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FIELD MEASUREMENT OF HIGH TEMPERATURE BULK REACTION RATES I: THEORY AND TECHNIQUE

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ABSTRACT. Knowledge of metamorphic reaction rates is crucial to accurately interpret rock and mineral chemistry. The local equilibrium assumption, used in geochronology, geothermobarometry, and material flux estimates, requires that local reaction rates among system phases are fast relative to local rates of P-T-X change. Natural metamorphic reaction rates are essentially unknown and difficulties and disagreements exist regarding extrapolations of existing laboratory data to natural conditions. Growing recognition of natural effects that could be attributed to slower reaction rates justifies the need for a field-based quantification of reaction rates to assess the accuracy of lab-based predictions. We describe in detail the theory and methodology of a technique for extracting bulk reaction rates directly from isotopic data derived from natural samples (Baxter and DePaolo, 2000). Reaction rates measured using this technique may be judiciously applied to isotopic exchange or net reaction kinetics in other natural systems. The technique requires collection of whole rock and garnet $^{87}Sr/^{86}Sr$ data along a sampling traverse normal to a lithologic contact where there was, prior to metamorphism, a sharp isotopic discontinuity. Garnet data provide information on syn-metamorphic conditions and the time interval for the exchange process. Forward modeling of the reactive transport process using numerical methods and the equations for diffusive reactive transport allow determination of the reaction rate and bulk Sr diffusivity that provides the best fit to the data. Measurement of reaction rates is best constrained if an isotopic step is preserved at the contact, the size of which is directly proportional to the bulk reaction rate. This contribution is intended to serve as a template for future use and development of this technique to acquire natural reaction rate data from metamorphic systems.

INTRODUCTION

The chemical and isotopic compositions of rocks and minerals are used to determine the history and timing of pressure (P), temperature (T) and chemical (X) evolution in the Earth during mountain building episodes. Interpretation of these data is often based on the assumption of local equilibrium, first defined by Thompson (1959). Many geochemical techniques employ the assumption of local equilibrium including radiogenic isotope isochron geochronology (for example Nicolaysen, 1961), thermodynamic geothermobarometry (for example Spear, 1993), stable isotope thermometry (for example O'Neil, 1986) and studies of chemical and fluid fluxes through geologic media (for example Brady, 1977; Ferry, 1986; Baumgartner and Rumble, 1988; Knapp, 1989; Bickle and Baker, 1990; Cartwright and Valley, 1991; Bickle and others, 1995, 1997). The local equilibrium assumption, which we examine in more detail below, essentially requires that the rate at which local reactions proceed towards equilibrium is fast compared to the rates of local P-T-X change that generate departures from equilibrium. In such a case, the system of mineral and fluid phases is able to adjust its compositions and modes rapidly and "keep up" with any changes in the equilibrium state defined by the local P-T-X conditions.

It is difficult to ascertain whether reaction rates are indeed this fast in high temperature geologic systems. However, it may be the case that certain applications

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*Present address: Division of Geological and Planetary Sciences, California Institute of Technology, MC 170-25, Pasadena, California 91125 based on the local equilibrium assumption may still be useful even if reaction rates are not this fast. For example, it is widely accepted that conclusions reached via equilibrium thermodynamics, particularly regarding P-T-t histories of metamorphic terranes, are typically reasonable although it might be impossible to prove their accuracy. Microanalysis of mineral grains in rocks allow investigators to focus on subdomains in crystals (for example, grain rims) that are more likely to be near equilibrium with other phases than interior domains. In this way, partial local equilibrium among discrete portions of system phases may still yield useful results. Nevertheless, the actual bulk rates of exchange between system phases is important to constrain, as it may affect the interpretation of P-T-t reconstructions, the use of rock chemistry and mineralogy in material flux estimates (for example Ferry, 1986; Bickle, 1992; Ague, 1998; Lasaga and others, 2001), geochronology (DePaolo and Getty, 1996), and also the relationship between reactions that produce mineralogical changes and the deformation of rocks during metamorphism (Baxter, ms, 2000; Baxter and DePaolo, 2002a).

Researchers have relied heavily upon laboratory-based kinetic data to predict and model the rate of approach to equilibrium in natural systems. Such extrapolations of laboratory-based kinetic data for high temperature (300°-700°C) metamorphic reactions (for example Wood and Walther, 1983; Helgeson and others, 1984; Matthews, 1985; Rubie and Thompson, 1985; Tanner and others, 1985; Lasaga, 1986; Schramke and others, 1987; Dachs and Metz, 1988; Heinrich and others, 1989; Kerrick and Others, 1991; Lüttge and Metz, 1991, 1993; Hacker and others, 1992; Jove and Hacker, 1997; Lüttge and others, 1998; Winkler and Lüttge, 1999, and references therein) are subject to large uncertainties because the reaction mechanisms (see Dachs and Metz, 1988; Lüttge and Metz, 1991, 1993; Hacker and others, 1992; Barnett and Bowman, 1995; Jove and Hacker, 1997; Mosenfelder and Bohlen, 1997; Ganor and Lasaga, 1998; Penn and Banfield, 1999; Zheng and others, 1999; Lasaga and Lüttge, 2001) and controlling parameters (for example affinity for reaction, and reactive surface area) are variable and may not be consistent between the lab and nature. Thus, while the theory of reaction rates and chemical transport in fluid-rock systems has been the topic of extensive study (Aagaard and Helgeson, 1982; Walther and Wood, 1984; Lasaga, 1989, 1998; Bickle and McKenzie, 1987; Richter and DePaolo, 1987; Baumgartner and Rumble, 1988; Blattner and Lassey, 1989; Lassey and Blattner, 1988; Knapp, 1989; Bickle, 1992; Lasaga and Rye, 1993; Lichtner, 1993, 1996; Bowman and others, 1994; Johnson and DePaolo, 1994; Steefel and Lasaga, 1994; DePaolo and Getty, 1996; Steefel and MacQuarrie, 1996; Abart and Sperb, 1997; Ague, 1998; Ague and Rye, 1999; Lasaga and others, 2000, 2001; Cole and Chakraborty, 2001), successful application of the theory to natural metamorphic systems remains a difficult endeavor.

Understanding Reaction Rates in Nature

Figure 1 illustrates the current state of understanding and predicting natural reaction rates. Conceptually, we identify three scientific components which, together, are fundamental to this endeavor: (1) Laboratory based kinetic data where we have the ability to control and observe system properties and mechanisms directly, (2) Extrapolation of laboratory based kinetic data to nature using kinetic theory and an understanding of the governing parameters and mechanisms, and (3) Field based measurement of reaction rates with which we can evaluate whether extrapolations of lab data yield reasonable predictions of natural reaction rates. Let us treat these each in turn.

Laboratory-based kinetic data.—The experimental data shown in figure 1 are rate constants (normalized to the geometric surface area of the rate limiting mineral) for different metamorphic reactions. These data have been used as a guide for the kinetics of metamorphic reactions in general. The Wood and Walther (1983) paper presented a compilation of existing lab-based kinetic data on a variety of reactions, much of which derived from powder experiments. They showed that a single, linear rate law could

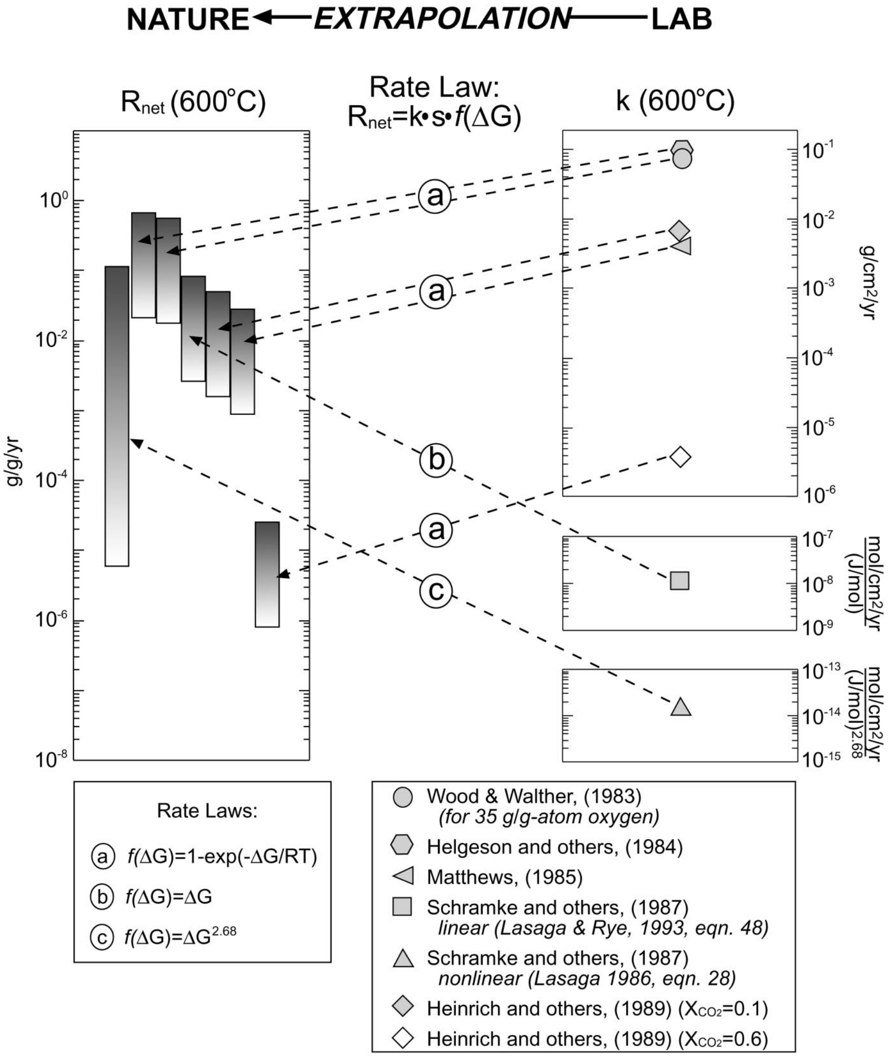

Fig. 1. The three components to understanding reaction rates: (1) **lab**-based kinetic data, (2) theory and governing parameters for **extrapolation**, and (3) **natural** kinetic data. Extrapolations are labeled with the form of *f*(ΔG) in the rate law. Rate law "a" is equivalent to ΔG/RT for ΔG<0.4RT (Walther and Wood, 1984). In the extrapolations, a geometric surface area (s) of 20 cm^2/g was used, representative of 100 micron radius spherical grains of the rate limiting mineral comprising 20 percent by volume of the rock. The bars in the "nature" column show the predicted R_{net} values for ΔG ranging from 3200 J (top of bar) to 80 J (bottom of bar). Note the absence of any *field-based* kinetic data in the "nature" column.

explain all the data. Helgeson and others (1984) reviewed much of the same experimental data as Wood and Walther (1983) and their pH-independent linear rate law for feldspar hydrolysis at 600°C is virtually identical to Wood and Walther (1983). Also shown are rate constants (denoted k^+ in these papers) extracted from two more recent studies: Matthews (1985) on the breakdown of zoisite, and Heinrich and others (1989) on the reaction 1 tremolite + 11 dolomite = 8 forsterite + 13 calcite + 9 CO_2 + 1 H_2O for two different fluid compositions (using equation 8 for n=1, of Heinrich and others, 1989, dolomite surface area normalized). Two interpretations of the data of Schramke and others (1987) on the dehydration of muscovite are shown in figure 1 as well. From this dataset, Lasaga and Rye (1993) extracted a linear rate law (with a different form than Wood and Walther (1983). Lasaga (1986) proposed a non-linear rate law as an alternative fit to the Schramke and others (1987) data. Recent studies involving high temperature metamorphic processes that mention or use kinetic data (for example Walther, 1996; Valley and others, 1997; Ague 1998; Ague and Rye, 1999; Lasaga and others, 2000, 2001; Gillis and others, 2001; Widmer and Thompson, 2001) typically rely upon one of the kinetic studies cited in this paragraph.

Extrapolation of laboratory-based kinetic data to nature.—Figure 1 shows that the kinetic data and rate laws of these studies predict values for the net reaction rate in nature (R_{net}) ranging from 10^0 to 10^{-6} g/g/yr, for a representative rate limiting surface area, s, of 20 cm^2/g. These extrapolations are for ΔG ranging from 80 joules - representative of a ~1°C reaction overstep of a typical metamorphic reaction (the suggested overstep of Walther and Wood, 1984, 1986), to 3200 joules - representative of a 40°C overstep (as suggested by Waters and Lovegrove, 2002; and comparable to the range of overstepping suggested by Ridley and Thompson, 1986; Lasaga and Lüttge, 2001). Most of these rates suggest reaction timescales ($1/R_{net}$) of 1 to 1,000 years, which in turn suggest that reactions will proceed very rapidly compared to regional metamorphic timescales of 10^6 to 10^7 years. It was on this basis that Wood and Walther (1983) and Walther and Wood (1984, 1986) concluded that reaction rates during regional metamorphism are very fast such that equilibrium is easily maintained. Note that the non-linear rate law for smaller ΔG predicts much slower net reaction rates. Extrapolation of non-linear rate laws to small ΔG is tenuous because they are often based only on data at large ΔG (for example Lasaga, 1986; Kerrick and others, 1991), and furthermore do not always appear to reproduce the limited small ΔG data that do exist (for example, the non-linear rate law of Lasaga, 1986, predicts a rate three orders of magnitude slower than the data of Schramke and others, 1987, table 7, for $\Delta G=59.5$ J). It is illustrative of the difficulties inherent in extrapolating lab based data to nature that two rate laws (that is Lasaga and Rye, 1993; and Lasaga, 1986) derived from the same experimental dataset yield natural reaction rates which can vary by orders of magnitude.

The natural kinetic dataset for high temperature systems.—Since the Wood and Walther (1983) paper, many studies (for example Rubie and Thompson, 1985; Ridley and Thompson, 1986; Kerrick and others, 1991; Hacker and others, 1992; Lüttge and Metz, 1993; Jove and Hacker, 1997) have called for cautious evaluation of the applicability of laboratory experimental data – in particular powder experiments – in predicting reaction kinetics in natural systems. Furthermore, in the last decade, there has been a growing recognition of effects in nature that could be attributed to slower reaction or exchange rates in natural high temperature systems (for example, Lasaga and Rye, 1993; Barnett and Bowman, 1995; DePaolo and Getty, 1996; Eppel and Abart, 1997; Jove and Hacker, 1997; Skelton and others, 1997; Ague, 1998; Lewis and others, 1998; Abart and Pozzorini, 2000; Baxter and DePaolo, 2000; Ferry, 2000; Lasaga and Lüttge, 2001; Waters and Lovegrove, 2002). Major discrepancies between field based and lab based measurements of low temperature weathering rates have been well documented (for example, Velbel, 1993; White and Brantley, 1995) and research in that discipline has been directed specifically towards addressing these complexities. However, save for our recent report (Baxter and DePaolo, 2000), which is discussed in Part II of this study (Baxter and DePaolo, 2002b), *no well-constrained field-based measurement of reaction rates exists* for high temperature regional metamorphic systems. Such field-based data are required to serve as a "ground truth" for applications of geochemical kinetics. In the absence of quantitative field based kinetic data, we have no way to assess the accuracy of existing extrapolations (fig. 1).

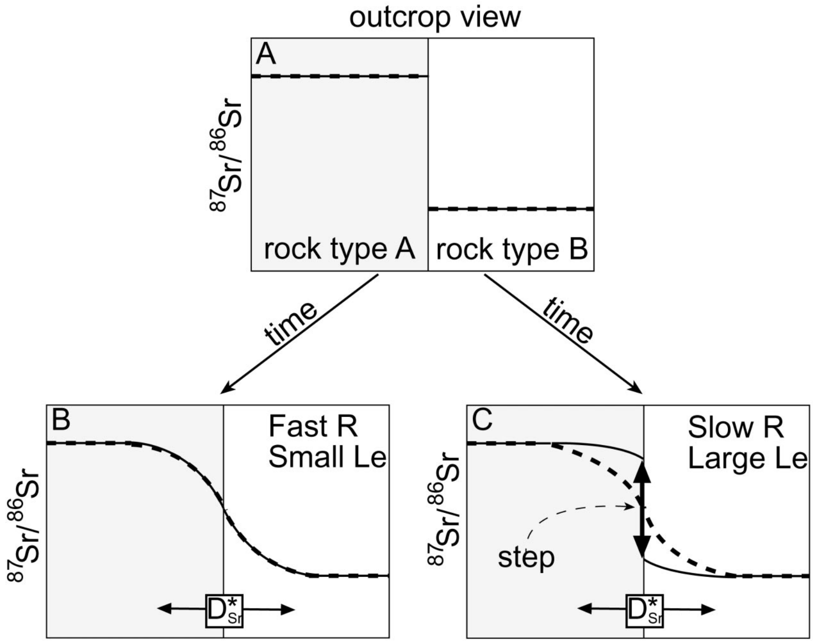

Fig. 2. Concept for measuring bulk fluid-rock exchange rates. (A) Initial isotopic "step" in $^{87}Sr/^{86}Sr$ at the contact between two different rock types. The thin solid line is the bulk solid $^{87}Sr/^{86}Sr$ and the dashed line is the ITM $^{87}Sr/^{86}Sr$. (B) $^{87}Sr/^{86}Sr$ profiles as the result of ITM-meditated diffusional transport across the contact after some time, t, for rapid R and small Le. (C) Similar to (B) but for slow R and large Le. D* is the effective bulk diffusivity of Sr in the rock. The size of the isotopic step remaining at the contact (if any) is proportional to ⟨Rt⟩.

In this paper, we detail the development and methodology of a technique to measure bulk high temperature metamorphic reaction rates using isotopic measurements of metamorphic rocks and minerals (Baxter and DePaolo, 2000). Even with the uncertainties inherent in a field based analytical approach, by having at hand a quantitative constraint on the actual reaction rates in nature we may then return to kinetic theory and better evaluate the dominant parameters, mechanisms, forms of the rate law, and rate-limiting steps in the process. Furthermore, such data may enable us to better assess the local equilibrium assumption and the utility of existing lab data. Ultimately, the goal is to provide a template with which we can gain a better understanding of the rates at which geochemical processes occur in the Earth.

MEASURING PALEO - REACTION RATES IN METAMORPHIC ROCKS

Since we do not normally have access to active metamorphic environments, we rely on the geologic record preserved in exposed metamorphic rocks to infer the conditions and processes operating in paleo-metamorphic environments. The approach focuses on analysis of natural isotopic variations along transects normal to lithologic contacts where there were, before metamorphism, sharp, step-like contrasts in isotopic ratios (fig. 2). During metamorphism, chemical potential (and isotopic) gradients across the contact become more or less smoothed due to cross layer chemical and isotopic exchange. The nature and extent of the smoothing of the original chemical and isotopic contrast contains information on the rates of material exchange between the intergranular transporting medium (typically a fluid) and the minerals of the rock.

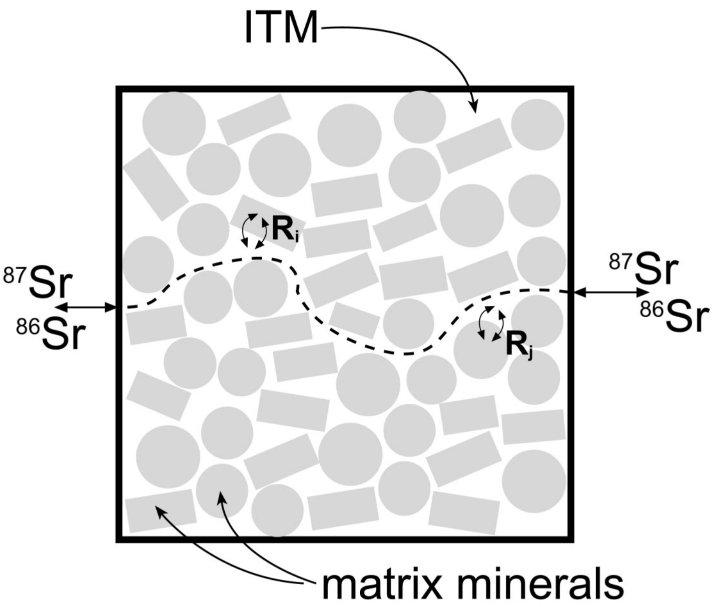

Fig. 3. Cartoon sketch of the rock at any point in the system. As Sr isotopes (and other elements) diffuse through the ITM (dashed line) driven by long scale isotopic gradients (or chemical potential gradients), the local minerals (i, j, et cetera) react and exchange with the ITM at rates, R_i, R_j, et cetera, for each mineral.

This approach is in principle applicable to any of a number of commonly used isotopic systems, such as O, C, Sr, Nd, Pb, Hf, and Os. We have concentrated on Sr isotopes for a number of reasons. It is fairly easy to find large Sr isotopic discontinuities in layered metamorphic rocks (see later discussion). This makes the Sr isotope approach relatively widely applicable. It also appears that Sr is sufficiently soluble in metamorphic fluids (in comparison to Nd, Pb, and Hf for example) that there is measurable transport at scales of several centimeters to meters. Also, unlike O and C isotopes, there is no temperature-dependent fractionation factor to further complicate data analysis. Nevertheless, it is desirable to have data from more than one isotopic system that may be transported at different rates to further evaluate the results derived solely from Sr isotopes. Nd is a suitable secondary system to Sr as it behaves fundamentally differently (though it may be readily transported in carbonate or phosphate rich fluids) and large Nd isotopic variations are also common in the same settings where Sr isotope variations occur.

Diffusion Through the Intergranular Medium (ITM)

Diffusional transport across lithologic boundaries presumably occurs via an intergranular medium that by definition surrounds all mineral grains (fig. 3). This intergranular transporting medium, herein referred to as the ITM, may be a free fluid, dry grain boundaries, or some combination of the two. The nature of the ITM is not prescribed by the model, although inferences about its characteristics may be drawn from the data. The presence and importance of the ITM as the primary medium for transport on scales larger than a few tens of microns is essentially required by the fact that grain volume diffusion is far too slow at metamorphic temperatures. Both dry grain-boundary and fluid mediated diffusion in the ITM (see Farver and Yund, 1995) are several orders of magnitude faster than volume diffusion. Volume diffusion is thus ignored as an outcrop scale transport mechanism, although it may come into play in terms of limiting the rate of mineral-fluid exchange due to the sluggishness of intragranular diffusion of key elements. In our model, we assume that all isotopic and chemical exchange through the rock matrix is accommodated by diffusion through the ITM. The ITM itself is assumed in our model to remain stationary (at least with respect to layer perpendicular motion). Transport could also occur by an advection of fluid, but numerous studies (for example Ferry, 1994; Kohn and Valley, 1994; Vyhnal and Chamberlain, 1996) have shown that cross-contact advection is limited and, where present, can usually be recognized by the characteristics of isotopic profiles across the contacts. In particular, a significant cross-layer component of advection would skew the isotopic profile in the direction of advection, resulting in a lack of symmetry about the contact. Layer-parallel advection will not affect the cross-layer isotopic pattern, except due to the effects of transverse dispersion, which simply add to the effective diffusivity.

The Rate of Local Solid-ITM Exchange

In our model, the sole mechanism by which the solid minerals change isotopic composition is by dissolving, at some rate R, and precipitating as either new mineral phases or the same mineral with a different chemical composition determined by the local P,T and chemical composition of the ITM (fig. 3). Exchange between neighboring minerals must involve exchange through the ITM as an intermediate step. Consequently, the bulk solid isotopic profile about the contact changes in different ways depending on the relative rates of cross-contact intergranular diffusive transport and local solid-ITM exchange. The cross-contact diffusional transport can be described in terms of an effective bulk diffusivity (D*) and the local solid-ITM exchange by the reaction time constant, R. Figure 2 shows two extreme cases. If the rate of local solid-ITM exchange, R, is very fast compared to D*, the solid and the ITM have the same local isotopic composition everywhere, or in other words can be considered to be in “isotopic equilibrium” everywhere. This situation is the isotopic version of “local equilibrium” and can occur only if the reaction rate is infinitely larger than the transport rate, or if there are no isotopic gradients. Given an initial isotopic discontinuity or “step”, the effect of having local equilibrium will be that the isotopic step in both the solid and the ITM degrades to a smooth error-function profile, with no discontinuity at the contact. At the other extreme, if R is very slow compared to D*, the solid isotopic composition will not “keep up” with the changes in the local ITM and, in general, will not have the same isotopic composition as the local ITM. In this case, the isotopic step will degrade to an error function profile in the ITM but with preservation of some proportion of the original step at the contact in the solid as it continues to slowly react towards the ITM profile. As we show in more detail below, the degree of preservation of the isotopic step in the solid is dependent solely on R and the duration of the metamorphic event.

The Equilibrium Lengthscale: Le

The balance between D* and R can be expressed in terms of Le, the diffusive equilibration length (see Phillips, 1992; DePaolo and Getty, 1996):

$$Le_{Sr} = \left(\frac{D^{*}_{Sr}}{R}\right)^{1/2} \tag{1}$$

where,

$$D^{*}_{Sr} = \frac{D_{Sr}\tau}{MK_{Sr}} \tag{2}$$

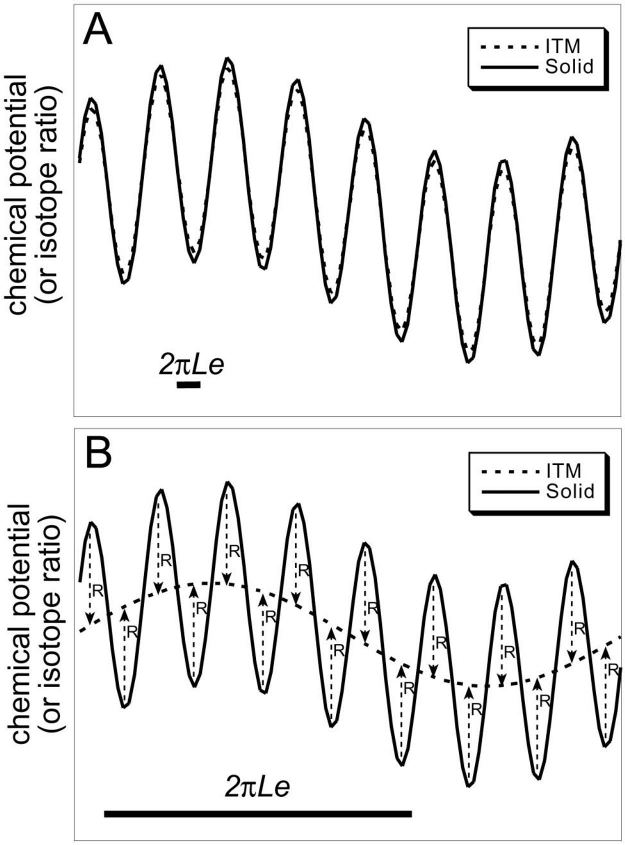

Fig. 4. Significance of Le. Given a chemically or isotopically layered solid as shown, the wavelength of chemical layering or heterogeneity compared to the system Le will determine if solid-ITM disequilibrium will persist. (A) Very small Le. Here, the solid reacts quickly and maintains equilibrium with the ITM for the chemical heterogeneities of wavelength greater than 2πLe (dark bar). (B) Large Le. Here, the short wavelength variations are smeared out via rapid diffusion in the fluid, but the ability of the solid to shift and reach equilibrium with the fluid is limited by the exchange rate, R. The component of long wavelength heterogeneity in the solid, which is longer than 2πLe, does match the fluid. See DePaolo and Getty (1996) for additional discussion.

and D_{Sr} is the diffusivity of Sr in the ITM, τ is tortuosity, $M = \frac{\rho_s(1-\phi)}{\rho_f\phi}$, the mass ratio of solid to fluid, ρ is density, ϕ is porosity, and K_{Sr} is the equilibrium solid/fluid distribution coefficient for Sr. Le is the length scale over which the ability of the solid to attain equilibrium with the fluid is limited by the exchange rate, R. Solid-ITM disequilibrium will persist at scales less than Le in heterogeneous systems where the ITM isotopic profile is changing. It is important to realize that, in a defined closed system given infinite time to react, the solid can always eventually reach equilibrium with the fluid, even for very slow reaction rates, though the time required may exceed that available. Le may also be related to a wavelength of heterogeneity, 2πLe, within which fluid-solid disequilibrium will persist (fig. 4). The assumption of perfect local equilibrium corresponds to the case where Le = 0, or functionally, when Le is smaller than the average grain size of the rock.

Constraints from Field Data

Application of the method is complicated by the fact that a metamorphic rock outcrop represents material that has gone completely through a metamorphic event (sometimes more than one) and has then been returned to surface conditions. This history may span tens of millions of years. The rock exposed at the surface, and its isotopic characteristics, represent integrated records of the diagenetic, metamorphic, and post-metamorphic history. In order to recover estimates of R at critical parts of the metamorphic history, a minimum amount of information is needed. Field measurement of, (1) the bulk solid isotopic profile, (2) a proxy for the ITM isotopic profile, (3) constraints on an initial condition and, (4) constraints on the timescale (Δt) for the reactive transport process will allow determinations of R, D* and Le. The pattern of isotopic ratios in the solid and the ITM about the contact allows us to constrain the value of Le, and the integrated amount of reaction, $\langle Rt \rangle$:

$$\langle Rt \rangle = \int_{t_{init}}^{t_{final}} R(t)\,dt \tag{3}$$

Independent geochronology can provide absolute values (or at least reasonably useful constraints) for t_{init}, and t_{final}. From the geochronologic data and $\langle Rt \rangle$, we can estimate R. From R and the spatial pattern of isotopic variations about the contact we can then infer values for D*.

DEFINITION OF "R"

The observable parameter, R, is the fractional rate at which the tracer isotope (in this case Sr) contained in the bulk solid is exchanged with the local ITM. We assume that Sr is released from the solid phase mainly by dissolution of minerals. For most purposes this rate can be assumed to equal the rate by which Sr is returned to the solid phase via precipitation. Any Sr released by volume diffusion from the mineral grains will also contribute to the observed value of R. Experimental studies suggest that dissolution-precipitation is the dominant reaction mechanism for metamorphic rocks at the conditions we are concerned with (see for example, Schramke and others, 1987; Lüttge and Metz, 1991, 1993). Available Sr volume diffusion rates (for example, Cherniak and Watson, 1994; Giletti and Casserly, 1994), suggests that dissolution-precipitation should be much faster than diffusion and dominate R; but that may be tested.

R has units of reciprocal time, and can be related to the dissolution rates of the individual minerals in the rock by:

$$R = \sum_i R_i \cdot M_i \cdot \frac{C_{Sr,i}}{C_{Sr,bulk}} \tag{4a}$$

where R_i are fractional dissolution rates (mass dissolved/mass of mineral/time) for each mineral, M_i is the mass fraction of the mineral in the rock, $C_{i,Sr}$ is the average strontium concentration in the mineral, and C_{Sr} is the strontium concentration for the bulk rock. Note that this formulation assumes that the dissolving material has the average isotopic composition of the existing bulk solid. The actual bulk dissolution (and precipitation) rate of the rock material, denoted as R_{BULK}, is:

$$R_{BULK} = \sum_i R_i \cdot M_i \tag{4b}$$

The Sr isotope ratio is a *passive* tracer of the bulk solid reactivity. The individual mineral dissolution rates are assumed to be independent of the isotopic ratios, and governed by departures from equilibrium involving the major chemical constituents of the rock. The driving potential for metamorphic reactions is provided by some combination of the overall chemical affinity (see Aagaard and Helgeson, 1982; Lasaga, 1998) and the strain energy (Stunitz, 1998). The overall chemical affinity is a measure of the sum, over all independent chemical reactions, of the free energy departure from equilibrium. The assumption that the isotopic exchange is passive stems from the fact that the contribution of isotopic exchange reactions to the overall chemical affinity is negligible (see Cole and Chakraborty, 2001).

A note about "net" versus "gross" reaction rates.—Transition state theory dictates that metamorphic reactions proceed towards equilibrium at a rate, R_{net}, which is the difference between a gross forward reaction rate (R_f) and a gross backward reaction rate (R_b). Gross forward (and backward) dissolution and precipitation are driven by the free energy difference between reactants (or products) and the activated complex (Lasaga, 1998). At dynamic equilibrium, $R_f = R_b$ and there is no *net* reaction progress in the system with time (that is, $R_{net} = 0$). R_{net} and R_f are related to each other by transition state theory according to the relation (Lasaga, 1998):

$$\frac{R_{net}}{R_f} = 1 - e^{-\Delta G_r/\Re T} \tag{5}$$

In general, the net reaction rate is smaller than the gross forward rate. The passive isotopic exchange responds to the gross reaction rates. Thus, the isotopic method used here essentially measures the gross forward rate (that is, $R \approx R_f$) as immediate dissolution of product minerals has a reduced effect on the isotopic composition of the ITM. Therefore, if the departure from equilibrium (ΔG_r) is small relative to $\Re T$, then R_{net} may be much smaller than R_f. However, for $\Delta G_r \approx \Re T$, R_f and R_{net} will differ only by a factor of about 1.6.

APPLICATION OF REACTION RATES MEASURED BY THIS TECHNIQUE

To apply a reaction rate, R, measured with this technique to other natural metamorphic systems first requires the rate to be normalized to the surface area (s) of the rate limiting mineral. Based on equation 4a, the rate limiting mineral in this case will be the one for which $M_i \cdot \frac{C_{Sr,i}}{C_{Sr,bulk}}$ is the greatest; that is, the mineral which dominates the Sr budget of the bulk rock. The surface area normalized reaction rate, $\bar{R}$ in g/cm^2/yr, may then be used in different ways depending on the specific application. The most straightforward application would be to modeling the kinetics of bulk isotopic exchange between solid and fluid (ITM), such as we do here for Sr (see eqs 8 and 9 below). In this case, $\bar{R}$ may be used as the overall rate constant for isotopic exchange:

$$\frac{dr_s}{dt} = -\bar{R} \cdot s \cdot (r_s - r_f) \tag{6}$$

(r_s and r_f are isotope ratios in solid and fluid) with appropriate additional factors for equilibrium isotope fractionation as needed (Cole and Chakraborty, 2001). For modeling the net progress of metamorphic reactions (R_{net}), the usage of R depends on the assumptions made about the functional dependence on ΔG. If ΔG (in the system to be modeled) is simply assumed to be similar to the ΔG at the field site where $\bar{R}$ was measured, we can write:

$$R_{net} \leq \bar{R} \cdot s \tag{7}$$

This is the most conservative, and accurate, usage for metamorphic reactions in general. Alternatively, in light of equation 5, it is tempting to use $\bar{R}$ as an effective rate constant in a rate law, which includes a specific functional dependence of R_{net} on ΔG (for example, rate law "a" in fig. 1). However, this must be done cautiously as $\bar{R}$ itself may also depend on ΔG. For example, numerous studies have shown that the rate ($\bar{R}$) of pure isotopic exchange via bulk dissolution-precipitation may itself be enhanced by increased ΔG of the overall reaction (see for example, Beck and others, 1992; Cole and Chakraborty, 2001).

GOVERNING EQUATIONS

The following equations (Richter and DePaolo, 1987; DePaolo and Getty, 1996) are used to model the evolution of the $^{87}Sr/^{86}Sr$ ratio in the ITM (r_f) and the solid (r_s):

$$\frac{\partial r_s}{\partial t} = -R(r_s - r_f) + \lambda r_{ps} \tag{8}$$

and

$$\frac{\partial r_f}{\partial t} = MK_{Sr}D^*_{Sr}\left(\frac{\partial^2 r_f}{\partial x^2} + 2\,\frac{\partial \ln(C_f)}{\partial x} \cdot \frac{\partial r_f}{\partial x}\right) + RMK_{Sr}(r_s - r_f) + \lambda r_{ps} \tag{9}$$

where x is the spatial coordinate normal to the lithologic contact, C_f is the concentration of Sr in the ITM, and λr_{ps} accounts for radioactive decay of ^{87}Rb to ^{87}Sr. The decay constant for ^{87}Rb, λ, is 1.42×10^{-11} yr^{-1}. r_{ps} is the $^{87}Rb/^{86}Sr$ ratio of the solid. The r_{ps} profile may be set to measured values and kept constant in time. Dimensional analysis, analytical solutions, and numerical models all confirm that system behavior is insensitive to changes in the product MK (DePaolo and Getty, 1996). In this model, the system behavior is fully described by the two adjustable parameters R and D^*_{Sr}. The above equations are only valid for spatially constant D* and porosity, though a shift at the contact alone may be accommodated by an appropriate boundary condition. R and D* may vary with time.

The term $\frac{\partial \ln(C_f)}{\partial x}$ is related to $\frac{\partial \ln(C_s)}{\partial x}$ for constant K_{Sr}, and may thus be monitored by field measured C_s values (C_s is the concentration of Sr in the solid). To fully model system evolution would require knowledge of an initial Sr concentration profile and the ability to quantitatively model the thermodynamics of Sr transport. In a fluid that has the same major chemical composition throughout (such as H_2O), the chemical potential of Sr should scale with concentration (Henry's Law). But in the solid, the chemical potential may vary complexly with the other major element bulk chemical and phase variations, perhaps producing complex patterns of change (see for example, Lescher, 1994; Richter and others, 1999). Therefore, for simplicity, C_s may be fixed at the measured values. This simplification has little effect on the results of the modeling. For constant C_s throughout the system, $\frac{\partial \ln(C_f)}{\partial x} = 0$, and that term drops out of the equation. For model simulation including spatially variable C_s, the steady state C_f profile may be determined from the following equation:

$$\frac{\partial C_f}{\partial t} = MK_{Sr}D^*_{Sr}\frac{\partial^2 C_f}{\partial x^2} + RM(C_s - K_{Sr}C_f) \tag{10}$$

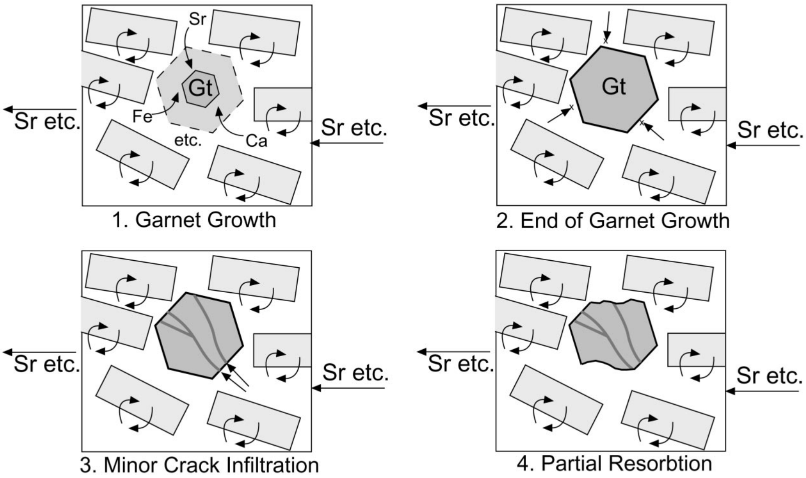

Fig. 5. Sketch of garnet uptake and retention of the ITM isotopic signature. After taking on the local isotopic signature of the ITM during growth, the garnet is resistant to further exchange with its surroundings while the other matrix minerals continue to react and exchange at some rate, R (see text). Minor crack infiltration or partial resorption after garnet growth will not significantly affect the chemistry of the remaining garnet measured in the rock today.

LIMITATIONS OF PREVIOUS STUDIES OF LITHOLOGIC CONTACTS

The idea of studying fluid-rock interaction by measuring cross-contact chemical profiles is not new. The approach is broadly similar to previous studies involving measurement of whole-rock $^{87}Sr/^{86}Sr$ in samples about a lithologic contact (Collerson, 1983; Springer and others, 1983; Collerson and others, 1984; van Breeman and Dallmeyer, 1984; Bickle and others, 1988, 1994, 1995, 1997; Bickle and Chapman, 1990). However, none of these studies were designed to measure reaction rates, instead neglecting reaction kinetics and assuming equilibrium. Other studies involved measurement of stable isotope profiles (Nagy and Parmentier, 1982; Baker and others, 1989; Bickle and Baker, 1990; Cartwright and Valley, 1991; Ganor and others, 1991; Puris and Wickham, 1994; Gerdes and others, 1995; van Haren and others, 1996; Vyhnal and Chamberlain, 1996; Bickle and others, 1997; Eppel and Abart, 1997). Stable isotopes alone yield no geochronological data, and without information about timescales, quantification of the rates of processes is difficult. Some stable isotope studies have constrained timescales with intragrain diffusive profiles and known diffusivities (see for example, van Haren and others, 1996). Furthermore, stable isotopes have the added complication of temperature dependent isotope fractionation between phases. Additionally, purely whole rock studies (such as many of the above referenced) lack the ability to differentiate between diagenetic effects and high temperature metamorphic effects because the whole rocks record the sum of all exchange processes leading up to the end of metamorphic exchange. That crucial information - a constraint on a syn-metamorphic initial condition and a specific time interval, Δt, over which the subsequent changes occurred - is provided in the current study by the analysis of garnets.

GARNETS AS RECORDERS OF THE ITM ISOTOPIC PROFILE

An important aspect of our approach is the use of garnet porphyroblasts. Garnet porphyroblasts preserve a record of the ITM isotopic profile from the time of garnet growth (fig. 5). When garnet (or any other mineral) first nucleates and grows it takes on the local ITM (fluid) isotopic composition. Unlike most other minerals, garnet is resistant to further exchange due to its exceedingly slow intracrystalline diffusivity (see for example, Chakraborty and Ganguly, 1991; Burton and others, 1995) and refractory nature. As the ambient P-T-X conditions change, new garnet with the new equilibrium chemistry simply grows around older garnet, like a snowball (Rosenfeld, 1968) effectively isolating earlier growth from further reaction. Cations may diffuse into the rims of garnet porphyroblasts, as is commonly observed, but the bulk garnet interior compositions are preserved. It is possible that some garnet may be resorbed by garnet consuming reactions. But these reactions do not affect the *remaining* garnet, which we measure today. The ability of garnet to retain the composition from the time of its first growth has been well documented (Loomis, 1986; Tracy, 1982) and this property of garnet has elsewhere been exploited to determine metamorphic chemical, P-T-t, and deformation histories (see for example, Spear and others, 1982; Spear and Selverstone, 1983; Vance and O'Nions, 1992; Christensen and others, 1989, 1994; St. Onge, 1987; Burton and O'Nions, 1991; Kohn and others, 1993). Certainly there are cases, in particular for higher temperature settings, where garnet does appear to have re-equilibrated, but this is evident by a lack of internal zoning, and generally is unlikely in metamorphic environments below granulite grade. Whitney (1996) discussed the possibility of garnets remaining open to chemical and isotopic exchange subsequent to growth, predominantly by fluid access to garnet interiors through cracks. The net volume of garnet affected by any infiltration along cracks will still be limited by the slow chemical and isotopic diffusivities in garnet, and hence will be minimal in comparison to the total volume of the garnet in most cases.

The age of garnet growth (or daughter nuclide retention) can be constrained by isotope geochronology, such as the Sm-Nd or Rb-Sr isochron technique. For garnets growing below their closure temperature for a given isotopic system, about ~650° to 700°C for Sr or Nd (Burton and others, 1995; Ganguly and others, 1998), the age recorded is the actual growth age. The age of garnet growth is used as the t_{init} for modeling purposes.

Because it is possible that garnet will preserve a Sr isotopic ratio which is not in equilibrium with its surrounding matrix and/or included minerals, particular care must be taken to ensure that a pure garnet separate is analyzed. A combination of crushing, hand picking, magnetic separation and partial acid dissolution treatment techniques (for example, Baxter and others, 2002) is recommended for this purpose. Note that analyses of bulk garnet samples represent a specific time *interval* – that of garnet growth. Thus the measured age and isotopic content of a bulk garnet sample will correspond to an average time, and average Sr isotopic ratio, within that interval. Due to the open system behavior characterizing a sample located within a distance Le of a chemical heterogeneity (that is, lithologic contact), meaningful geochronologic data for garnet growth must be collected from samples located beyond a distance Le from the contact. So, while garnet-whole rock isotopic data collected <Le from the contact provide information about R and D*, garnet-whole rock pairs collected >Le from the contact provide the needed geochronology.

ESTABLISHING THE SYN-METAMORPHIC INITIAL CONDITION

The initial condition used for the modeling of syn-metamorphic reactive-transport is not the same as the pre-metamorphic protolith condition. The protolith could have been affected by diagenetic or other processes. Herein, the "initial" condition refers to the condition *at the time of garnet growth*, from which modeling proceeds. As described above, the garnet isotopic profile equals the initial ITM isotopic profile. We know that the initial bulk solid isotopic profile must have either matched or lagged the ITM (garnet) profile at the time of garnet growth, because the solid $^{87}Sr/^{86}Sr$ changes only by exchanging with the ITM. Furthermore, a quasi-steady state

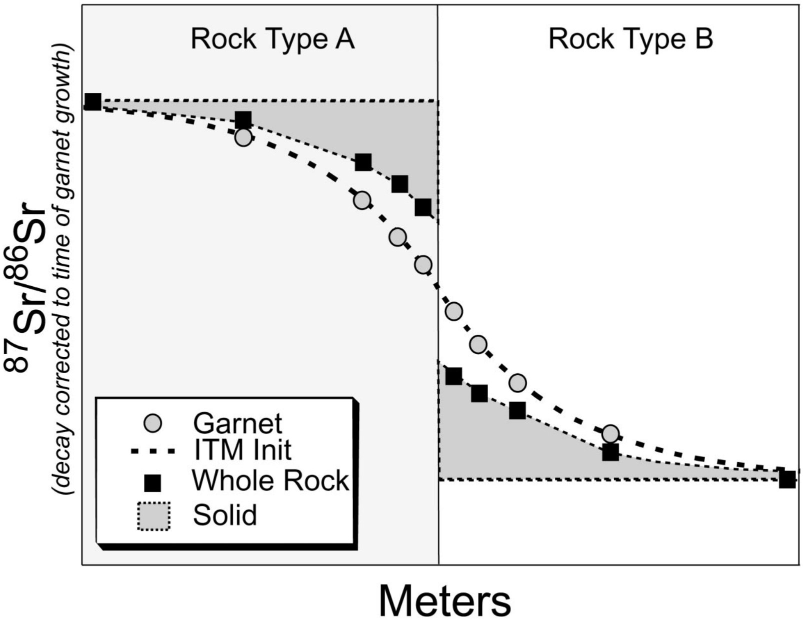

Fig. 6. Constraints on the syn-metamorphic initial condition used in modeling. The garnet data collected about the contact constrain the ITM profile at the time of garnet growth as shown. The initial solid profile (accounting for Sr concentration variations) is constrained to be within the shaded region. Constraints on the initial solid profile include, (1) the garnet data, and (2) the solid data far from the contact above which (for A) or below which (for B) the solid could not have been (assuming initial homogeneity). The exact shape of the solid profile within the shaded region may vary, but must conform to a quasi-steady state fit with the ITM profile (see text).

exists between the fluid and solid profiles defined by the initial values of R and D* and equations 8 and 9 (see DePaolo and Getty, 1996) which provides a further constraint on the initial solid profile. The quasi steady state is reached after diffusion has smoothed out variations in the ITM profile of wavelength less than 2πLe. Subsequent changes in the solid and ITM are limited by the bulk reaction rate, R. The initial quasi-steady state ITM and solid profiles are established by allowing the ITM profile to adjust in a short period of time (1-1000 years) to a quasi steady state; with a given initial solid profile. This quasi-steady state initial ITM profile must be fit to the garnet data. It is possible that the solid initially contains shorter wavelength variations that are smeared out by the end of metamorphic exchange, but relatively immobile Nd isotopes may be used to evaluate the extent of initial isotopic heterogeneity within each rock. Once the initial solid and ITM profiles are established, modeling of the reactive transport process may proceed. The initial solid profile which generates a quasi-steady state ITM profile satisfying the garnet data is non-unique within the bounds shown in figure 6. But, a unique initial solid profile that ultimately permits a fit to the final whole rock data after modeling may be determined iteratively. Subsequent changes in the WR and garnet Sr isotopic ratios must have been generated between the time of garnet growth and the cessation of metamorphic exchange, eliminating the possibility of confusing earlier, diagenetic exchange with metamorphic processes (for example, Bickle, 1992; Vyhnal and Chamberlain, 1996).

PLAGIOCLASE: RECORDER OF THE END OF METAMORPHIC EXCHANGE

For most typical metasedimentary (metapelites) or metavolcanic (amphibolites) assemblages, plagioclase is the most common dominant Sr bearing mineral. Plagioclase typically has hundreds to thousands of ppm Sr which is at least 10-100 times more Sr than other major phases like amphibole (10-50 ppm), mica (5-20 ppm), almandine rich garnet (<2 ppm), grossular rich garnet (10-30 ppm), or quartz (<<1 ppm). Accessory phases such as apatite, sphene, calcite, or epidote may have significant Sr concentrations, but are typically small enough volumetrically not to play a major role in the bulk rock Sr budget. Therefore, the time at which the plagioclase (or whatever the dominant Sr bearing mineral is) closes to further exchange of Sr with the ITM is also effectively the time at which the entire rock ceases to exchange of Sr. The ending time of metamorphic exchange, t_{final}, is taken to be the age given by a Rb/Sr plagioclase-whole rock isochron, which indicates the time at which plagioclase ceases to exchange with its surroundings, *by any mechanism*, with respect to Sr. Using the closure equation (Dodson, 1973) and diffusion parameters (see Cherniak and Watson, 1994; Giletti and Casserly, 1994), a diffusional closure temperature may be assigned to this time. The diffusional closure temperature for plagioclase is useful as a constraint on the *maximum* temperature that could be associated with the Rb/Sr plagioclase age. In order for the plagioclase (and the bulk rock system) to remain open to further Sr exchange to lower temperatures would require a mechanism other than volume diffusion, such as dissolution-precipitation to mediate Sr isotopic exchange.

FIELD SITE SELECTION

In order for this technique to succeed, the ideal field site must have several key characteristics, some of which may be pre-screened, and others which may only become evident after preliminary analysis. Below, these characteristics are listed and discussed. As will become apparent, location of an adequate field site for this purpose is quite difficult.

Sharp lithologic contact between rocks of differing $^{87}Sr/^{86}Sr$.—The field site must include a sharp, well defined and well preserved primary lithologic contact between two different rock types. In order to minimize the impact of analytical uncertainties (for $^{87}Sr/^{86}Sr$: ± 10-20 ppm), and increase the chances of being able to discern an isotopic step at the contact, it is desirable to find a lithologic contact between rocks with a maximum initial difference in $^{87}Sr/^{86}Sr$. Metapelites typically have high $^{87}Sr/^{86}Sr$ ratios given their high Rb/Sr, whereas calcsilicates or amphibolites typically have low $^{87}Sr/^{86}Sr$ due to their low Rb/Sr. Amphibolites are particularly desirable because their protoliths, probably mafic volcanics or intrusives, likely are initially homogeneous in their chemistry. Measurement of a relatively immobile chemical tracer, such as the $^{144}Nd/^{143}Nd$ ratio, may be used to assess protolith homogeneity.

Abundant garnet porphyroblasts.—Ideally, both lithologies should include abundant garnets. If garnets are large enough, separate core and rim analysis may be undertaken to gain further details of the fluid (ITM) profile evolution. Often, only one of the two lithologies includes garnet, in which case the constraint on the fluid (ITM) initial profile will be limited to one side of the contact. Generally, given the symmetry of the diffusional exchange for spatially constant D*, garnet data on one side of the contact is adequate.

Evidence of significant cross-layer transport.—If little or no diffusional transport has occurred, it may be difficult to discern a true isotopic step from a steep but smooth diffusional profile, rendering a precise measurement of Le, D* and R impossible. It is difficult to pre-screen a site for this criteria without preliminary $^{87}Sr/^{86}Sr$ analysis of a few samples near the contact. However, mineralogical trends about the contact may indicate the presence of major element diffusional transport (for example, increasing biotite mode as an indicator of K diffusion) which may hint of significant isotopic diffusion as well. Continuous, centimeter scale sampling immediately adjacent to the contact on both sides is very helpful in illuminating the diffusive profile and an isotopic step, if it exists.

Closed system.—The lithologic contact must be a closed system at the outcrop scale. That is, all cross-contact variations observed must be due to diffusional exchange between the two rock types alone and not from exchange with an exotic source, such as a through-going fluid. Evidence for advection could include veining or other notable mineralogical characteristics suggestive of metasomatism. Mass balance analyses of the Sr isotopes about the contact may also be used to reveal the possible presence of open system behavior. As long as the system is closed, then the isotopic pattern about the contact will exhibit diffusional symmetry.

"Unfinished" reaction at contact.—The ideal case for this method is to find a lithologic contact which indeed preserves an isotopic step. The magnitude of D* has no effect on the size of the isotopic step at the contact. For any lithologic contact where there is significant cross-layer diffusion, a measurable isotopic step will be preserved only if, (1) R is slow enough, (2) the total duration, Δt, is short enough, or (3) the initial difference in isotope ratio across the contact is extremely large. Possibility #3 has already been addressed above. Possibilities #1 and #2 may be combined into a single term, $\langle \text{Rt} \rangle$ (eq 3), which is the total time integrated amount of reaction. Ultimately, the isotopic step will be directly proportional to $\langle \text{Rt} \rangle$ (fig. 7). Reaction between solid and ITM immediately at the contact of lithologies A and B may be described by equation 8 alone (neglecting ^{87}Rb decay), where, $r_f = \frac{r_{s(A)} + r_{s(B)}}{2}$ for the constant concentration model. Equation 8 may be solved and the progress towards solid-ITM equilibrium at the contact expressed as

$$\frac{r_{s(t)} - r_f}{r_{s(init)} - r_f} = e^{-\langle Rt \rangle} \tag{11}$$

where $r_{s(t)}$ and $r_{s(init)}$ are the solid isotope ratio at the contact in either lithology at times t and 0, respectively, and r_f is the constant ITM isotope ratio at the contact. When $\langle Rt \rangle = 4$, the isotopic step at the contact is only 1.8 percent of what it initially was. This isotopic difference may be discernable from an analytical standpoint; but, depending on the density of sampling near the contact and the diffusivity, it may be difficult to discern a true step from a smooth profile from a modeling standpoint. So, field sites for which $\langle Rt \rangle < 4$ would be preferable for successful and unambiguous measurement of reaction rate. Some datasets of cross-contact Sr isotopic analyses may not clearly reveal a strong isotopic step preserved at the contact (Bickle and Chapman, 1990; Bickle and others, 1995; Bickle and others, 1997). In such cases, this is because either $\langle Rt \rangle$ was too high to preserve it and/or spatial sampling was not sufficiently dense to discern it. Field sites that do not preserve an isotopic step provide only a minimum constraint on $\langle Rt \rangle$ and, if an estimate of Δt is available, a minimum R.

Young metamorphism.—The errors associated with the age correction, based on Rb/Sr ratios, of the data back to the time of the end of metamorphism are smaller for young metamorphic rocks than for old metamorphic rocks. This reduction in errors for young metamorphic rocks will be particularly significant for a metapelite layer given its characteristically high Rb/Sr. Furthermore, older metamorphic rocks simply have a greater possibility of having been disturbed by later non-metamorphic processes.

NUMERICAL MODELING AND MEASUREMENT OF R, D*, AND LE

Once the whole rock (final solid) and garnet (initial fluid) profiles are collected from the field site, and the Sm/Nd or Rb/Sr garnet-whole rock age (t_{init}) and Rb/Sr plagioclase-whole rock age (t_{final}) are measured, providing the Δt for the simulation, the reactive transport process may be modeled using the equations given above. A FORTRAN90 code was written for this purpose. A mass conserving equal flux bound-

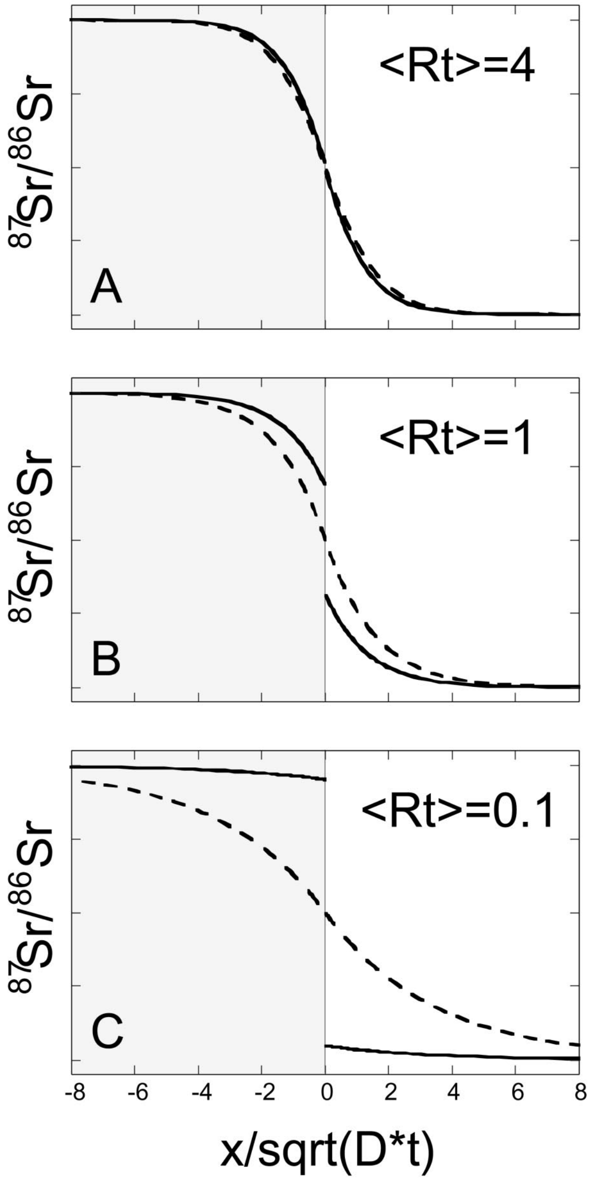

Fig. 7. Model isotopic profiles after metamorphic exchange for (A) ⟨Rt⟩ = 4, (B) ⟨Rt⟩ = 1, and (C) ⟨Rt⟩ = 0.1. For ⟨Rt⟩ greater than 4, the isotopic step in the solid (solid line) at the contact is lost. For ⟨Rt⟩ less than 0.1, there is so little reaction that it cannot be discerned and accurately interpreted. The best constraints on R come from field sites with ⟨Rt⟩ between 0.1 and 4. Note also that the greater the value of sqrt(D*t), the greater our ability to resolve an isotopic step with reasonable sampling density. Dashed line is the ITM isotopic profile.

ary condition (Crank, 1975, p. 149-150) is required at the contact in the case where D* varies between lithologies. A variable step size is used with a high density of nodes near the contact where most of the change occurs and more widely spaced nodes further from the contact. The extreme boundary nodes on either side of the model system, set beyond significant effects of diffusion, are fixed with a no-flux boundary condition. The code uses an explicit numerical scheme and employs a dynamic timestep variable to ensure stability and optimize run-time. Ultimately, the best fit for the adjustable parameters R and D* is sought which satisfies both: (1) a fit of the initial fluid profile to the garnet data, and (2) a fit of the final solid profile to the whole rock data.

CORROBORATING MAJOR ELEMENT EVIDENCE

We assert, as explained above, that the Sr isotopes used to measure the bulk reaction rate are not driving the reaction, but rather it is the overall affinity for reaction, dominated by the major element components of the system, that drive the reactivity. It is therefore worthwhile to seek corroborating evidence for major element processes, namely the extent of post garnet growth cross-layer diffusive transport, and the extent of local ITM-solid disequilibrium, which may be similar to the phenomena that the Sr isotope analysis documents.

Several studies (for example Fischer, 1973; Fischer and Elliot, 1974; Brady, 1977; Joesten, 1977; Frisch and Helgeson, 1984) have discussed in great detail the processes, thermodynamics, and consequences of "diffusion metasomatism" whereby two mineral assemblages in contact with one another react and diffusively exchange major element components. Theoretically, this produces a sequence of local-equilibrium controlled metasomatic reaction bands parallel to the contact. These studies have laid the groundwork for detailed modeling and interpretation of such processes. However, the assumption of local equilibrium, which is required in order to follow the theory outlined by these authors, is the very assumption being tested in our study, rendering this approach less useful for the current endeavor. Lasaga and Rye (1993) showed that incorporation of reaction kinetics, instead of assuming local equilibrium, could generate a non-equilibrium steady state pattern of mineral assemblage zoning and fluid composition.

We suggest a simple thermodynamic approach to examine major element equilibrium: an approach that can test the existence of the local equilibrium assumption rather than assume it *a priori.* If, and only if, local equilibrium prevails, any balanced chemical reaction written among end-member components of existing phases in an assemblage, by definition, must yield a single value of the reaction quotient, Q_r, unique for a given P and T, regardless of bulk chemistry. Where local equilibrium holds, $Q_r = K_{eq}$, the equilibrium constant. This is the basis of the Law of Mass Action (for discussion see Aagaard and Helgeson, 1982; Spear 1993). To review the fundamental relations, for a general reaction of the form

$$aA + bB = cC + dD \tag{12}$$

where lower case letters stand for the stoichiometric coefficient and upper case letters stand for a pure mineral end-member component in a particular phase:

$$Qr = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} \tag{13}$$

where a_X^x stands for the activity of the mineral endmember component, X, in a given phase, raised to the stoichiometric coefficient, x. The thermodynamic basis for the case when $Q_r = K_{eq}$ (when the local equilibrium condition exists) is:

$$log(K_{eq}) = \frac{-\Delta G_{r(P,T)}}{\Re T} \tag{14}$$

where ΔG_r is the free energy of the balanced chemical reaction at pressure and temperature, $\Re$ is the gas constant, and T is the temperature in degrees Kelvin.

Consideration of the Q_r values measured at several locations in an outcrop reveals whether or not the local equilibrium approximation holds and over what lengthscale. Perfect local equilibrium at every point in the system would yield a single Q_r value equal to the K_{eq} for the P and T at which those phase compositions last equilibrated (assuming the entire system experienced the same P-T history).

Most important in evaluating the lengthscale for major-element diffusive-reactive processes (and potential disequilibrium) is the consideration of reactions both with and without garnet. Since garnet preserves a record of the local ITM composition at the time of its growth, reactions including garnet may show a skew in Q_r within some distance of the contact. Such a Q_r skew would be due to either or both, (1) garnet-whole rock disequilibrium with respect to major elements at the time of their growth, or (2) continued open system major element diffusive transport through the ITM and reaction of the other matrix phases subsequent to garnet growth.

SUMMARY

A new technique for measuring bulk reaction rates directly from field data has been presented. Three key requirements are essential for successful quantitative measurement of reaction rates from modeling of field data: (1) constraint on an initial syn-metamorphic condition, (2) constraint on a time interval of observed metamorphic processes, (3) analysis of an "unfinished" reaction/exchange process. This technique provides all three. The major steps required for implementation of the method may be summarized as follows.

1. Selection of an appropriate field site with a sharp lithologic contact
2. Collection of closely spaced whole rock and garnet samples for isotopic analysis from both sides of the lithologic contact
3. Measurement of garnet-whole rock Rb/Sr isochron age from samples located far from the contact beyond the open system effects of cross layer diffusion
4. Measurement of plagioclase-whole rock Rb/Sr isochron age
5. Establishment of an initial syn-metamorphic condition using the equations for diffusive-reactive transport and the garnet isotopic data
6. Use of numerical modeling to simulate system evolution and find the best fit values of $\langle Rt \rangle$, Le, D*, and R

Part II of this study (Baxter and DePaolo, 2002b) details the implementation and results of this technique at a field site near Simplon Pass, Switzerland. Only by combining *lab-based* kinetic data, kinetic *theory*, and quantitative *field-based* kinetic data such as that provided by this method, will we achieve the necessary advances to understand natural geochemical kinetics. We hope that this field-based method will be applied and refined by geochemists in many varied geological settings in order to contribute to this ultimate understanding.

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