

Metamorphic reaction rate laws and development of isograds

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ABSTRACT. New data on the kinetics of dehydration of muscovite+quartz suggest the necessity for a careful treatment of *both* surface kinetics and diffusion processes in metamorphic reactions. A new model is proposed that illustrates the relative role of diffusion and surface reactions in the overall metamorphic process. The rate law for the reaction at mineral surfaces derived from the experimental data is shown to be probably non-linear and similar to rate laws derived from Monte Carlo calculations. The experimental rate data is then used in a heat flow calculation to model the evolution of the muscovite isograd in the field. The position of the isograd, the temperature oversteps above equilibrium, and the width of 'reaction zones' are then analysed as a function of intrusion size and kinetic parameters.

KEYWORDS: metamorphic reactions, surface kinetics, diffusion, rate laws.

THE focus of metamorphic petrology today is shifting from a static mode based on the thermodynamics of mineral assemblages to a dynamic mode aimed at the quantification of the processes that produced the metamorphism. As a result, the non-equilibrium aspects and the kinetics of metamorphic processes are being increasingly studied. The proper role of equilibrium versus kinetics in describing metamorphism is still being debated today. As petrologists initially tackled the complexities of the texture and mineralogy of metamorphic rocks, many of which could not coexist according to an equilibrium model, the concept of *local* equilibrium (Thompson, 1959; Helgeson, 1968; Fisher and Elliott, 1974) was born. In this fashion, equilibrium was maintained at least on a local scale, which meant essentially for surfaces of mineral grains in physical contact with each other. Isotope studies (Lattanzi *et al.*, 1980; Rumble *et al.*, 1982; Rumble and Spear, 1983; Tracy *et al.*, 1983) have investigated the length scale of equilibrium and found many cases where it was only a few centimetres.

Closer inspection of the chemical composition of minerals has unearthed a wide variety of zoning profiles which preserve, albeit encoded by the

kinetics, the details of the metamorphic history. The ubiquitous zoning found in several metamorphic minerals has led to recent papers on their kinetic significance (Lasaga *et al.*, 1977; Lasaga, 1983; Ozawa, 1984; Smith and Ehrenberg, 1984; Wilson and Smith, 1984, 1985; Smith and Wilson, 1985; Docka *et al.* (in press).

More recently, the kinetic study has been extended to the generation, motion and characterization of metamorphic fluids. Within the assumption of local equilibrium, it was logical to assume that the local mineral assemblage would control or buffer the composition of the fluid phase during dehydration/hydration and decarbonation/carbonation reactions and that the kinetics were fast enough to be ignored. This control, however, can *only* be achieved by the continuous and concurrent dissolution and growth of one or several minerals. As Greenwood (1975) has shown, the amount of fluid involved during evolution along univariant isobaric $T-X_{CO_2}$ paths is minor compared with the amount involved in the reactions at isobaric invariant points. The latter are of central importance because they represent boundaries separating the presence or absence of one or more minerals and therefore are the traditional mappable isograds. Recent papers (Matthews, 1980; Walther and Orville, 1982; Ferry, 1983*a, b*; Wood and Walther, 1983; Walther and Wood, 1984; Rubie and Thompson, 1985; Tanner *et al.*, 1985; Schramke *et al.*, 1986*a*) have begun to address the kinetic descriptions of these reactions. We want to extend these treatments in this paper.

Kinetics of metamorphic fluid-rock reactions

As has been pointed out before (e.g. Yardley, 1977; Fisher, 1978; Rubie and Thompson, 1985), there are several processes which must be quantified and understood to describe the result of fluid-rock metamorphic reactions: (a) heat transport processes both conductive and convective; (b) fluid mass transfer processes; (c) solute mass transfer

processes—convective and diffusive; (d) mineral surface reaction processes, both dissolution and growth; and (e) nucleation of new minerals. Unfortunately much more data are needed to complete this task. This absence of data has led to numerous theoretical models (e.g. heat, diffusion or surface control models), which are hard to test. However, some recent experimental data (e.g. Tanner *et al.*, 1985; Schramke *et al.*, 1986a) can begin to provide the type of answers that are needed.

In discussing concepts such as heat flow control of metamorphic reactions, one basic concept which must be introduced at the outset is that of external versus internal control of intensive variables within a metamorphic volume unit. Given a particular volume of rock, there are fluxes of heat and mass into the volume that are governed externally, i.e. irrespective of any reactions taking place within the volume. Thermal evolution models (Jaeger, 1968; Bottinga and Allegre, 1976; England and Thompson, 1984; Thompson and England (in press)) can provide possible P - T - t paths either regionally or in contact metamorphism. These models can provide a basis for obtaining the external source of heat in various parts of a metamorphosed assemblage. Within the particular

volume, reactions involving heat and mass will take place. These internal reactions may dominate the external fluxes and control the concentration of particular chemical species or the temperature of the locality as advocated by the proponents of equilibrium models. The actual evolution of the mineral assemblage is determined by the interplay of the internal and external controls and will be explored in detail in later sections. For example, if reactions are extremely slow, the temperature in a given region is controlled externally and can be calculated by solving the heat equations with the appropriate external boundary conditions. However, if the reactions are very fast, the temperature may be maintained close to the equilibrium temperature of a particular reaction or sequence of reactions (i.e. a heat-flow control process). It is this distinction between internal and external control that is essential to the description of metamorphic processes.

To unravel the types of control that may be encountered in nature we must (1) understand the chemical kinetics of metamorphic reactions and (2) couple the heat transport to the chemical reactions.

We will begin by discussing recent experimental data on relevant chemical reactions and use them to

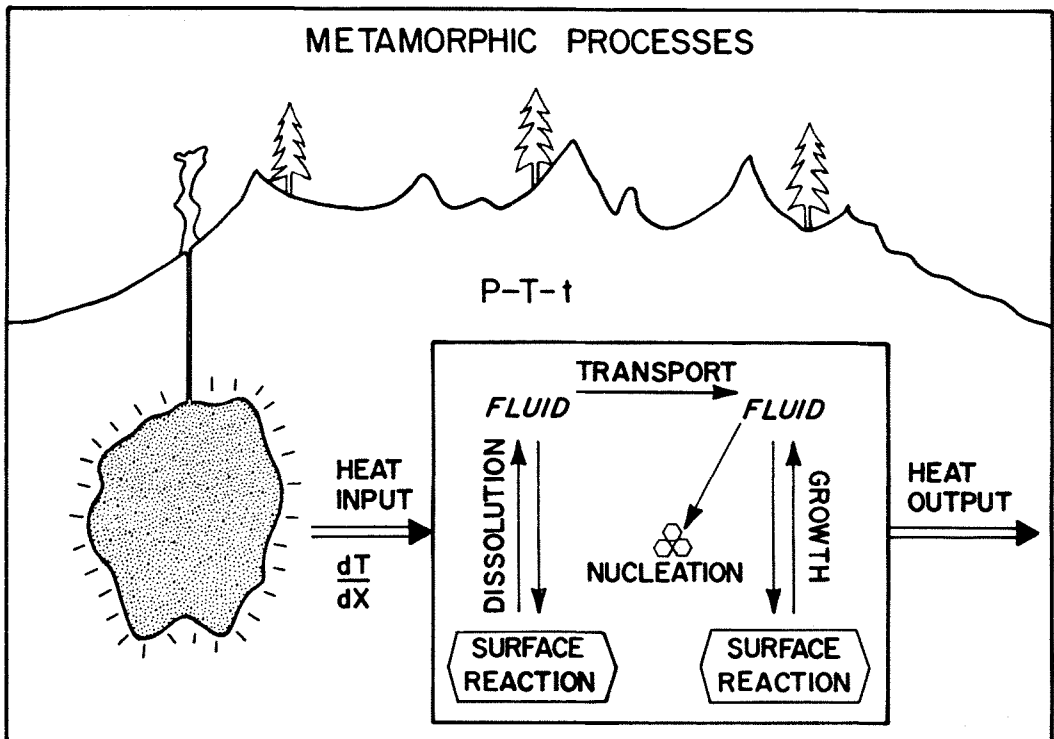


FIG. 1. Sketch of basic kinetic processes controlling the evolution of a metamorphic assemblage.

illustrate the key kinetic concepts needed to answer question (1). Then we will apply these data to a simple metamorphic model and answer question (2). Finally, we will generalize the results.

Fig. 1 illustrates the basic kinetic processes relevant to metamorphic fluid reactions. Many earlier papers focused on the description of transport control during metamorphic reactions, in particular diffusion control (Fisher and Elliott, 1974; Joesten, 1974, 1977, 1983; Fisher, 1975, 1978; Frantz and Mao, 1975, 1976; Weare *et al.*, 1976). The description of diffusion was amenable to treatment by the theory of irreversible thermodynamics. Further papers (Fisher, 1973; Joesten, 1977; Fisher and Lasaga, 1981) discussed these applications. The diffusion model requires fast surface reactions (for *all* minerals in the particular reactions) relative to the rates of diffusion so that 'local equilibrium' can be established between the 'fluid' (i.e. bulk fluid or an intergranular adsorbed fluid, or a grain boundary fluid) adjacent to each mineral and each mineral in the assemblage. The diffusion and heat flows obey the so-called linear kinetics:

$$\vec{J}_i^p = -\sum_j D_{ij} \vec{\nabla} C_j \quad (1)$$

$$= -\sum_j L_{ij} \vec{\nabla} \mu_j \quad (2)$$

$$\vec{J}_Q = -K \vec{\nabla} T \quad (3)$$

where J_i^p and J_Q are the diffusion flux of species i and the heat flux, respectively; D_{ij} is the multi-component diffusion coefficient matrix; L_{ij} is the multicomponent phenomenological coefficient matrix, C_j is the concentration of the species j in the 'fluid', μ_j is the chemical potential of species j and K is the thermal conductivity. One important distinction between L_{ij} and D_{ij} should be stated. The size of D_{ij} in 'fluids' is generally restricted over a couple of orders of magnitude (10^{-5} to 10^{-3} cm²/sec) over the metamorphic range of P and T (Nigrini, 1970). However, for a tracer (Fisher and Lasaga, 1981):

$$L_{ii} = \frac{D_{ii} RT}{C_i} \quad (4)$$

Because L_{ii} contains the added dependence on C_i , the L_{ii} can and will vary over many more orders of magnitude. These linear laws (equations 1–3) have been upheld in both extensive theoretical and experimental works. It should be noted that the fluxes in equations (1) and (2) are based on unit area of fluid. To convert to fluxes based on unit area of rock, we must incorporate the values of the porosity and tortuosity as will be done below.

There are some broad and pertinent comments that should be also stated at this point. The first

use of diffusion-controlled growth models came from material scientists, for example in studying corrosion mechanisms or powder reactions. In many cases, and under their experimental conditions, the materials were much more reactive than minerals in the field. The use of diffusion-control models in metamorphic reactions has *not* been proven universally, especially in reactions other than those involving carbonates. It is important to stress that even so-called 'diffusion' textures may not be uniquely assigned to diffusion control as will be shown below (that is a typical problem with kinetics!). Only by careful experimental *data*, as well as modelling and field data, can these questions be answered. It is important, therefore, not to use diffusion models indiscriminately because of their convenience.

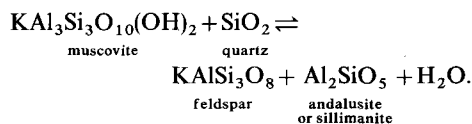
The description of nucleation and growth or dissolution at mineral surfaces is not as advanced as that of diffusion. This was recognized by Fisher (1978) in his useful summary of the earlier kinetic work. By far the most common assumption has been to use a linear theory

$$R_i = -\sum_j L_{ij}^R \Delta G_j \quad (5)$$

where R_i is the rate of a particular metamorphic reaction and ΔG_j are the free energies of the various reactions describing the kinetic process [sometimes affinities ($-\Delta G$) are used in (5)]. Although Fisher (1978) tried to give some justification for equation (5), it is clear that it does not have such a sound theoretical basis as equations (2) and (3). Transition state theory (Lasaga, 1981; Aagaard and Helgeson, 1982) can be used to justify the form of equation (5) when $\Delta G_j \ll RT$. However, such justification requires a number of assumptions, including the absence of linear and planar defects (Lasaga, 1981), which must be satisfied but which for some heterogeneous kinetic processes may not be fully valid.

Recently, Walther and Wood (1984) have extended Fisher's (1978) paper with additional calculations on the relative rates of diffusion, fluid flow and surface reaction. Many of these earlier treatments are necessarily oversimplified because adequate experimental data are lacking. Now that new data are available, we want to discuss further some of the earlier points.

One of the central reactions in the low-pressure high-grade metamorphism of pelitic rocks is the dehydration of muscovite:



This reaction is probably typical of those involving aluminosilicates. The kinetics of this reaction have been studied recently by Schramke *et al.* (1986a). Several important results from that work which shed light on the previous discussion of metamorphic fluid-mineral reactions will be summarized here. First, the reaction, *under the conditions studied* (350–700 °C, 1–3 kbar), is ‘surface-controlled’ and specifically depends on the reaction at the surface of the andalusite crystals. Therefore, each total reaction rate (an extensive property) was normalized to unit area of andalusite. This result is very important as it challenges the usual simple notions that diffusion-control is pervasive in metamorphic reactions (although, of course, life would be much simpler for theoreticians if it were!). The extension of the data to field conditions and the possibility of surface control in nature will be further quantified below. We should stress that in metamorphic reactions controlled by surface processes it is usually *one* mineral surface that is important, as obtained by Schramke *et al.* (1986a). Which mineral surface controls the kinetics must be determined experimentally and, of course, *may* vary if the relative abundances of the reactants or products change sufficiently. In general, however, it is expected that low solubility minerals will be the more likely candidates for surface control.

Any discussion of ‘diffusion control’ or ‘surface control’ must begin with the vital acknowledgment that after a microscopically small time period, the rate of transport of components away from the surface of any mineral, by diffusion, fluid flow or both, must necessarily *equal* the reaction rate at the surface of that mineral. The discussion about whether diffusion or surface processes ‘control’ the rate really refers to the question: ‘are the concentrations in the fluid adjacent to mineral surfaces the *equilibrium* concentrations?’ In the case of slow surface rates, we *do not* expect the concentrations to be the local equilibrium ones. The proper understanding of the interplay between surface reaction and diffusion in metamorphic reactions is so fundamental that we have developed a general (though simplified) model to show the salient kinetic relationships in detail. This model is the topic of the next section.

A metamorphic reaction model

The understanding of the results of the experiments on muscovite and their relation to general metamorphic fluid reactions can be achieved with a useful model. The interplay between transport (e.g. diffusion), surface reaction and the surface area dependence of the overall rate are illustrated in fig. 2. Most simple examples in the literature (except

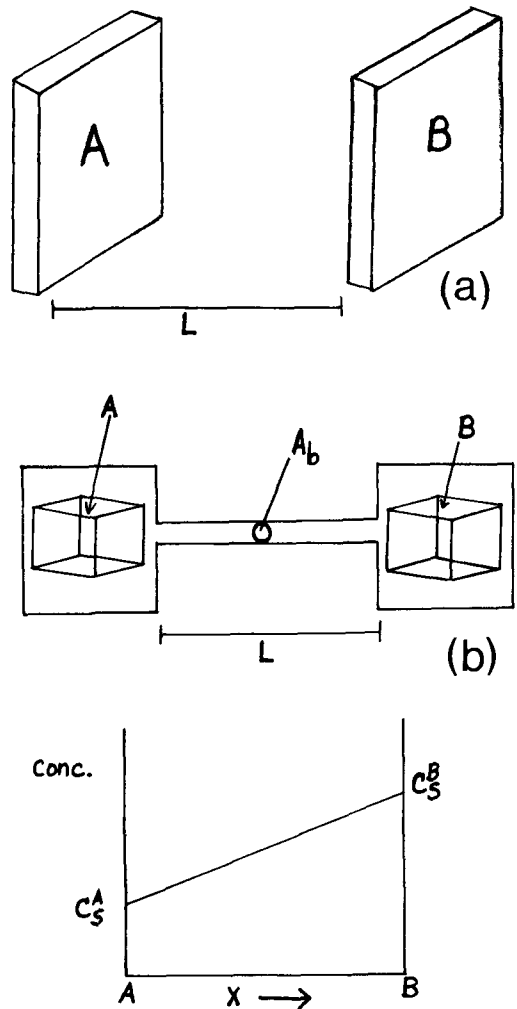


FIG. 2. (a) Metamorphic reaction model. Minerals *A* and *B* are assumed infinitely planar at a distance *L*. The concentration of component in fluid is given below. (b) Simplified model of three-dimensional case where finite minerals *A* and *B* communicate through a boundary fluid of effective area A_b .

for the pure diffusion models) deal with one solid reacting with a fluid or many solids reacting only by diffusion processes (e.g. metasomatic models). For metamorphic reactions, we must develop a *new* and broader model which includes surface reaction as well as diffusion between minerals *A* and *B* mediated by some metamorphic fluid. Let us assume, with no loss of generality, that *B* dissolves to make *A*. Fig. 2a illustrates the situation where there is infinite surface area for planar *A* and *B*. The minerals are separated by a distance *L*. For the sake

of simplicity, assume that the process is governed by the transport and reaction of one component (e.g. Al or Si). Ideally, this treatment can (and probably should) be extended to several components. If C_{eq}^A and C_{eq}^B are the equilibrium concentrations of the component in the 'fluid' in contact with minerals A and B respectively, then the surface reaction rates, R_A and R_B , and the diffusion flux, J , will be given by

$$R_A = k_A(C_S^A - C_{\text{eq}}^A)^{n_A} \quad (6)$$

$$R_B = -k_B(C_{\text{eq}}^B - C_S^B)^{n_B} \quad (7)$$

$$J = -D \frac{C_S^B - C_S^A}{L} \quad (8)$$

where C_S^A , C_S^B are the concentrations of the component at the surface of A and B respectively and D is the diffusion coefficient in the fluid medium. k_A and k_B are rate constants, and n_A and n_B are real numbers; these latter parameters are determined from experimental data such as in Schramke *et al.* (1986a). The important point made earlier is that, at all times, the rates are equal (ignoring signs):

$$R_A = R_B = J \quad (9)$$

$$\text{or } D \frac{C_S^B - C_S^A}{L} = k_A(C_S^A - C_{\text{eq}}^A)^{n_A} = k_B(C_{\text{eq}}^B - C_S^B)^{n_B} \quad (10)$$

Equation (10) can be solved, in general, for the two unknowns, C_S^A and C_S^B . However, if n_A and n_B are not equal to a small integer, the solutions must be done numerically. None the less, the key kinetic concepts are all obtained if we approximate $n_A \approx n_B \approx 1$. (This is not to say that deviations of n_A or n_B from 1 are not important in the actual kinetics.) Now we have:

$$D \frac{C_S^B - C_S^A}{L} = k_A(C_S^A - C_{\text{eq}}^A) \quad (11)$$

$$k_A(C_S^A - C_{\text{eq}}^A) = k_B(C_{\text{eq}}^B - C_S^B) \quad (12)$$

Equations (11) and (12) are easily solved for C_S^A and C_S^B :

$$C_S^A = \frac{\gamma_B C_{\text{eq}}^B + (\gamma_B + 1)\gamma_A C_{\text{eq}}^A}{(\gamma_B + 1)(\gamma_A + 1) - 1} \quad (13)$$

$$C_S^B = \frac{(\gamma_A + 1)\gamma_B C_{\text{eq}}^B + \gamma_A C_{\text{eq}}^A}{(\gamma_B + 1)(\gamma_A + 1) - 1} \quad (14)$$

where the dimensionless variables, γ_A and γ_B , are defined by

$$\gamma_A \equiv \frac{k_A L}{D} \quad (15)$$

$$\gamma_B \equiv \frac{k_B L}{D} \quad (16)$$

Now, if we take into account the finite size of A and B , we can approximate the generally three-dimensional problem by a model such as in fig. 2b. Here it is assumed that the surface region all around A is 'stirred' and maintained at some uniform value, C_S^A , and similarly for B . In between, we must transport the component from B to A across a distance L . Now, the equality of surface reaction and diffusion flux is identical to that given earlier except that the rates are

$$R_A = k_A A_A (C_S^A - C_{\text{eq}}^A)^{n_A} \quad (17)$$

$$R_B = -k_B A_B (C_{\text{eq}}^B - C_S^B)^{n_B} \quad (18)$$

$$\text{and } J = -\frac{D}{L} A_b (C_S^B - C_S^A) \quad (19)$$

where A_A and A_B are the surface areas of A and B . A_b is an effective grain boundary or intergranular cross-sectional surface area for transport between A and B . In this case, the solutions to C_S^A and C_S^B are *identical* to equations (13) and (14), except that now we use γ_A' and γ_B' instead of γ_A and γ_B :

$$\gamma_A' \equiv \frac{k_A L}{D A_b} A_A \quad (20)$$

$$\gamma_B' \equiv \frac{k_B L}{D A_b} A_B \quad (21)$$

Let us analyse equations (13) and (14). If the rate of surface reaction is fast for mineral A , γ_A (or γ_A') will become very large. In this case, the numerator in (13) will become $(\gamma_B + 1)\gamma_A$ (drop the 1). Because γ_A is very large, we can also ignore the first term in the numerator of (13). Therefore, C_S^A equals C_{eq}^A . Similarly, if the rate of surface reaction of mineral B is large, C_S^B will become C_{eq}^B . If *both* rates are high, $C_S^A = C_{\text{eq}}^A$ and $C_S^B = C_{\text{eq}}^B$ and we obtain

$$R_A = R_B = J = \frac{D}{L} (C_{\text{eq}}^B - C_{\text{eq}}^A) A_b \quad (22)$$

(again ignoring \pm signs). Equation (22) is the usual 'mass-transport controlled' model. On the other hand, for slow surface rates the situation is not as simple. Now, the best way to proceed is to insert equations (13) and (14) for C_S^A and C_S^B into equation (23)

$$R_A = R_B = J = \frac{D}{L} A_b (C_S^B - C_S^A) \quad (23)$$

and using γ' rather than γ , obtain

$$R_A = R_B = J = \frac{D A_b}{L} \frac{\gamma_A' \gamma_B' (C_{\text{eq}}^B - C_{\text{eq}}^A)}{(\gamma_B' + 1)(\gamma_A' + 1) - 1} \quad (24)$$

Equation (24) is the general equation for the overall rate, of which equation (22) is but a special case.

There are some interesting results of equation

(24). First, the general equation (24) is proportional to $(C_{eq}^B - C_{eq}^A)$. Therefore, it is clear that, even in cases controlled by linear surface kinetics, the overall rate (including the diffusion flux) can be written as if the whole process were diffusion-controlled [equation (22)] but with an effective diffusion coefficient defined as

$$D_{eff} = \frac{D\gamma'_A\gamma'_B}{(\gamma'_B + 1)(\gamma'_A + 1) - 1}. \quad (25)$$

This result is very important because it illustrates that applying models that use diffusion control to model successfully field data does not imply that diffusion control is operative at all! Only in the case where both γ'_B and γ'_A are large does D_{eff} become equal to the true D and we obtain real diffusion control. Care should be taken to distinguish D_{eff} from D in equation (25) in interpreting field data. Of course, if the surface reaction kinetics are very non-linear then even equation (24) does not hold and it should be easier to separate the models based on diffusion control from those based on surface control.

Let us now investigate a situation where surface reaction at B is very fast but surface reaction at A is very slow (high γ_B and low γ_A), the denominator in equation (24) becomes γ_B and we obtain

$$\text{Rate} = \frac{DA_b}{L} \gamma_A (C_{eq}^B - C_{eq}^A) = k_A A_A (C_{eq}^B - C_{eq}^A). \quad (26)$$

Note that although equation (26) looks similar to equation (22), if γ'_A is very small ($\gamma'_A \ll 1$) and γ'_B is large ($\gamma'_B \gg 1$), as in this case, equations (13) and (14) yield

$$\begin{aligned} C_S^B &\rightarrow C_{eq}^B \\ C_S^A &\rightarrow C_{eq}^A \end{aligned}$$

so that the fluid is fairly homogeneous and close to C_{eq}^B in composition. Therefore, the fluid is quite different from the fluid expected in the diffusion control case. Equation (26) shows how the surface area of only one mineral (in this case A) becomes the rate-controlling factor as observed in the experimental data of Schramke *et al.* (1986a). Similarly if the rate of surface reaction of B were slow, the rate would depend on A_B . However, if the rates of A and B are slow but similar, the overall rate will not have a simple dependence on surface area.

The model developed here does indeed account for the dependence of the overall rate on one mineral surface area in most cases. The same calculations can be generalized to other n_A and n_B as well as several components. None the less, it is hoped that even at this level, the explanation of the

role of surface versus transport terms in the overall rate of metamorphic reactions is greatly clarified.

Experimentally determined surface rate laws

Because the muscovite reaction is not 'controlled' by diffusion transport (under the experimental conditions of Schramke *et al.*, 1986a), the dependence of the rate on ΔG may not be linear. In fact, recent Monte Carlo simulations (Blum and Lasaga, 1985; Lasaga and Blum, 1986) indicate that if defects, such as dislocations, are present, the growth rate may vary as $\Delta G^{2.6}$ to $\Delta G^{2.9}$. To analyse the data in Schramke *et al.* (1986a), the 2 kbar dehydration rates (in units of moles water/cm² area andalusite/sec) were plotted versus the free energy of the hydration reaction in fig. 3. A least-squares fit of a rate law such as

$$R = k\Delta G^n \quad (27)$$

yields

$$R = 4.38 \times 10^{-22} \Delta G^{2.68} \text{ moles cm}^{-2} \text{ sec}^{-1} \quad (28)$$

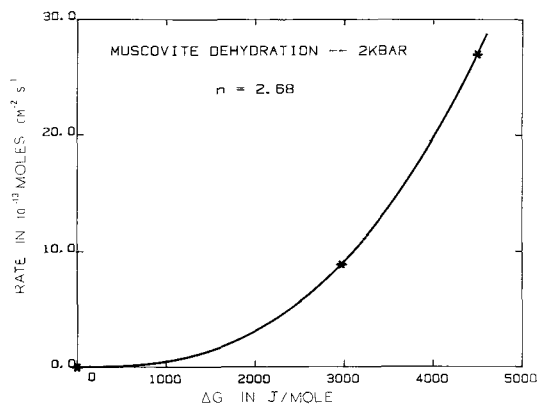


FIG. 3. Plot of muscovite dehydration rate as a function of ΔG for the 2 kbar data of Schramke *et al.* (1986a). Data are shown by * and the solid line is the theoretical fit of equation (26).

with ΔG in Joule/mole. Even with the small data set, the agreement with the Monte Carlo predictions is striking. If one plots the rate data versus ΔT , where ΔT is the increase in temperature above the equilibrium temperature (601 °C here), the results are as shown in fig. 4. Because ΔG and ΔT are nearly linear in this region, the rate law is now

$$R = 2.51 \times 10^{-17} \Delta T^{2.69} \text{ moles cm}^{-2} \text{ sec}^{-1}. \quad (29)$$

Fig. 4 will be useful in the later sections.

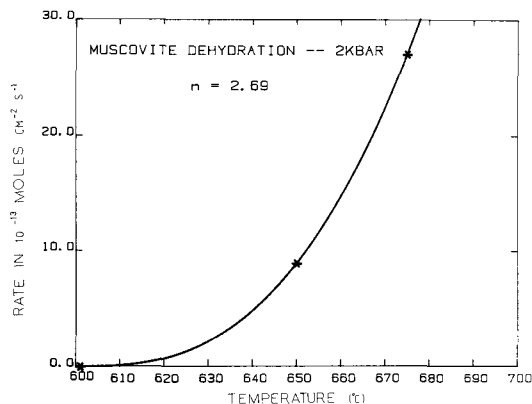


Fig. 4. Plot of muscovite dehydration rate as a function of temperature. The equilibrium value of T under these conditions is $601\text{ }^{\circ}\text{C}$ from the data of Schramke *et al.* (1986a).

Fig. 5 illustrates the same behaviour for the 1 kbar dehydration data. Now, the rate data obey

$$R = 2.73 \times 10^{-20} \Delta G^{2.08} \text{ moles cm}^{-2} \text{ sec}^{-1}. \quad (30)$$

Again, we obtain a highly non-linear behaviour. The exponents obtained in the Monte Carlo calculations and in the analysis of the experimental data above, are both similar to those expected from the classical BCF theory of crystal growth. According to that theory, the growth occurs on the steps of a spiralling screw dislocation by surface diffusion of adsorbed atoms and the theory predicts (e.g. Christian, 1975):

$$\text{Growth Rate} = k\Delta G^2. \quad (31)$$

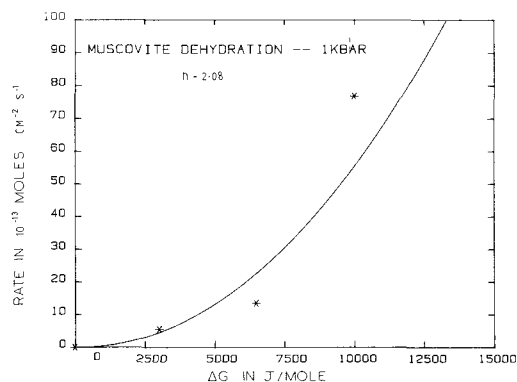


Fig. 5. Plot of muscovite dehydration rate as a function of ΔG for the 1 kbar data of Schramke *et al.* (1986a). Data are shown by * and the solid line is the theoretical fit of equation (26).

The usual method of writing the rate law as used by several workers (Schramke *et al.*, 1986a; Lasaga, 1981; Wood and Walther, 1983) based on transition state theory is

$$R = Ae^{-E/RT}(1 - e^{-\Delta G/RT}) \quad (32)$$

where E is an activation energy and n is some number on the order of unity. Equation (32) becomes a linear rate law if $\Delta G \ll RT$, similar to equation (5), and is thus essentially different from equation (31). Schramke *et al.* (1986a) had problems fitting the experimental data to this equation, however. While equation (32) has general validity within the assumptions of transition state theory, it encounters difficulties if defects (such as at surface reactions) dominate the kinetics. It is this role of defects which was investigated by the Monte Carlo studies of Lasaga and Blum (1986).

The importance of these non-linear rate laws lies in their qualitative shape. Close to equilibrium ($\Delta G = 0$), the slope of the rate curve is nearly zero (e.g. fig. 4). The 'flatness' of the curves near $\Delta G = 0$ means that the system will respond very feebly to an initial deviation from equilibrium (e.g. an overstep in temperature above the equilibrium temperature). It is not until a more sizeable deviation from equilibrium occurs that the rate will increase dramatically and produce an appropriate negative feedback to decrease the overstep (see below). In short, it is much easier to deviate from equilibrium (for 'small' deviations) for non-linear rate laws than for linear ones. On the other hand, it is very difficult to incur sizeable deviations in a non-linear system because the slope of the rate *vs.* ΔT curve finally increases to very high values.

Application of reaction data to simple metamorphic models

The data of Schramke *et al.* (1986a) can now be used to quantify general metamorphic models. We will begin by analysing some simple cases and then tackle the detailed problem of coupling heat fluxes and chemical kinetics.

At the outset, any model of heterogeneous kinetics must deal with the value of the specific surface area (\bar{A}). In our case, we need the specific surface area of andalusite. To estimate this value in the field, we can use the formula in Lasaga (1984),

$$\bar{A}_\theta = \frac{1000}{\rho} \frac{3X_\theta}{100r_\theta} \text{ cm}^2/\text{kg rock} \quad (33)$$

where X_θ = volume % of mineral θ

\bar{A}_θ = specific surface area of mineral θ

r_θ = mean radius of mineral θ

ρ = density of solids.

Using $X_{\text{And}} = 5\%$, $r_{\text{And}} = 0.1 \text{ cm}$; $\rho = 2.6 \text{ g/cm}^3$ yields

$$\bar{A} = 577 \text{ cm}^2/\text{kg rock}.$$

Knowing \bar{A} , the time for completion of metamorphic reactions can be estimated. Using the dehydration data at 2 kbar and equation (29) (where $T_{\text{eq}} = 601 \text{ }^\circ\text{C}$), an overstep of $50 \text{ }^\circ\text{C}$ yields a rate of $9 \times 10^{-13} \text{ moles cm}^{-2} \text{ sec}^{-1}$ while an overstep of $5 \text{ }^\circ\text{C}$ yields $1.9 \times 10^{-15} \text{ moles cm}^{-2} \text{ sec}^{-1}$. The total rate will be given by the product of the specific surface area, \bar{A} , and the rate per unit area; i.e. $R_{\text{tot}} = 5.19 \times 10^{-10}$ to $1.10 \times 10^{-12} \text{ moles/kg rock/sec}$ for the range of temperature oversteps from 50° to 5° . In estimating the amount of muscovite, we will obtain an upper boundary if the mean water content of pelites is used. Based on the data in Holland (1984), the H_2O content of shales is around 3–6 wt. %. Using the value of 4.5 wt. %, one kilogram of rock will contain 2.5 moles of water. Using similar arguments Walther and Wood (1984) obtained 2 moles H_2O /kg rock. In general, therefore, if the 'intrinsic' rate is given by R (moles $\text{cm}^{-2} \text{ sec}^{-1}$) and the specific surface area by \bar{A} ($\text{cm}^2/\text{kg rock}$), the minimum time needed to reach completion for the dehydration reaction will be given by

$$t = \frac{2.5}{R\bar{A}}. \quad (34)$$

Based on the \bar{A} value obtained above, we can vary \bar{A} from 100 to 1000 cm^2/kg (of course, it can deviate even further) and for various temperature oversteps compute the reaction times. The results are given in Table I. Obviously there is a wide range of times possible. Whether or not these times are considered 'long' depends on the rates of the other processes during the metamorphic event and will be investigated further below.

TABLE I. Times to muscovite dehydration

ΔT ($^\circ\text{C}$)	\bar{A} (cm^2/kg)	t (yrs)
50	1000	84
50	100	840
5	1000	41,516
5	100	415,160
10	1000	6,424
10	100	64,240

There are a few comments which should be added based on the experimental data and its theoretical implications. A general question in metamorphic kinetics is the role of diffusion in the intergranular fluid as a possible limiting rate for the chemical reactions as discussed earlier. The diffusion flux of a species in the field can be written as

(omitting multicomponent diffusion—e.g. Lasaga, 1979):

$$J = -\frac{D\phi}{\theta^2} \frac{\partial C}{\partial x} \quad (35)$$

where D is the diffusion coefficient of the species in the intergranular fluid, ϕ is the porosity and θ is the tortuosity. Values of D vary with species as well as with pressure and temperature. However, they generally fall in the range $10^{-5} \text{ cm}^2/\text{sec}$ to $10^{-3} \text{ cm}^2/\text{sec}$ (Nigrini, 1970; Ildefonse and Gabis, 1976; Balashov *et al.*, 1983; Brady, 1983). For our purposes, we can choose $D = 10^{-4} \text{ cm}^2/\text{sec}$, $\phi = 0.001$, $\theta = 1$. It is important to note that the surface reaction rates obtained by Schramke *et al.* (1986a) will be valid *regardless* of the porosity of the rock. However, the speed of diffusion in the field will depend strongly on ϕ . Using the values just mentioned, the diffusion flux will be given by

$$J = 10^{-7} \frac{\Delta C}{\Delta x} \text{ moles cm}^{-2} \text{ sec}^{-1}. \quad (36)$$

The hardest term to constrain is the size of the concentration gradient. We can estimate $\Delta C/\Delta x$ by using solubility data. For example, the solubility of quartz at $600 \text{ }^\circ\text{C}$ and 2 kbar is around $10^{-4} \text{ moles/cm}^3$ (Fournier and Potter, 1982). The value of C near quartz could be close to this C_{eq} if the surface kinetics are fast (i.e. see equation 13 or 14). Close to the surface of a mineral like andalusite, C_{eq} will be much smaller and by inference so will C . Therefore, we can estimate $\Delta C/\Delta x$ by $10^{-4}/\Delta x$ moles/ cm^4 (Δx in cm). Δx in this case is the distance between the region close to saturation with quartz and the region close to the andalusite surface. It will roughly correspond to the physical separation of grains and thus will typically be 0.1–10 mm. Leaving Δx as a parameter to be varied, we can use the value of $10^{-11}/\Delta x$ for the diffusion flux under 'diffusion-controlled' conditions to find out the cases where it is valid. If the temperature oversteps the equilibrium temperature by an amount ΔT , the surface rate will be given by equation (29). If this rate is much smaller than the diffusion flux estimated above, then the conditions for 'transport-control' are not valid, as shown earlier. We can find out the boundary between 'surface-control' and 'diffusion-control' by setting

$$k\Delta T^n = \frac{10^{-11}}{\Delta x}. \quad (37)$$

Using equation (29), we obtain a plot of ΔT versus transport distance, Δx , for the boundary as given in fig. 6. It is clear that, in general, unless Δx is quite large, the required values of ΔT for 'diffusion-control' are high. In fact, the ΔT values in fig. 6 will be shown to be greater than the actual values

obtained in the model of contact metamorphism to be carried out below. These calculations suggest that not only are the experimental data controlled by the surface kinetics but also this control is expected to extend in the case of aluminosilicate reactions to the field situations.

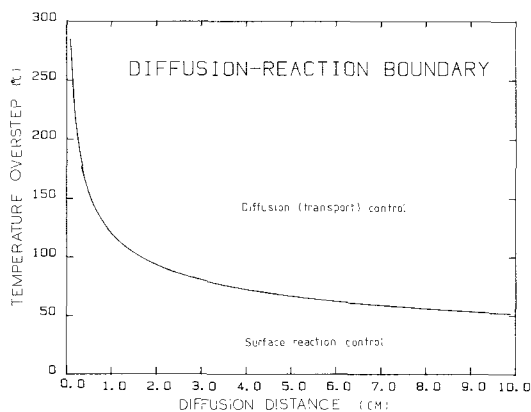


FIG. 6. Temperature overstep required for diffusion to match surface reaction rates as a function of diffusion distance between the minerals. For temperature oversteps higher than those in the figure, diffusion will dominate the rate.

Of course, there are other chemical reactions which may very well be governed by the rates of mass transfer in fluids (e.g. the calcite-wollastonite reaction, Tanner *et al.*, 1985). Much more experimental data are needed to discern the ultimate kinetic controls on the major metamorphic reactions.

Heat flow and reaction

The effect of metamorphic reactions on the external heat flow in a tectonic event and vice-versa is a key problem for petrologists and geophysicists. Using the previous data, we can begin with some simple calculations. The thermal history of a region and any chemical reactions that occur are coupled by the enthalpy of the reactions, ΔH_r . For the muscovite dehydration reaction, $\Delta H_r = 18$ kcal/mole H_2O (Kerrick, 1972). We would like to compare the internal heat sink induced by the reaction to the external heat inputs. To do this, the thermal history resulting from the intrusion of an igneous body can be calculated and used as a zeroth order reference point.

The heat flow is essential to the operation of these endothermic reactions. In fact, it is critical to decide whether the external sources control the heat or the

reaction itself. At this point, it is useful to carry out some calculations on the cooling of a magmatic intrusion. If the pluton is $2a \times 2b \times 2c$ in size, the initial magmatic temperature is T_0 and the initial country rock temperature is T_1 , then the temperature at position x, y, z is (Jaeger, 1968)

$$T = T_1 + (T_0 - T_1) f\left(\frac{x}{a}, \frac{kt}{a^2}\right) f\left(\frac{y}{b}, \frac{kt}{b^2}\right) f\left(\frac{z}{c}, \frac{kt}{c^2}\right) \quad (38)$$

where

$$f(u, \tau) \equiv \frac{1}{2} \left[\operatorname{erf}\left(\frac{u+1}{2\sqrt{\tau}}\right) - \operatorname{erf}\left(\frac{u-1}{2\sqrt{\tau}}\right) \right] \quad (39)$$

and u, τ are defined by the expressions in parentheses in equation (38). If this equation is used to compute T at several distances from a mafic intrusion $1 \times 10 \times 10$ km in size (essentially a one-dimensional problem—e.g. a dyke or a sill) with $T_0 = 1200^\circ\text{C}$ and $T_1 = 200^\circ\text{C}$, the result is as given in fig. 7.

To proceed further we could set $T_{eq} = 600^\circ\text{C}$ as the dehydration temperature (i.e. the equilibrium value for the 2 kbar pressure, Schramke *et al.*, 1986a). This temperature is shown as a dashed line in fig. 7. As can be seen, 50 m away from the contact the temperature exceeds 600°C after close to 600 years, reaches a maximum of 644°C 2000 years later and finally drops below 600°C at $t = 8000$ years. The time interval for reaction is then 7400 years. Of course, the time interval involved decreases as the distance from the contact is increased (fig. 7), until at 110 m from the contact, the temperature never exceeds 600°C . Using a simple petrologic model (including neglect of nucleation), the reaction isograd would be sharp and coincide with this last distance.

Let us now look at the actual heat flow, for the case discussed above. At a distance of 50 m the rate of temperature rise, as 600°C is first exceeded, is

$$\frac{dT}{dt} = 0.07^\circ\text{C/yr.}$$

If the heat capacity is set to $0.25 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$, this temperature rise can be converted to a net input of heat in a unit volume of $0.0175 \text{ cal g}^{-1} \text{ yr}^{-1}$ or $5.5 \times 10^{-7} \text{ cal kg}^{-1} \text{ sec}^{-1}$.

It is important to compare the external heat source with the heat sink represented by the dehydration reaction. If the temperature is allowed to increase by 50°C above equilibrium, equation (29) shows that the rate of reaction will be $5.19 \times 10^{-10} \text{ moles kg}^{-1} \text{ sec}^{-1}$. If the enthalpy of dehydration is taken as 18 kcal/mole (Kerrick, 1972) then the heat sink is

$$9.3 \times 10^{-6} \text{ cal kg}^{-1} \text{ sec}^{-1}.$$

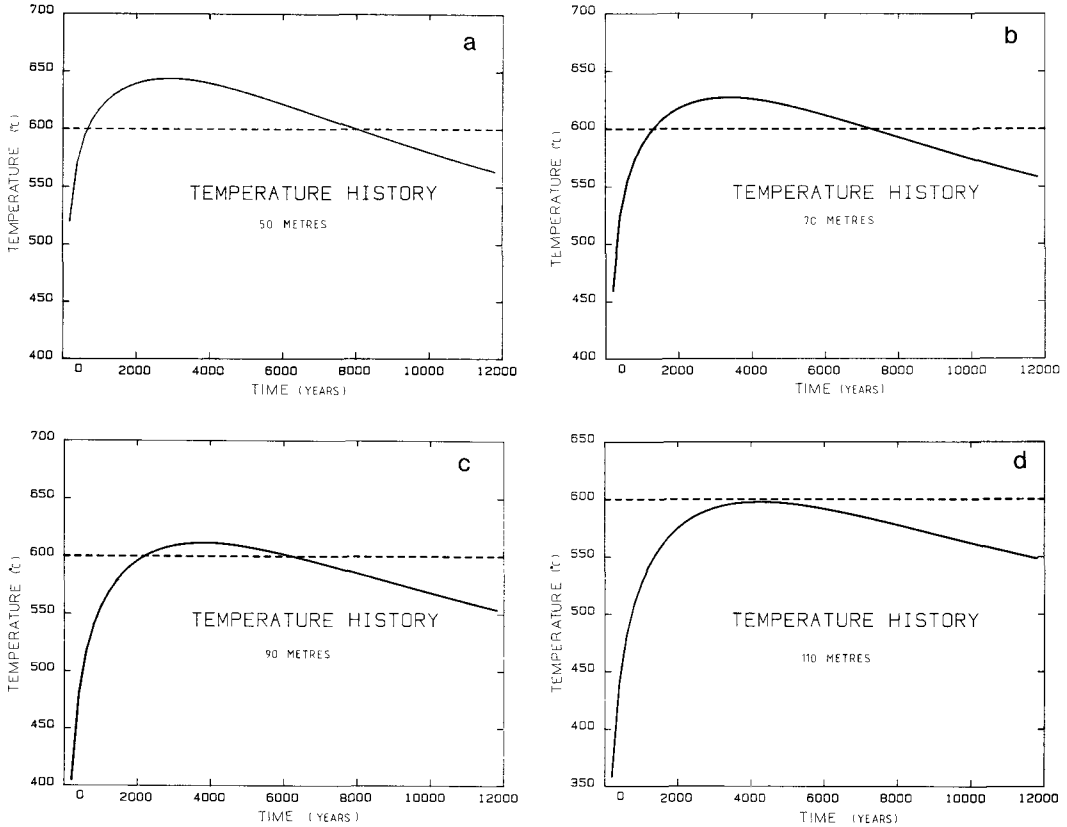


FIG. 7. Temperature-time history for positions at various distances from the intrusive contact. $T_0 = 1200^\circ\text{C}$, $T_1 = 200^\circ\text{C}$, half-width $a = 500$ m. Dashed line marks the equilibrium temperature (601°C) for muscovite breakdown at 2 kbar. Distance from contact: (a) 50 m; (b) 70 m; (c) 90 m; (d) 110 m.

If the $\Delta T = 5^\circ\text{C}$, then the heat sink is now

$$1.98 \times 10^{-8} \text{ cal kg}^{-1} \text{ sec}^{-1}.$$

Comparing these reaction heat sinks suggests that the control resulting from coupling between the external heat and the chemical reactions may range from external to internal control depending on the size of the intrusion and the rate parameters (including the \bar{A} term). The description of the system, in this case, required a more careful account of the heat flux-chemical reaction equations.

The heat equation with chemical reaction is given by

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} + \frac{\Delta H_r R_{\text{tot}}}{\rho C_p}. \quad (40)$$

κ , the thermal diffusivity, is typically $\sim 0.01 \text{ cm}^2/\text{sec}$. ΔH_r is the enthalpy of reaction (cal/mole); R_{tot} is the rate of reaction (moles $\text{cm}^{-3} \text{ sec}^{-1}$); ρC_p is the volume heat capacity in $\text{cal cm}^{-3} \text{ K}^{-1}$. Note that direct solution to equation (40) transcends the

simpler discussions of 'heat flow control' versus 'reaction control' of metamorphic reactions. Equation (40) was solved by the implicit Crank-Nicholson finite difference method. The initial conditions assume a 1 km wide 'infinite' intrusion at temperature 1200°C (e.g. a large mafic dyke or sill) and a country rock at an initial temperature of 200°C . These conditions correspond to the calculations shown in fig. 7. Due to symmetry, only one side of the system needed to be modelled. The boundary conditions were

$$\frac{\partial T}{\partial x} = 0 \text{ at } x = 0 \quad (41)$$

$$T = T_0 \text{ at } x = x_{\text{max}}. \quad (42)$$

Equation (41) follows from the symmetry of the problem. Equation (42) sets T equal to the initial country rock value, T_0 , at some distance, x_{max} , sufficiently removed from the contact to validate the approximation. As a self-consistency check on

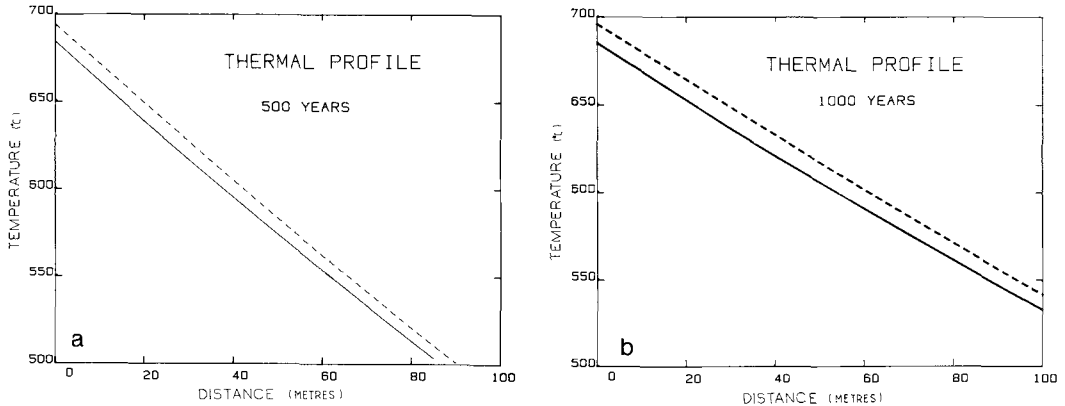


FIG. 8. Thermal profile for the intrusive used in fig. 7 but now allowing for metamorphic reaction. The dashed line gives the case with no reaction and the solid line the results with reaction. (a) 500; (b) 1000 years.

equation (42), the values of T in the numerical results were checked to be close to T_0 before reaching x_{\max} .

In the numerical calculations, κ , ΔH_r , ρ , and C_p were kept constant. A pressure of 2 kbar was assumed. The surface area \bar{A} was taken as 577 cm²/kg rock based on the earlier calculations. The reaction term, R_{tot} , in equation (40) is given by $\bar{A}R$, where R is zero if $T < 601$ °C and is calculated from equation (29) if $T \geq 601$ °C ($\Delta T = T - 601$). The total number of moles of water given off was monitored in the calculations. If the moles given off exceeded 2, it was assumed that all the muscovite had disappeared and R was set back to zero (even if $T > 601$ °C). The accuracy of the numerical scheme was checked by comparing the calculations for $R = 0$ with the analytic solution [equations (38) and (39)]. Finally, the calculations assumed that the water of dehydration was removed quickly from the system. Therefore, we did not include the hydration rate data, which is also available in Schramke *et al.* (1986a).

Fig. 8a, b compares the temperature profile with and without chemical reaction after 500 and 1000 years. The effect of the heat sink caused by the dehydration reaction is to lower the temperature (solid line) for the first 100 m by between 5–10 °C for the 500 year thermal profile, and by 10–15 °C for the 1000 year thermal profile.

Fig. 9 analyses in detail the evolution of the muscovite isograd as the intrusion cools and the country rock is invaded by a thermal pulse. The width of the isograd can be inferred from the place where the number of muscovite moles is 2 per kg (no reaction) and the place where there is no muscovite left. Fig. 9a yields 15 m for $T = 500$ years. This width grows to 20 m by the time the

'molar profile' has ceased to vary (fig. 9f). If we place the isograd at the point where $n_{\text{musc}} = 0$ for first time, we see in fig. 9 that the isograd moves steadily outward as time progresses. The isograd lies at $x = 15$ m at $T = 500$ years and the final value occurs at $x = 65$ m ($T \geq 6000$ years). This value contrasts with the simple value of 105 m discussed earlier. This contraction of the isograd around the intrusion is caused by: (1) the lowering of T due to the heat sink of the reaction; and (2) the sluggishness of the reaction itself.

Greenwood (1975) and many others after him have focused on isobaric invariant points as the unique thermodynamic loci, which define isograds and buffer the temperature of the assemblage. This tenet of faith can now be scrutinized with the results in fig. 9. The regions with $n_{\text{musc}} = 0$ or 2 are not on the invariant point. Hence, the region of interest is that where $0 < n_{\text{musc}} < 2$. According to the thermodynamic data and the local equilibrium assumption, the temperature throughout this region should be 601 °C. Fig. 9 shows that the temperature can overshoot the invariant point by nearly 40 °C.

As a comparison, if the surface rates are increased by three orders of magnitude (more comparable to carbonate reactions), the results above become more in line with the invariant buffer assumption. The results are shown in fig. 10. Note that now the temperature deviation is only a few degrees and that the isograd exhibits a much sharper spatial front.

Table II summarizes the results for a variety of surface area terms and intrusion sizes. Obviously the range of widths can easily reach up to 100 m for large intrusives (> 1000 m). It is interesting to note that Tyler and Ashworth (1982) observed 'reaction

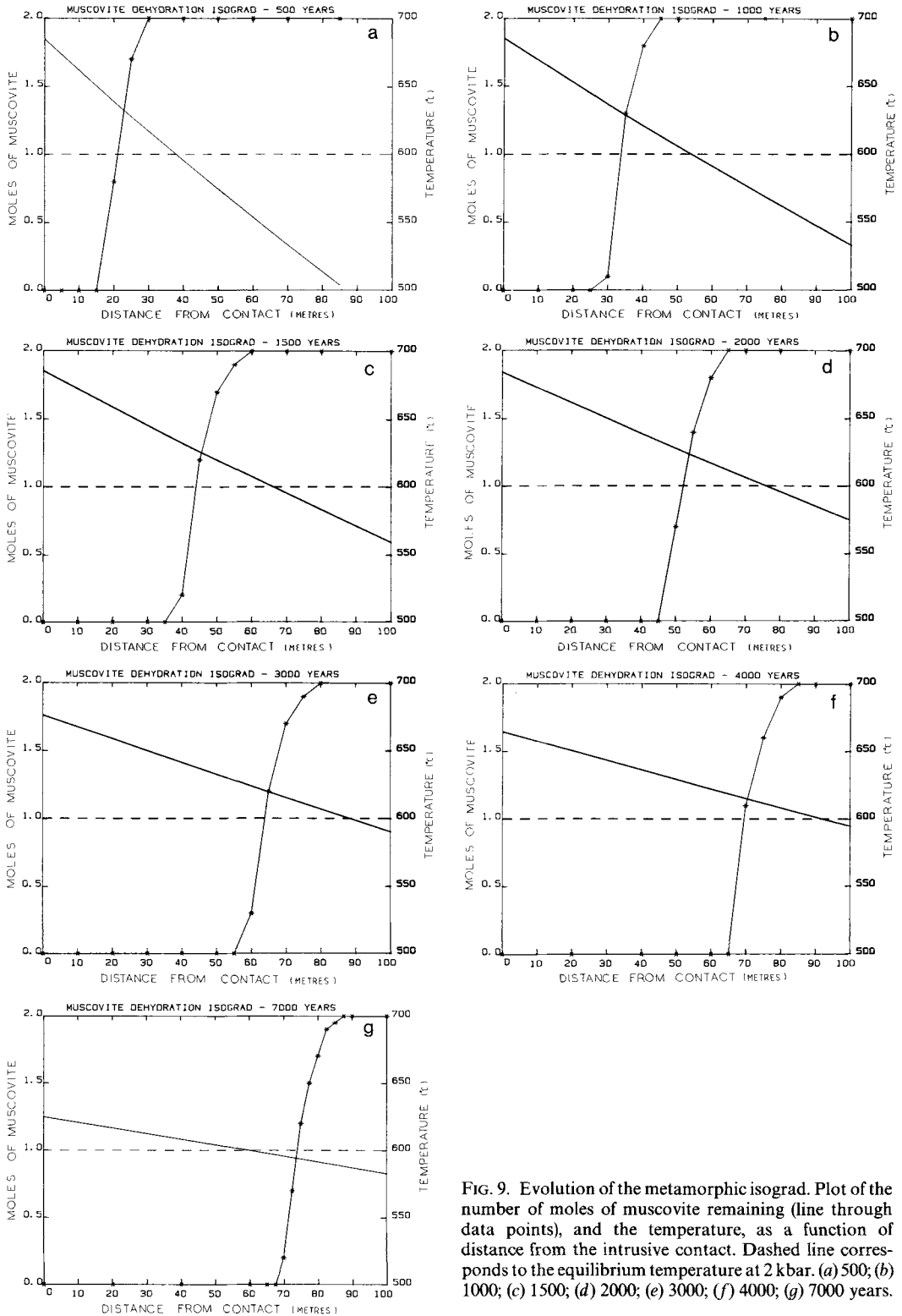


FIG. 9. Evolution of the metamorphic isograd. Plot of the number of moles of muscovite remaining (line through data points), and the temperature, as a function of distance from the intrusive contact. Dashed line corresponds to the equilibrium temperature at 2 kbar. (a) 500; (b) 1000; (c) 1500; (d) 2000; (e) 3000; (f) 4000; (g) 7000 years.

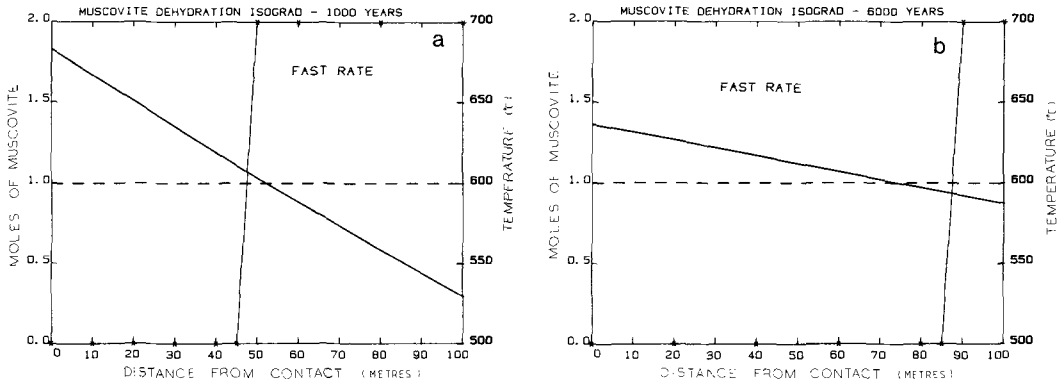


FIG. 10. Same as fig. 9 but now the rate constant is increased by three orders of magnitude. (a) 1000; (b) 6000 years.

zones' on the order of 300 m for the muscovite isograd in the contact metamorphic zone around the Strontian granodiorite (~ 2000 m half width), Scotland. They ascribe the width to the variation arising from varying X_{H_2O} . There is no question that added thermodynamic variables (in the phase rule sense) can affect the isograd development. However, using the kinetic data available now, our results show that kinetics can indeed play just as major a role in the interpretation of the reaction widths.

TABLE II. Isograd width (metres)

Half-width a (metres)	\bar{A} (cm ² /kg)	11.5	115	577	1150
100	7 ^a	13	9		
250	32.5 ^a	22.5	15		
500	50	27.5	20		
1000	70	35	25		20

^a no muscovite out region

Table III gives a variety of results from the calculations. The maximum ΔT refers to the maximum temperature overstep observed. Obviously this ΔT can reach values of 60–90 °C, especially for small intrusions. The column 'isograd position' gives the distance (in m) from the contact where the $n_{musc} = 0$ boundary is to be found, i.e. the position of the muscovite-out isograd. It is interesting to note that in a one-dimensional model (i.e. an intrusive sheet of half-width a), the place where $T_{max} = 601$ °C (for out T_0 and T_1 values) is given by $x = 1.2196a$. If the kinetics were infinitely fast and their effect on the thermal evolution small (i.e.

$\Delta H \sim 0$), then we would expect the isograd at position $1.2196a$ or $0.2196a$ m from the contact. This value corresponds to 22, 55, 110, and 220 m for the $a = 100, 250, 500,$ and 1000 m cases illustrated in Table III and is clearly an upper boundary. The two places marked by — in the table correspond to situations where muscovite persisted right up to the contact.

TABLE III. Isograd widths, positions and T oversteps

Half-width a (metres)	\bar{A} (cm ² /kg)	Isograd width (metres)	Max. ΔT (°C)	Isograd position (metres)
100	577	9	60	7
250	577	15	40	27.5
500	577	20	41	67.5
1000	577	25	29	150
100	11.5	8	91	—
250	11.5	32.5	92	—
500	11.5	50	95	25
1000	11.5	70	45	90

One aspect that has not been treated in detail here is the rate of nucleation. Nucleation rate data are almost non-existent for metamorphic reactions. However, in our experimental study of the muscovite breakdown kinetics, nucleation experiments were included. These data are just now being sorted out (Schramke *et al.*, 1986b). A proper treatment of simultaneous nucleation and growth would incorporate models such as those developed by Avrami (see Kirkpatrick, 1981), or more likely new extension of these earlier models that incorporate heterogeneous nucleation and pre-existing crystals. We are currently working on these theoretical developments. In developing nucleation models it is imperative that experimental data be obtained and used. One reason for this is that the theory of nucleation is in worse shape than the theory of growth. We cannot be content to just borrow the

very simple formulae from materials science. Therefore, we do not claim to put nucleation phenomena in our results. None the less, given all the caveats above, one can crudely 'simulate' a nucleation effect by requiring that a certain temperature overstep be reached before reaction takes place. This modification was included in the model and the results also given in Table IV.

TABLE IV. Effect of nucleation on isograds

Nucleation overstep °C	\bar{A}^*	Reaction zone width (metres)	Max. ΔT (°C)	Isograd position (metres)
0	577	20	k1	67.5
5	577	17.5	k2	67.5
25	577	2.5	k2	60.0
0	11.5	50	95	25
5	11.5	50	95	25
25	11.5	42.5	95	25

* $\text{cm}^2/\text{kg rock}$

A nucleation-induced overstep of 5 °C did not change the results significantly. The maximum temperature oversteps remained about the same, as well as the position of the isograd. Only the width of the 'reaction zone' was decreased slightly, for example from 20 to 17.5 m in the $\bar{A} = 577 \text{ cm}^2/\text{kg}$ case (Table III). Increasing the nucleation-induced overstep to 25 °C, significantly decreased the 'reaction zone', while the isograd position changed slightly. In this case, the reason for the relative abruptness of the 'reaction zone' stems from two factors. On the one hand there is no reaction until the temperature exceeds $T_{\text{eq}} + 25 \text{ °C}$; but at this point the reaction proceeds at a very fast pace, because the overstep is so large. Therefore, regions which either never exceed $T_{\text{eq}} + 25 \text{ °C}$ or do so very briefly will now remain 'unreacted'. These results suggest that nucleation can have an effect on the width of the 'reaction zone' only if the effective overstep is large enough. Based on the abundance of heterogeneous nucleation sites and our preliminary data, I do not feel that the $\Delta T = +25 \text{ °C}$ case is likely. However, it is safest to wait for new experimental data on nucleation to have the last word.

Summary

The effectuation of metamorphic reactions necessitates the operation of many kinetic processes involving both heat and mass transfer. New kinetic data enable us to appraise the importance of several of these processes. In particular, the inter-

play of diffusion and surface reactions in the breakdown and growth of metamorphic minerals is elucidated by the new data and by the formulation of a metamorphic reaction model. For reactions involving low-solubility aluminosilicates, the rates at the mineral surface of one of the reactants or products may control the overall rate and not the diffusion transfer. However, both surface reaction and diffusion must occur at equal rates.

A reaction-diffusion model was developed to analyse the interplay of surface kinetics and diffusion fluxes in the overall reaction rate. The dependence of the rate on the surface area of one mineral (reactant or product) in the case of slow surface kinetics was shown quantitatively by the model. The model included the usual diffusion-control term as a limiting case of very fast surface kinetics. An important result of the model for the case of near-linear surface reaction rate laws is the possibility of recasting the overall rate as a 'diffusion-control' model with a new effective diffusion coefficient.

The kinetic description of surface reaction rates may require the use of non-linear terms. The new data on muscovite dehydration predicts a non-linear dependence on ΔG or on the temperature overstep ΔT that seems to be in agreement with theoretical Monte Carlo simulations of growth and dissolution in the presence of linear defects. While some reactions may obey linear kinetics, the results presented here strongly suggest that more metamorphic reactions be studied in detail.

The reaction rate equations can be coupled with the heat flux equations to enable a description of the overall processes in the field. The numerical modelling carried out here shows that the usual assumptions regarding the buffering of temperature and composition at univariant reaction points have to be modified, especially for the sluggish reactions involving silicates. Furthermore, the sharpness of an isograd is clearly dependent on the thermal evolution and the rates of reaction. For the examples carried out in the text, the width of the isograd varied from a few metres to nearly 100 m as the rates of reaction and the size of the intrusion were varied over ranges easily expected in the wide range of metamorphic conditions. The expression of these kinetic results in field observations should be further studied.

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