. Quartz precipitates in areas of down-temperature flow and dissolves in zones of up-temperature flow. With time (10^4 years) flow is focused into regions where fluids move up temperature gradients and is dispersed where fluids move down temperature. Local equilibrium between fluid flowing through fractures and host rock is generally nearly attained at temperatures above approximately 200°C where permeabilities are on the order of 10^{-15} to 10^{-14} m^2 and fracture spacing is less than approximately 100 m. Local disequilibrium prevails in the vicinity of permeable thermal boundary layers. These results lend credibility to many petrological studies of metamorphic fluid flow that assume local equilibrium.

Multidimensional numerical models were also used to study fluid flow through metamorphosing rock on the meter and centimeter scales. *Gerdes et al.* [1993] constructed a finite element model that links compressible

fluid flow, thermal transport, and advective and dispersive material transport to kinetics of oxygen and carbon isotope exchange between fluids and rocks. The model can be used to simulate the formation of isotopic exchange fronts in two-dimensional flow systems.

Detailed simulations of the effects of fluid flow on mineral parageneses have been carried out independent of hydrodynamic considerations. *Symmes and Ferry* [1991] used equilibrium thermodynamics coupled with mass balance constraints to show that mineral assemblages representing pelitic rocks of the classic Barrovian metamorphic sequence can only be reproduced faithfully if aqueous fluid, in quantities equivalent to time-integrated aqueous fluid fluxes of $\geq 10^2 \text{ m}^3/\text{m}^2$, are included. *Foster* [1993] formulated a combined equilibrium and nonequilibrium thermodynamic numerical approach that enables simulation of rock textures formed during mineral growth in the presence of flowing fluid.

Reactions as Monitors of Fluid Flow

Although imperfect, distinction between fluid-driven reactions and gradient reactions is nevertheless convenient when describing the development of concepts pertaining to metamorphic fluid flow that occurred over the last quadrennium. Categorization of fluid-rock effects in this report is not intended to enforce or advocate a form of semantics. Instead, the author finds that it serves to underscore differences and, indeed, *similarities* between the various processes considered.

Fluid-driven reactions are those for which the sole (or principal) driving force is continued ingress of fluid that enters the flow system out of equilibrium with the reacting rock. In contrast, gradient reactions arise where flowing fluids enter in, and maintain, equilibrium with host rocks. Reaction progress in a fluid-driven reaction occurs as the rock strives to achieve equilibrium with the flowing fluid. Cessation of flow causes desistance of reaction. In the case of gradient reactions, reaction progress occurs in response to the prolonged availability of fluid combined with flow along existent gradients in factors of state other than fluid composition such as temperature and pressure. Reaction ends if either the flux of fluid or gradients in state variables fade.

Fluid-driven reactions result in abrupt changes in physical and chemical properties affected by reaction that propagate in the direction of flow. Gradient reactions allow for gradual changes in the physico-chemical parameter of interest. However, exploration of these concepts has shown that discontinuities similar to those associated with fluid-driven reactions can result from gradient reactions in the event that the capacity of the rock to react with fluid is exhausted (e.g., loss of a reactant mineral). Similarly, fluid-driven reactions can give rise to broad gradients in chemistry and mineralogy in some circumstances. Of course, fluid entering in a state of disequilibrium and flowing along gradients in state variables will produce a hybrid force with components of both fluid-driven and gradient reactions.

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_{front} is the tracer front displacement, ψ is a "carrier porosity" equivalent to $\phi/(\phi + (1 - \phi)k)$ in terms of interconnected porosity ϕ 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 ψ 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 ψ , 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 down stream 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 , and 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,

$$\Delta n_i = \nabla \cdot (x_i \mathbf{J}_t),$$

can be rearranged to yield a straightforward equation that relates time-integrated molar fluid flux $\mathbf{J}_t$ (mol/m²) to reaction progress ξ :

$$\mathbf{J}_t = \frac{\xi(\nu_i - x_i \sum_j \nu_j)}{\nabla x_i}$$

where n_i is the total moles of fluid species i produced or consumed per unit rock volume, x_i is the mole fraction of i in the fluid phase, and ν_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, $\mathbf{J}_t$ 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 ∇x_i to yield:

$$\mathbf{J}_t = \frac{\xi(\nu_i - x_i \sum_j \nu_j)}{\left(\frac{\partial x_i}{\partial T}\right)_P \nabla T + \left(\frac{\partial x_i}{\partial P}\right)_T \nabla P}.$$

The specified changes in x_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 ∇T and ∇P are the driving forces. The flux $\mathbf{J}_t$ 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 ∇T and $\mathbf{J}_t$. *Phillips* [1991] noted that the product $\mathbf{J}_t \cdot \nabla T$ 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 $(\partial x_i / \partial T)_P$. The sign of the rock alteration index, and hence the polarity of reaction progress, is then determined by the sign of ∇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, ∇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*:

$$\alpha \mathbf{J}_{18O} = - \frac{\delta^{18O}_{\text{rock}} - \delta^{18O}_{\text{rock}}^0}{\left(\frac{\partial(\delta^{18O}_{\text{fluid}})}{\partial T}\right)} \nabla T$$

where α is the equilibrium rock/fluid isotope ratio fractionation factor (essentially 1), $\mathbf{J}_{18O}$ is a time-integrated flux of fluid oxygen (as traced by ¹⁸O, parameter Bt of *Dipple and Ferry*), and $\delta^{18O}_{\text{rock}}^0$ (δ^{18O} is the per mil deviation of ¹⁸O/¹⁶O from a standard) signifies the initial δ^{18O} for the rock at a particular position along the flow path. *Dipple and Ferry* presented detailed δ^{18O} 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 ¹⁸O and ¹⁶O between fluid and rock; in the absence of a temperature gradient ∇T , no shift in rock δ^{18O} occurs and the extent of isotopic alteration is a function of the rock alteration index $\mathbf{J}_{18O} \cdot \nabla T$. For the typical case of flow of H₂O through carbonate or quartzo-feldspathic lithologies, $(\partial \delta^{18O}_{\text{fluid}} / \partial T)$ is positive so that flow up temperature, or positive ∇T , results in a decrease in rock δ^{18O} at any location on the flow path, while flow down temperature, or negative ∇T , results in an increase in rock δ^{18O} .

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 ¹⁸O¹⁶O₋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 δ^{18O} to be propagated downstream, as there is in a fluid-driven front. The gradient front is therefore defined by a discontinuity in δ^{18O} rather than a step. The difference between fluid-driven and gradient exchange δ^{18O} fronts is topologically reminiscent of the dissemblance between first-order and second-order reaction enthalpies, respectively (for the thermodynamically inclined reader). Upstream of the gradient isotope exchange front $\delta^{18O}_{\text{fluid}}$ is constant and equal to the initial value at the inlet of the flow system. Rock δ^{18O} values are controlled by this constant initial fluid δ^{18O} and temperature. Downstream the system exhibits the gradual changes typical of gradient reactions.

The Nature of Permeability

From the perspective of pure continuum theory, permeability in rocks can be treated as a statistical problem. In a recently published monograph, *Turcotte* [1992]

provided an overview of this probabilistic view of permeability. This sort of analysis predicts that there will be a sudden onset of macroscopic, inter-REV permeability at some critical value of porosity. Accordingly, metamorphic fluid flow is expected to be episodic if porosity is altered by reactions and strain.

Identification of the physical features that actually give rise to metamorphic permeability at sub-REV scales remained an active area of research (see *Brenan* [1991] for a summary through 1991). Connected grain edges, microcracks, and fractures are all posited as being potent determinants of permeability. The effects of fluid composition on formation and persistence of these features was recognized as an issue of cardinal importance in the last quadrennium.

The role of intergranular permeability depends on the extent to which fluid-filled grain edges are connected. It is now well established that upon attainment of textural equilibrium, grain-edge connectivity occurs in isotropic porous media when the solid-solid-fluid dihedral angle Θ is less than 60° (for realistic porosities). Assessment of the efficacy of pervasive intergranular fluid flow during metamorphism is underway and entails identification of the factors that control grain-edge fluid connectivity in different mineral-fluid systems.

Following original experiments by *Watson and Brenan* [1987], *Lee et al.* [1991], *Laporte and Watson* [1991], *Holness* [1992], and *Holness* [1993] examined the effects of pressure, temperature, and fluid composition on intergranular connectivity of H_2O - CO_2 -alkali-halide salt fluids in polycrystalline SiO_2 . In concert, the experimental data show a broadly negative correlation between pressure and Θ , a positive correlation between the mole fraction of CO_2 in the fluid phase (X_{CO_2}) and Θ , and a negative correlation between concentrations of dissolved alkali-halide salt and Θ . One concludes that quartzose lithologies in textural equilibrium will be permeable to intergranular flow of H_2O and aqueous brines in the upper and middle crust (≤ 0.6 GPa) if temperatures are less than ca. 400° to 500° C, respectively. Pervasive intergranular flow of aqueous fluid during high-grade metamorphism in upper- and middle-crustal quartzites is apparently precluded. Intergranular flow of CO_2 -rich fluid ($X_{\text{CO}_2} > 0.5$) in quartzite at all metamorphic conditions also appears unlikely.

Holness and Graham [1991] demonstrated that Θ for calcite and aqueous fluid decreases with increasing NaCl concentration, consistent with the results obtained previously for quartz and water-rich fluid [e.g., *Watson and Brenan*, 1987]. In contrast to quartz-fluid experiments, however, *Holness and Graham* [1991] also found that calcite-calcite- $(\text{H}_2\text{O}$ - $\text{CO}_2)$ fluid Θ does not increase monotonically with X_{CO_2} in the fluid phase. Instead, Θ exhibits a minimum at $X_{\text{CO}_2} = 0.5$ for a temperature and pressure of 650° C and 0.1 GPa, respectively. The critical condition for connectivity, $\Theta < 60^\circ$, was found to occur for X_{CO_2} between 0.2 and 0.6. These data suggest that the effects of fluid composition on Θ can be highly mineral specific. Relations in the calcite- H_2O - CO_2 system are as yet unresolved, however, as *Koga*

[1993] reports a monotonic increase in calcite-calcite- $(\text{H}_2\text{O}$ - $\text{CO}_2)$ fluid Θ with X_{CO_2} at higher pressures.

The implications of these data are far reaching. Permeability enhancement or diminution is revealed to be chemical and not simply mechanical. Feedback effects in which buffering of infiltrated fluid composition alters the permeability of the host rock must now be considered.

Anisotropic interfacial energies will affect solid-fluid dihedral angles. The 60° critical value is therefore not necessarily applicable in polymineralic metamorphic

rocks. In order to circumvent reliance on dihedral angles, and to assess the robustness of the Θ criterion in anisotropic media, measurements of bulk transport properties of fluid-bearing rock materials at relevant P-T conditions are being used to determine intergranular fluid connectivity. Diffusivities of oxygen and chlorine in porous polycrystalline quartz measured by *Farver and Yund* [1992] and *Brenan* [1993], respectively, exhibit positive correlation with textural evidence for grain-edge fluid connectivity. The diffusion data corroborate many of the relations between fluid composition and intergranular fluid connectivity previously derived mainly from measurements of Θ , although the Θ -criterion was shown to be fallible at very low porosities [*Brenan*, 1993].

Where fluid composition or ambient conditions prevent intergranular flow, microcracks and fractures must accommodate fluid advection. *Brantley* [1992] showed that, in general, fluid compositions that promote grain-edge connectivity (e.g., aqueous brines) also promote healing of microcracks in quartz. These data suggest a possible delineation of intergranular flow and microfracture flow regimes in quartzose rocks on the basis of fluid composition. Healing in all fluid compositions was shown by *Brantley* to be virtually instantaneous (≤ 100 years), however, and so it appears that fluid overpressures are required to maintain flow along connected microfracture networks during metamorphism regardless of fluid composition. *Dutrow* [1994] concluded that such overpressures will produce diachronous and episodic fluid flow during metamorphism. Episodic fracture flow was also predicted by *Germanovich and Lowell* [1992].

Fisher and Brantley [1992] used textural observations, vein distributions, and kinetic model calculations to investigate the time scale of fracture flow in slates from Kodiak and Afognak Islands, Alaska. They concluded that crack and seal events lasted approximately 10^2 to 10^4 years with a cumulative duration of 10^3 to 10^6 years. Some veins show textural evidence for having remained open for 10^5 to 10^6 years.

The potential extent of fluid-rock interaction afforded by fracture flow is controlled by the spatial distribution of fractures. *Manning* [1994] showed that the distributions of subparallel veins (representing fluid pathways) in several amphibolite to greenschist facies metamorphic terranes are self similar. *Manning* suggested that the fractal dimension of each vein set can therefore be used to quantify the degree to which fracture flow was channelized or pervasive.

Isotope Tracers

Rumble *et al.* [1991] found that $^{18}\text{O}/^{16}\text{O}$ values for marbles from southern Maine are consistent with *either* extensive fluid-rock interaction during metamorphism or premetamorphic diagenesis. Until recently, the ambiguity suffered by Rumble *et al.* was indicative of a nagging foundational uncertainty in the study of oxygen isotopes in metamorphic rocks; *indisputable* evidence that observed heterogeneities in mineral $^{18}\text{O}/^{16}\text{O}$ indicative of fluid flow occurred *during* metamorphism was lacking. Measurements of small-scale intracrystalline $^{18}\text{O}/^{16}\text{O}$ variations in metamorphic minerals during this past quadrennium have provided us with this previously lacking evidence.

Chamberlain and Conrad [1991] measured $^{18}\text{O}/^{16}\text{O}$ in four metamorphic garnets from three localities using the CO_2 laser-heating fluorination method described by Sharp [1990]. One of the analyzed garnets, from the Gassetts schist of southeastern Vermont, exhibits a decrease in $\delta^{18}\text{O}$ of 2‰ from core to rim that can only be explained by exchange with a mobile fluid phase. By documenting the existence of this pattern of oxygen isotope zoning in a patently metamorphic mineral, it was shown unequivocally that externally derived fluids were the progenitors of significant shifts in $^{18}\text{O}/^{16}\text{O}$ during metamorphism. Chamberlain and Conrad suggested that the zoning profile of this garnet resulted from exchange with a low- $\delta^{18}\text{O}$ fluid phase that infiltrated the rock during late stages of garnet growth.

Young and Rumble [1993], studying a sample of Gassetts schist similar to that examined by Chamberlain and Conrad [1991], illustrated the usefulness of millimeter-scale measurements of $^{18}\text{O}/^{16}\text{O}$ in several minerals for chronicling both fluid-rock reaction histories and durations of fluid flow during metamorphism. Young and Rumble's analysis suggests that oxygen carried by advecting fluid can find its way into minerals even after cessation of flow by action of net-transfer reactions. Thus the presence of fluid-derived oxygen in a metamorphic mineral, as ascertained from measured $\delta^{18}\text{O}$, does not *a priori* constitute evidence for growth *during* fluid infiltration. In the case of the Gassetts schist sample, it was shown that the fluid-borne low- $\delta^{18}\text{O}$ oxygen evidenced by garnet zoning may have been sequestered by the rock initially in the mineral chlorite during hydration reactions, and that garnet acquired this low $\delta^{18}\text{O}$ oxygen from chlorite during subsequent post-fluid mineral-mineral reaction. The small-scale isotope measurements suggest that fluid infiltration during metamorphism of the sample studied must have been short-lived with the total duration of flow being $\leq 10^5$ years. Preservation of nonequilibrium $\delta^{18}\text{O}$ values between two different mica minerals with similar oxygen diffusivities was a crucial observation in this work.

The importance of these types of measurements should not be overlooked. Previously published geochronology data suggest garnet growth in pelitic rocks may take approximately 10^7 years. If so, the study by Chamberlain and Conrad [1991] implies protracted continuous

flow of water spanning millions of years. Alternatively, the analysis of Young and Rumble [1993] indicates fluid that was the source of the low $^{18}\text{O}/^{16}\text{O}$ oxygen flowed for 100,000 years or less.

Chamberlain and Conrad [1993] attributed meter-scale spatial variations in the amplitude of metamorphic garnet $^{18}\text{O}/^{16}\text{O}$ zoning to growth of garnet during passage of an oxygen isotopic front propagated by advecting fluid over a period of 10 Ma. Such a long period of flow of exogenous fluid has testable consequences for the $^{18}\text{O}/^{16}\text{O}$ composition of other minerals in the rock. For example, mica minerals, which have comparatively large oxygen diffusivities, should show $\delta^{18}\text{O}$ values reflective of equilibrium with the fluid upstream of the front (for micas, see below) regardless of their role in the garnet-producing reaction.

The study by Chamberlain and Conrad [1993] raises the issue of how to define $^{18}\text{O}/^{16}\text{O}$ fronts in polymineralic rocks imparted by flow of nonequilibrium fluid. Recalling that the displacement of a $^{18}\text{O}/^{16}\text{O}$ front is a function of the amount of exchangeable oxygen in the solid, and considering that the amount of exchangeable oxygen is a function of oxygen diffusivity, a parameter that varies over fifteen orders of magnitude from mineral to mineral in some rocks, it is clear that there will be different $^{18}\text{O}/^{16}\text{O}$ front positions for different minerals. Moreover, mineral-specific fronts may only be evident in portions of individual grains as a result of diffusion-limited zoning.

The high spatial resolution that is unique to the ion microprobe also contributed to our understanding of isotope exchange between fluid and rock during metamorphism through the advent of new methods and instrumentation. Valley and Graham [1991] used this technology to measure magnetite $^{18}\text{O}/^{16}\text{O}$ on an unprecedented small scale. Although the analytical precision of the analyses is an order of magnitude larger than laser-heating and conventional bomb analyses, the data reveal a dramatic 9‰ decrease in $\delta^{18}\text{O}$ at the outer 10 μm edge of the magnetite grains that could not have been identified by other means. Valley and Graham concluded that the narrow zones of ^{18}O depletion are the result of diffusive exchange of oxygen with a hydrous fluid during the waning stages of granulite facies metamorphism. The width of the depleted edges and known oxygen diffusivities in magnetite were used to infer that retrograde fluid flow apparently lasted between 1×10^7 and 9×10^3 years.

Sample charging has hampered similar efforts in insulating materials. New methods of analysis are nevertheless aiding in obtaining $^{18}\text{O}/^{16}\text{O}$ ion microprobe analyses of useful precision in silicates. Jamtveit and Hervig [1994] used "extreme energy filtering" to obtain $\delta^{18}\text{O}$ analyses of hydrothermal garnet with analytical precision on the order of $\pm 2\%$. The data are sufficient to delineate an abrupt decrease in $\delta^{18}\text{O}$ of 5‰ from core to rim with a spatial resolution of 50 μm . Jamtveit and Hervig attributed the shift to a transition from magmatic fluid to meteoric fluid compositions as the system evolved from a ductile to a brittle strain regime.

During this last quadrennium, several laboratories [e.g., *Weichert and Hoefs*, 1993; *Rumble et al.*, 1994] began investigations of the viability of substituting ultraviolet (UV) lasers for infrared lasers in order to obtain high-spatial resolution analyses of oxygen isotope ratios in minerals. Ultraviolet laser light is absorbed intrinsically by electronic transitions in minerals. Oxygen can therefore be liberated by UV irradiation without the localized heating that limits the spatial resolution of infrared laser methods. When combined with new He-entrainment mass spectrometry techniques [e.g., *Hayes et al.*, 1990], the UV laser may substantially improve our ability to probe mass transfer between fluids and metamorphic rocks on the micrometer scale.

Studies of small-scale variations in $^{18}\text{O}/^{16}\text{O}$ over the past several years showed that exchange of oxygen isotopes between metamorphic fluids and minerals can no longer be regarded as separate and independent from advance of net-transfer reactions. *Young* [1993] presented a methodology based on differential thermodynamics that constitutes a necessary framework for evaluating small-scale variations in $^{18}\text{O}/^{16}\text{O}$ in the context of metamorphic parageneses formed during fluid flow. Calculations of this type showed that net-transfer reaction paths can strongly influence the ability of an external fluid to effect changes in mineral $\delta^{18}\text{O}$ values.

Oxygen and carbon isotopes are well-suited as tracers of mass transfer and transport in metamorphic rocks, but the need to identify the *sources* of metamorphic fluids with improved certainty has prompted development of other isotope tracers over the last several years. Notable among these are the isotopes of the noble gases He, Ne, Ar, Kr, and Xe. *Irwin* [1993] reported preliminary results of laser microprobe noble gas mass spectrometry that illustrate the potential of the isotopes of heavy noble gas elements (Ar, Kr) for constraining the origin of fluid trapped in individual metamorphic mineral grains.

The Sign of $\mathbf{J} \cdot \nabla T$: 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 H_2O -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 $\delta^{18}\text{O}$ 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 $\mathbf{J}_t \cdot \nabla T$, 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 $\delta^{18}\text{O}$ with distance as is expected for gradient isotopic exchange. Up-temperature flow was invoked to explain the decrease in argillite $\delta^{18}\text{O}$ 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 $\mathbf{J}_t$ 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 $\delta^{18}\text{O}$ 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 ∇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 $\delta^{18}\text{O}$ values several per mil *greater* than indicated by equilibrium 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 $\delta^{18}\text{O}$ 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.

Allochemical Metamorphism by Fluid Flow

Allochemical metamorphism is an old idea recently revived by studies of metamorphic fluid flow in several diverse metamorphic settings. *Ague* [1994a, 1994b] examined mass transfer attending Barrovian style regional metamorphism of the Wepawaug Schist, Connecticut. He documented correlations among metamorphic grade, quartz vein density, and vein accessory-phase mineralogy. Amphibolite-facies veins were found to be surrounded by aluminous selvages, and staurolite and kyanite were seen to occur preferentially within the selvages. *Ague* calculated that the selvages are the result of a 35% reduction in mass during metamorphism, and he concluded that growth of staurolite and kyanite was the direct result of metasomatism born of regional-scale fluid flow. The implication is that the positions of staurolite and kyanite isograds in Barrovian metamorphic terranes delimit the locations of fossil fluid-filled fracture networks as well as pertinent isotherms and isobars.

Selverstone et al. [1991] found that fluid flow that accompanied ductile shearing in the Tauern Window of the eastern Alps, Austria, transformed metagrandiorite protolith into aluminous schist along a shear zone. Weight loss in this process was as much as 60%.

The aluminous composition caused by metasomatism of the shear zone resulted in formation of garnet-chlorite-staurolite schist during metamorphism to amphibolite facies conditions soon after shearing.

The process described by *Selverstone et al.* is essentially an extreme example of the phenomenon described by *Ague* brought about by comparatively large fluxes of fluid. *Ague* attributed metasomatism in the Barrovian terrane to a time-integrated fluid flux of $10^5 \text{ m}^3/\text{m}^2$. *Selverstone et al.* calculated a larger flux of $\geq 10^6 \text{ m}^3/\text{m}^2$ for shear-zone metasomatism.

Scales of Fluid Advection

Fluids derived from metamorphism of subducting lithosphere are often cited as agents for metasomatism of overlying mantle wedges in studies of arc magmatism. Two different views of the efficacy of mass transport by fluid advection during high-pressure low-temperature metamorphism of paleosubduction complexes emerged from studies in southern California, and in the eastern and western Alps.

Bebout and Barton [1993] described evidence for widespread metasomatism effected by flow of aqueous fluids in the Catalina subduction complex of Santa Catalina Island, southern California. The advected H_2O -rich fluids were apparently derived from sedimentary rocks of the complex. Structural discontinuities associated with mélange zones in the Catalina rocks facilitated large-scale (kilometer) flow at depths of 15 to 40 kilometers.

Unlike at Catalina, *Philippot and Selverstone* [1991] found fluid inclusion evidence for ubiquitous local heterogeneity of fossil fluid compositions in eclogite veins from the Monviso ophiolitic complex of the western Alps, and *Selverstone et al.* [1992] showed that mineral assemblages record similar heterogeneity in the eclogite zone of the Tauern Window, eastern Alps. *Philippot and Selverstone* and *Selverstone et al.* noted that heterogeneous fluid compositions are an indication that large-scale metamorphic fluid flow did not occur in these ancient subduction complexes. As the Tauern eclogites are remnants of lithosphere subducted to depths of 70 kilometers, these data imply that metasomatism of overlying mantle by fluid that flowed from subducting and metamorphosing lithosphere was unlikely. It follows that fluids may be entrained by the down-going lithospheric slab to zones of partial melting (thought to occur at depths of approximately 100 kilometers).

Our notion of the potential magnitude of the effects of fluid flow on the evolution of orogenic belts was altered in this last quadrennium. *Ferry* [1992], *Stern et al.* [1992], and *Léger and Ferry* [1993] proposed that Devonian Barrovian-type regional metamorphism in eastern Vermont, U.S.A., was influenced by the action of "giant" hydrothermal systems that operated at depths of 25 kilometers over an area of $\sim 2,000$ square kilometers for perhaps millions of years. They based their conclusions on the distributions of prograde net-transfer reaction progress indicators and time-integrated fluid fluxes implied by these indicators, and on carbonate $^{18}\text{O}/^{16}\text{O}$

and $^{13}\text{C}/^{12}\text{C}$ data in the region. Aqueous fluid is envisaged to have been focused through subhorizontal flow up temperature from the cool flanks of regional-scale antiforms toward their hotter cores. Up-temperature flow enabled progress of gradient reactions. Upon reaching the axes of the domes, fluids flowed subvertically down temperature as evidenced by abundant quartz veins. Ferry noted that the time-integrated fluxes of approximately 10^3 to 10^4 m^3/m^2 , combined with estimates for the duration of metamorphism of approximately 10^7 years, imply that the "giant" hydrothermal cells that attended Barrovian metamorphism had fluid fluxes equivalent to $\leq 2\%$ of the mean flux associated with mid-ocean ridge hydrothermal activity. The source(s) of the fluids are not known.

Depth of Meteoric Fluid Penetration

The maximum depth of meteoric fluid ingress into Earth's lithosphere is not well constrained. A principal barrier to surface fluid penetration is thought to be the transition from brittle to ductile stress-strain regimes in the crust because of the implicit shift from hydrostatic to lithostatic fluid pressures. Studies of Tertiary metamorphic core complexes exposed in the Cordilleran orogen of the southwestern United States addressed the question of whether or not surface fluids breached the ductile-brittle transition.

The lower plates of core complexes are exhumed along crustal-scale shear zones (detachment faults) that span the ductile-brittle transition. Lower-plate rocks have thus undergone ductile strain followed by brittle deformation during their unroofing. There is abundant evidence for reaction with fluids both above and below core complex detachment faults. Indications are that some of these fossil fluids were surface-derived. The timing of fluid-rock interaction below detachment faults therefore has important implications for the depth of meteoric fluid penetration.

Fricke *et al.* [1992] and Morrison [1994] examined indicators of fluid-rock reaction in the lower plates of the Ruby Mountains-East Humboldt Range core complex of northeastern Nevada and the Whipple Mountains core complex of southeastern California, respectively. Both studies found that quartz-feldspar $^{18}\text{O}/^{16}\text{O}$ systematics were indicative of exchange with meteoric fluid, but Fricke *et al.* concluded that $^{18}\text{O}/^{16}\text{O}_{-1}$ exchange occurred during the waning stages of ductile deformation of the lower plate while Morrison asserted that exchange occurred after passage of the lower plate rocks into the brittle regime. The critical question of whether or not meteoric fluids passed through the ductile-brittle transition remains unresolved. Outstanding difficulties include estimating depths from temperatures in tectonically active terranes, and accounting for the complexity of variable strain rates.

Acknowledgments. The author has benefitted from valuable discussions with D. Rumble, R. Ilchik, D. Bell, J.D. Frantz, J.M. Brenan, J.M. Palin, and J. Morrison during

compilation of this report. Reviews by two anonymous referees, J.M. Brenan, K. Verosub, and R. Pielke improved the clarity of presentation.

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- (Received August 18, 1994; revised January 6, 1995; accepted February 2, 1995.)