

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/227055152>

# Inverse modeling approach for obtaining kinetic parameters of diffusion-controlled metamorphic reactions in the Kharlovo Contact Aureole (South Siberia, Russia)

Article in *Mineralogy and Petrology* · April 2001

DOI: 10.1007/PL00013506

CITATIONS

8

READS

94

5 authors, including:



**Igor Likhanov**

Sobolev Institute of Geology and Mineralogy

179 PUBLICATIONS 1,741 CITATIONS

SEE PROFILE



**Reverdatto Vladimir**

Sobolev Institute of Geology and Mineralogy

238 PUBLICATIONS 2,005 CITATIONS

SEE PROFILE



**Isabella Turbanti Memmi**

Università degli Studi di Siena

39 PUBLICATIONS 799 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



Metamorphic complexes of the Yenisei Ridge: geological evolution, sedimentary parent rocks, and resource potential. Funding: Russian Science Foundation • 21-77-20018. Principal Investigator: Igor Likhanov [View project](#)



Metamorphic and geodynamic evolution of orogenic belts along the continental margins of ancient cratons (on example of Yenisey Ridge, Urals, and Dzhugdzhur-Stanovoi fold belt) [View project](#)

# **Inverse modeling approach for obtaining kinetic parameters of diffusion-controlled metamorphic reactions in the Kharlovo Contact Aureole (South Siberia, Russia)**

**I. I. Likhanov<sup>1</sup>, A. A. Ten<sup>2</sup>, V. A. Ananiev<sup>1</sup>, V. V. Reverdatto<sup>1</sup>, and I. Memmi<sup>3</sup>**

<sup>1</sup> Institute of Mineralogy and Petrography, Novosibirsk, Russia

<sup>2</sup> Department of Geology and Geophysics and Supercomputer Institute, University of Minnesota, South Minneapolis, MN, USA

<sup>3</sup> Dipartimento di Scienze della Terra, Università di Siena, Italy

With 2 Figures

Received July 14, 1998;

revised version accepted June 28, 2000

## **Summary**

A new approach for deriving kinetic parameters of diffusion-controlled metamorphic reactions is described. It is based on comparison of models of temperature field evolution near a cylindrical intrusion and observable chemical changes in biotite at the contact aureole of the Kharlovo massif. Unlike other methods used to construct quantitative models of reactions which produce distinctly expressed zoned micro-textures, the proposed approach allows better understanding of the processes occurring in texture-homogeneous rocks, where complete consumption of some reactant mineral phases prevent accurate reconstruction of the metamorphic process. The calculations yielded estimates of the effective rates of metamorphic reactions ( $10^{-12} \text{ s}^{-1}$ ) and the effective diffusion coefficient ( $5.29 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ ). These values are consistent with experimentally and theoretically derived estimates of solid-state diffusion, including grain-boundary diffusion.

## **Zusammenfassung**

*Inverse Modellierung zur Bestimmung kinetischer Parameter diffusionskontrollierter metamorpher Reaktionen in der Kontaktaureole von Kharlovo (Südsibirien, Rußland)*

Ein neuer Ansatz zur Herleitung kinetischer Parameter diffusionskontrollierter metamorpher Reaktionen wird beschrieben. Er basiert auf einem Vergleich der Modelle für die Temperaturentwicklung um eine zylindrische Intrusion mit beobachtbaren

Änderungen im Chemismus von Biotit in der Kontaktaureole des Kharlovo Massivs. Im Unterschied zu anderen Methoden, die quantitative Modelle von Reaktionen mit deutlich zonierten Mikrotexturen verwenden, erlaubt dieser Ansatz ein besseres Verständnis der Prozesse in texturrell homogenen Gesteinen, in denen die vollständige Reaktion einiger Reaktanden (Mineralphasen) sonst die Rekonstruktion des Metamorphoseprozesses verhindert. Die Berechnungen erlauben eine Abschätzung der metamorphen Reaktionsraten ( $10^{-12} \text{ s}^{-1}$ ) und des effektiven Diffusionskoeffizienten ( $5.29 * 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ ). Diese Werte sind mit experimentell und theoretisch ermittelten Werten der Diffusion in Festkörpern, einschließlich der Diffusion entlang von Korngrenzen, konsistent.

## Introduction

The rates of metamorphic reactions and diffusion coefficients of components in solid phases need to be reassessed if metamorphic phenomena are to be adequately understood. Progress in this field could enable solution of a major problem of petrology, namely determination of the duration of metamorphic events. The study of reaction rates and diffusion coefficients is known as “chemical kinetics”. Some aspects of metamorphic reaction kinetics have been examined by *Walther* and *Wood* (1984), *Rubie* and *Thompson* (1985), *Lasaga* (1986), and others, and the subject has recently received much attention. These classic studies provided a basis for quantitative evaluation of the kinetics of metamorphic processes and estimation of the duration of successive stages of a metamorphic cycle.

A metamorphic process involves several local reactions in different microscopic domains of the rock. Components migrate from one domain to another. *Eugster* (1970) and *Fisher* (1970) investigated metamorphic processes of this kind, using a graphic approach to show that local chemical potential gradients of some components are in the right direction to account for the required material transport from one domain to another. However, it is difficult to use these methods to examine chemical potential gradients of more than a few components and to quantify the relative rates of transport and reaction which occur in different parts of a rock. More comprehensive analytical approaches have therefore been developed using irreversible thermodynamics to evaluate gradients, fluxes and reaction rates in metamorphic rocks. Irreversible thermodynamic models have become a powerful tool for understanding the processes involved in the formation of complex metamorphic textures. Detailed reconstruction of metamorphic processes has been based not only on reactants and products, but also on the observed spatial relationships between them in distinctly expressed zoned reaction textures, formed during kelyphite, coronite, symplectite and segregation formation (*Vidale*, 1969; *Fisher*, 1970; *Joesten*, 1974, 1977; *Sanford*, 1980; *Walther*, 1983; *Ashworth*, 1986; *Ashworth* and *Sheplev*, 1997; among others). Because these textures are disequilibrium features that record an intermediate stage in the production of a new equilibrium assemblage from its precursor, they provide unique information about the rates of metamorphic reactions. In particular, analysis of these textures may permit constraints to be placed on the relative rates of intergranular diffusion of the components involved in metamorphic reactions (*Carlson* and *Johnson*, 1991). Unfortunately, application of this technique for texture-homogeneous rocks is

impeded by the fact that all phases tend to react with each other until the reaction is over. For these metamorphic reactions, the complete consumption of some reactant mineral phases prevents accurate reconstruction of the the metamorphic process in the kinetic framework used to understand the zoned reaction textures. With some notable exceptions (e.g. *Carmichael*, 1969; *Foster*, 1977, 1981; *Ferry*, 1983, 1984; *Yardley*, 1977; *Atherton*, 1980; *Rice and Ferry*, 1982; *Menard and Spear*, 1996), no detailed studies on the precise mineralogical changes across isograds have been made. Some generalized characteristics of mass-transfer based on geological observations have been obtained in these studies, by examining rock textures and chemical heterogeneities in minerals and by mathematical modeling used to solve dynamic problems, given duration and PT parameters. However, progress in acquiring quantitative characteristics using these model approaches is restricted by the deficit of kinetic parameters. Experimental investigations aimed at ascertaining mineral nucleation centers, growth and dissolution rates and chemical diffusion coefficients are required to understand and substantiate mineral reaction mechanisms. Unfortunately, such experiments are not abundant for known metamorphic reactions. A deeper understanding of metamorphic reactions obviously requires more sophisticated models, applicable to particular reactions. In this connection, we now propose a novel approach to the quantitative determination of diffusion-controlled mineral reaction kinetics.

### **Rocks investigated, previous research and general characteristics of inverse approach**

The study area, previously well investigated (*Reverdatto et al.*, 1974, 1976, 1978; *Likhanov*, 1989, 1990) is the contact aureole of the Kharlovo gabbro massif. Emplacement of a composite stock of titanomagnetitic gabbro, forming a distinct “cylindric-shaped” structure with a radius of 1950 m, in Cambrian-Ordovician metapsammites of the Altay Mountains, regionally metamorphosed to greenschist facies conditions, produced an extensive contact aureole with distinct zonation characterized by muscovite and amphibole hornfels facies. Diffusion-controlled chemical reactions in the aureole and some changes in the mineral composition towards the intrusive contact had been investigated in detail by the authors (*Likhanov et al.*, 1994, 1995). These provided the opportunity to suggest and substantiate the possible mineral reactions mechanisms responsible for the formation of metamorphic microtextures along contact metamorphism isograds and to discuss the effect of changing thermodynamic conditions on their stabilization (*Likhanov et al.*, 1997). Quantitative models elaborated during mass transfer analysis allowed the authors to define the actual scales of mass transfer and to determine a differential component mobility sequence occurring as a result of specific metamorphic reactions, which are characterized by different mechanisms of mineral transformation in the matrix (*Likhanov et al.*, 1999). Because isochemical suites of rocks were available, mass-transfer quantitative analysis, carried out to derive the minimum volumes of material transport involved in metamorphic reactions, relied on an assessment of the material balance between reactants and products and detailed microtextural observations coupled with mineral chemistry. The balance of petrogenetic components was estimated for small microdomains and

aggregates of rock, assuming practically constant volume. Some of the component moles in these microdomains were compared before and after the reaction, which provided information about the character of the mineral transformations of mass-transfer scales. It was established that the mass transfer of major components for biotite-forming reaction was limited to very small volumes of the order of  $0.01 \text{ mm}^3$  (Likhanov et al., 1994). The estimates of the minimum volumes in which matter redistribution took place as a result of mineral reaction, is used in the present paper for the determination of an effective diffusion coefficient.

The contact aureole was chosen for solving the kinetic tasks for a number of reasons. On one hand, it is especially suitable for evaluating psammitic schist phase relations because the last metamorphism occurred in response to an isobaric thermal overprint by a gabbro intrusion. Variations in phases and their compositions therefore primarily express changes in temperature. On the other hand, contact aureoles provide an ideal natural experiment for the retrieval of kinetic coefficients of thermally activated processes. Both the starting materials and the reaction products, at various stages of reaction, are available for study in rocks within an aureole. Because each rock sampled in a contact aureole has been heated to a different temperature for a different period of time, the mineral assemblage of rocks sampled across an aureole records a range of temperature and run duration similar to that of a well-planned set of laboratory experiments. Unlike the products of a set of isothermal experiments, which yield the value of the kinetic coefficient for that temperature, each sample from a contact aureole records the integrated kinetic response to a heating-cooling cycle. Although it is possible to derive the value of the kinetic coefficient for a fixed, "time-averaged" temperature from analysis of a single sample, analysis of the full set of samples from an aureole yields a temperature-dependent function that describes the kinetic behavior of the system integrated over the range of temperatures recorded in the aureole. The time index for non-isothermal kinetic processes is the temperature-time integral of the kinetic equation, evaluated numerically using a calibrated thermal-history model for the intrusion (Joesten and Fisher, 1988).

The contact aureole is therefore a suitable object which may yield kinetic parameters. The direct approach is experimental determination of mineral reaction kinetics. For naturally-occurring objects, this means conducting natural experiments with natural materials. In contrast to experiments, where all ratios between reactant and product phases, duration and thermodynamic conditions are known, the study described in this paper obtains the kinetic parameters of metamorphic reactions by solving an inverse problem. By this approach, a bulk rate constant for metamorphic reactions is obtained from mineral chemical data and numerical modeling of the thermal evolution of the aureole. From this bulk reaction rate and information on the volumes of material redistribution, the effective diffusivities that controlled the reaction rate are obtained.

Average chemical compositions of biotites from the Kharlovo contact aureole's hornfelses, obtained by Camebax electron microprobe analyser (Institute of Mineralogy and Petrography, Novosibirsk), are given in Table 1. Biotite was chosen as the main mineral characterizing the "reaction product", for the following reasons. First, biotite is ubiquitous in all samples from the study area and is the most abundant and widespread ferromagnesian phase in all contact metamorphic zones

Table 1. Average biotite composition from hornfelses of the contact aureole

<i>l, m</i>	30	90	140	160	200	250	300	350	380	400	420
<i>L, M</i>	1980	2040	2090	2110	2150	2200	2250	2300	2330	2350	2370
SiO <sub>2</sub>	35.92	36.55	36.65	36.06	36.57	36.58	37.00	35.52	36.25	36.35	34.32
TiO <sub>2</sub>	3.28	3.12	3.36	3.15	3.38	3.19	2.67	2.32	2.36	2.37	2.33
Al <sub>2</sub> O <sub>3</sub>	19.52	18.84	19.24	18.48	17.05	18.32	16.96	18.43	18.25	19.31	18.36
FeO	16.85	17.33	17.72	17.32	19.55	19.26	18.02	19.13	19.86	20.51	21.56
MgO	10.65	9.86	9.04	11.17	9.75	8.32	11.85	11.79	8.73	8.45	8.81
CaO	0.01	0.05	0.02	0.01	0.03	0.04	0.01	0.18	0.05	0.01	0.14
Na <sub>2</sub> O	0.19	0.19	0.15	0.21	0.2	0.36	0.16	0.26	0.26	0.22	0.32
K <sub>2</sub> O	9.63	9.45	9.75	9.43	9.17	9.56	9.07	9.56	9.32	8.89	8.35
MnO	0.07	0.07	0.10	0.11	0.12	0.05	0.34	0.25	0.10	0.12	0.05
Cr <sub>2</sub> O <sub>3</sub>	0.07	0.18	0.06	0.03	0.18	0.01	0.11	0.02	0.19	0.02	0.38
Σ	96.19	95.64	96.09	95.97	96.80	96.69	96.19	96.97	95.61	96.68	95.16

Note: *l, m* distance from the intrusive contact; *L, m* distance from the center of the intrusion

and mineral assemblages. Second, it displays a clear trend of increasing TiO<sub>2</sub> content with increasing metamorphic temperature (e.g. *Miyashiro, 1958*). Since the study rocks include the Ti-bearing phases (ilmenite and titanomagnetite), the degree of isomorphism naturally increases with increasing metamorphic grade as a result of metamorphic reactions. An abrupt change in TiO<sub>2</sub> content (from 2.32 to 3.38 wt.%) coincides with the andalusite-in isograd of the middle zone of the contact aureole. All these data confirm that biotite took part in practically all local metamorphic reactions in the contact aureole and can be used in evaluating the rate of metamorphic reactions in which biotite participated directly.

### **Inverse modeling approach for obtaining kinetic parameters: mathematical model and computational results**

We modeled contact metamorphism by two concurrent processes. The first process was cooling and solidification of an igneous body due to heat conductivity, which necessarily involves a substantial temperature change in the surrounding rocks. This temperature change causes the second process which is alteration of the surrounding rock. The rock responds to heat with redistribution of chemical components among the mineral phases (assuming a closed system). If the rate of these changes is high enough, the new component distribution achieves an equilibrium state at a new temperature. Otherwise, the distribution is frozen in a non-equilibrium state or the rocks remain unaltered.

Metamorphic zoning is typically observed around an intrusion. Zoning of this kind implies relatively gradual changes within zones and abrupt transitions between them. Since metamorphism is a set of chemical reactions, one may expect reaction rates to depend on temperature exponentially. This relation implies that under the wide range of temperature conditions, metamorphic changes near an igneous contact should be step-like (e.g. *Reverdatto and Melenevsky, 1983; Clayton and Bostick, 1985*). As shown in Fig. 1, a compositional profile has two comparatively homogeneous zones with a narrow transition zone between them.

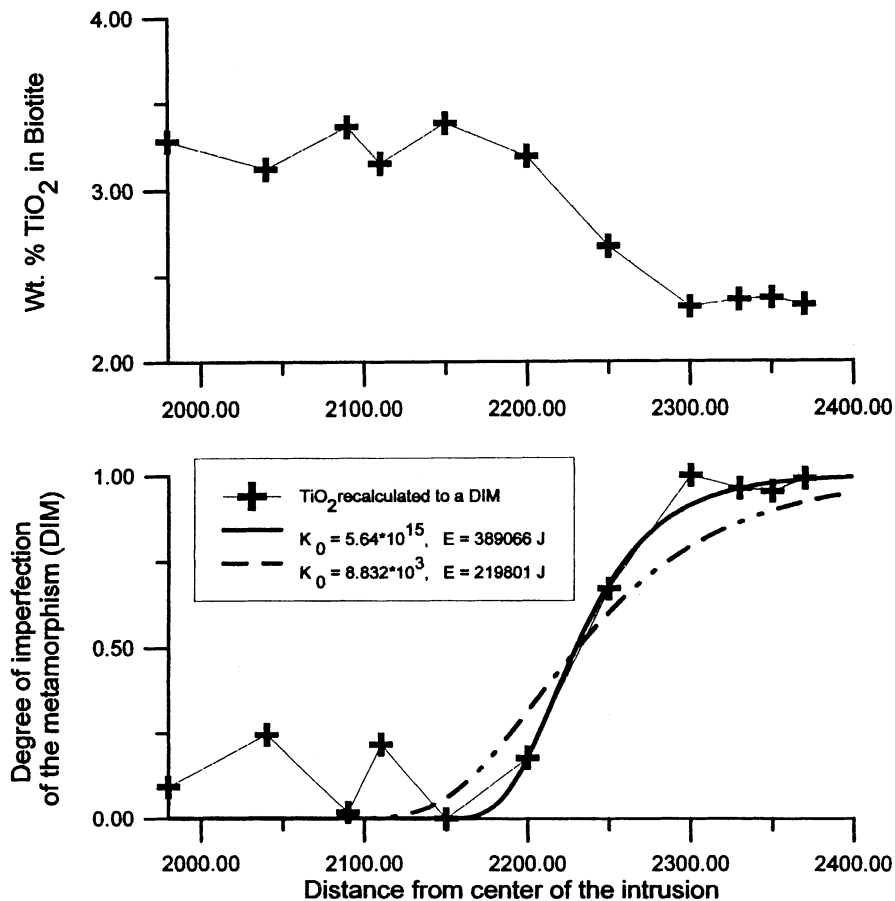


Fig. 1. Profile of TiO<sub>2</sub> content in biotite and model profiles. *Upper panel:* wt. % TiO<sub>2</sub> versus distance from center of intrusion. *Lower panel:* recalculated TiO<sub>2</sub> content result in the observed DIM profile. Two model calculations show good agreement with observed DIM

Step-like behavior is supported by another observation. Within a definite metamorphic zone, a mineral assemblage was stable. This fact implies that compositional variation in a particular mineral occurs mainly due to temperature variation across the zone. However, in an adjoining zone (with higher or lower temperatures) some reactions stop due to extremely low reaction rates, while others proceed due to a shift in chemical equilibrium. The combination of different temperatures and the shift in chemical equilibrium results in a different mineral assemblage (metamorphic zone). The shift of chemical equilibrium across the transition zone has a much more powerful effect on mineral compositions than that due to temperature variation within the zone (Ferry, 1983).

To represent metamorphic changes quantitatively, we need to introduce a formal criterion to characterize a metamorphic process. The extent ( $\xi$ ) of chemical changes during metamorphism at a given moment may be described in dimensionless, normalized form,  $d\xi$  – called *degree of advancement of reaction* (Prigogine, 1961;

*Helgeson*, 1968) or reaction progress variable (*Fitts*, 1962), which, for a mineral, may be defined as:

$$d\xi = \frac{\text{current quantity of a component}}{\text{quantity of a component at equilibrium}}$$

To avoid misunderstanding, we emphasize that *Ferry's* (1983) notion of reaction progress variable (or degree of advancement of reaction) is different from that defined above. The degree of advancement of reaction is a reasonable formal parameter for describing the dynamics of a metamorphic system. For the purposes of this paper, however, we used an inverse criterion:

$$y = 1 - d\xi,$$

where  $y$  is the degree of incompleteness (or imperfection) of reaction (DIM). The degree of incompleteness of reaction may also be interpreted as concentration (e.g. *Lasaga* and *Rye*, 1993; *Bolton et al.*, 1999).

This dimensionless parameter is equal to 1 for unaltered rock (before the intrusion) and equal to 0 for rock that has reached its equilibrium state for the PT-conditions of the contact metamorphism. The rock changes that are identified as metamorphism may be converted to DIM.

For example, a content of  $\text{TiO}_2$  in biotite may be measured at different distances from the center of the intrusion. The upper panel of Fig. 1 shows  $\text{TiO}_2$  variations versus distance from the center of the intrusion. A sharp drop between two relatively steady intervals is observed. A respectively uniform percentage of  $\text{TiO}_2$  at distances between 1980 and 2160 meters suggests that changes in biotite due to temperature reached the metamorphic equilibrium state ( $y = 0$ ), whereas at distances beyond 2300 meters  $\text{TiO}_2$  is uniform ( $y = 1$ ). After smoothing and scale attribution, this data could express DIM (lower panel of Fig. 1). The same method may be applied to any mineral. Less formal observations may also be quantified with this method. For instance, changes in modes or rock volumes which a rock undergoes could be plotted against metamorphic temperature or against distance in the field perpendicular to isograds.

Considering the form of the observed component profiles and the chemical nature of the metamorphism, we may reasonably assume that  $y$  is governed by the first order kinetic equation:

$$\frac{dy}{dt} = -y \cdot k_0 \cdot \exp\left(\frac{-E}{RT(x, t)}\right), \quad (1)$$

where  $E$  is activation energy,  $R$  the universal gas constant,  $k_0$  pre-exponential coefficient,  $T$  temperature,  $t$  time and  $x$  distance. This approach has been applied for mineral zoning (e.g. *Lasaga*, 1983; *Wilson* and *Smith*, 1985) and thermal alteration of organic-rich rocks (e.g. *Reverdatto* and *Melenevsky*, 1983).

Metamorphism is a set of complex chemical reactions coupled with no less complex transport processes, such as diffusion associated with thermal convection in porous media (*Skelton et al.*, 1997; *Ashworth et al.*, 1998, *Balashov* and *Yardley*, 1998, *Bolton et al.*, 1999). It is impossible to consider such a process in all its details. However, equation 1 should reflect the *cumulative dynamics* of the contact changes, including influence exchange reactions, porosity, grain size and all other



processes affecting metamorphism. Here we take the dynamics of metamorphism as an overall process of rock change, without decomposing it into its components. For example,  $\text{TiO}_2$  content is a result of the interaction of all agents acting during the metamorphism.

At the initial stage ( $t = 0$ ), the DIM ( $y$ ) equals 1, signifying unaltered rocks. The solution of differential equation (1) depends on the activation energy  $E$ , pre-exponential coefficient  $k_0$  and temperature. For a given geometry of the intrusion, the temperature evolution may be reliably calculated (Likhanov and Ten, 1994; Likhanov et al., 1996).

The temperature evolution is described by the heat balance equation:

$$\frac{\partial T}{\partial t} = \frac{1}{C_p} \text{div}(\chi \text{grad}(T)) \quad (2)$$

where  $T$  is temperature,  $t$  time,  $C_p$  effective heat capacity and  $\chi$  thermal conductivity. Since the intrusion is cylindrical, equation 2 may be rewritten as (e.g. Carslaw and Jaeger, 1959):

$$\frac{\partial T}{\partial t} = \frac{1}{rC_p} \frac{\partial}{\partial x} \left( r\chi \frac{\partial T}{\partial r} \right) \quad (3)$$

In this case  $r$  denotes distance from the center of the intrusion. In the dimensionless form,  $x = 1$  corresponds to the boundary of the intrusion. The furthest  $x$  of the calculation domain equals 10.  $C_p$  is the latent heat of crystallization (Jaeger, 1968):

$$C_p = \begin{cases} C_p^{add}, & T \notin [T_{solidus}, T_{liquidus}] \\ C_p^{add} + \frac{Q}{(T_{liquidus} - T_{solidus})}, & T \in [T_{solidus}, T_{liquidus}] \end{cases} \quad (4)$$

where  $C_p^{add}$  is the heat capacity and  $Q$  the crystallization heat. The thermal conductivity of the country rock is assumed to be constant; that of the intrusion depends on the state of matter:

$$\chi = \begin{cases} \chi_{liquidus}, & T \geq T_{liquidus} \\ \chi_{liquidus} \frac{T - T_{solidus}}{T_{liquidus} - T_{solidus}} + \chi_{solidus} \frac{T_{liquidus} - T}{T_{liquidus} - T_{solidus}}, & T \in (T_{solidus}, T_{liquidus}) \\ \chi_{solidus}, & T \leq T_{solidus} \end{cases} \quad (5)$$

This function describes a linear transition of thermal conductivity between solid and melt. We used a reflecting (symmetric) boundary condition in the center of the intrusion ( $x = 0$ ) and fixed temperature at the furthest end:

$$\begin{aligned} \frac{\partial T}{\partial r} \Big|_{r=0} &= 0, \\ T \Big|_{r=10} &= T_{background} \end{aligned} \quad (6)$$

At the initial moment ( $t = 0$ ) the temperature is equal to  $T_{intrusion}$  in the intrusion and  $T_{background}$  in the surrounding rocks.

Equations (1,3–6) describe a direct approach. The values of the parameters used in our model are shown in Table 2. We used a finite-difference approximation

Table 2. *Parameter descriptions and values*

Parameter	Description	Value	Units
$C_p^{add}$	Additive heat capacity	$2.52 \times 10^6$	$\text{J m}^{-3} \text{K}$
$Q$	Crystallization heat	$1.05 \times 10^9$	$\text{J m}^{-3}$
$\chi_{liquidus}$	Thermal conductivity of melt	1	$\text{J m}^{-3} \text{sec}^{-1}$
$\chi_{solidus}$	Thermal conductivity of solid	2.03	$\text{J m}^{-3} \text{sec}^{-1}$
$\chi_{country}$	Thermal conductivity of country rock	2.27	$\text{J m}^{-3} \text{sec}^{-1}$
$T_{intrusion}$	Initial temperature of intrusion	1473(1200)	$\text{K}(\text{C}^\circ)$
$T_{liquidus}$	Solidification temperature	1373(1100)	$\text{K}(\text{C}^\circ)$
$T_{solidus}$	Melting temperature	1323(950)	$\text{K}(\text{C}^\circ)$
$T_{background}$	Temperature of country rock before intrusion	353(80)	$\text{K}(\text{C}^\circ)$

to solve these equations. The heat balance equation was solved by the second order Crank-Nicolson method and equation 4 by the 4<sup>th</sup> order Runge-Kutta method. If all parameters were known, we could calculate the changes in rock composition in relation to distance. However, the kinetic parameters  $E$  and  $k_0$  are unknown, but we have the observed compositional profile expressed as DIM ( $y_{observed}$ ). The kinetic parameters should therefore be written in such a way that the difference between observed DIM and calculated DIM is minimum. To find a least-square minimum of  $|y_{observed} - y_{model}|$  we used the Nelder-Mead method (*Nelder and Mead, 1965*).

Figure 2 shows the calculated temperature dynamics for the cylindrical intrusion ( $R = 1950 \text{ m}$ ) for the parameters shown in Table 2. As shown in Fig. 2, relatively high temperatures persisted in the contact zone for about 150,000 years ( $\sim 5 \times 10^{12} \text{ sec}$ ). Writing equation 1 as follows:

$$\frac{dy}{dt} = \tilde{k}y,$$

where  $\tilde{k}$  is an effective reaction rate, we obtain the effective rate:

$$\tilde{k} \sim \frac{1}{t} = \frac{1}{5 \times 10^{12}} = 2 \times 10^{-13} \text{ sec}^{-1}.$$

This means that if metamorphic changes occurred in this time span, these changes should have a rate of about  $2 \times 10^{-13} \text{ sec}^{-1}$ . If the rate is much lower, metamorphic changes will be negligible, whereas too fast a rate will result in an implausibly large zone of contact metamorphism. Small dykes and regional metamorphism are end-member examples of relatively slow and fast processes, respectively.

For known temperature dynamics, we have minimized the difference between the model and observed DIMs. The wt. % of  $\text{TiO}_2$  in biotite was used as observed DIM (Fig. 1). The lower panel of Fig. 1 shows observed DIM and two model DIMs. As shown in the graph, both model DIMs with quite different  $E$  and  $k_0$  give a good approximation of the observed  $\text{TiO}_2$  profile. Errors in measuring  $\text{TiO}_2$  and the definitions of the model exceed the difference between the model DIMs. We therefore cannot prefer any curve in the error interval, although some of them seem to fit the observed data better. In spite of significant differences in the parameters, both model curves approximate the observation equally well. Although we only plotted two graphs on the figure, there is a continuous area in  $E$ - $k_0$  space, which

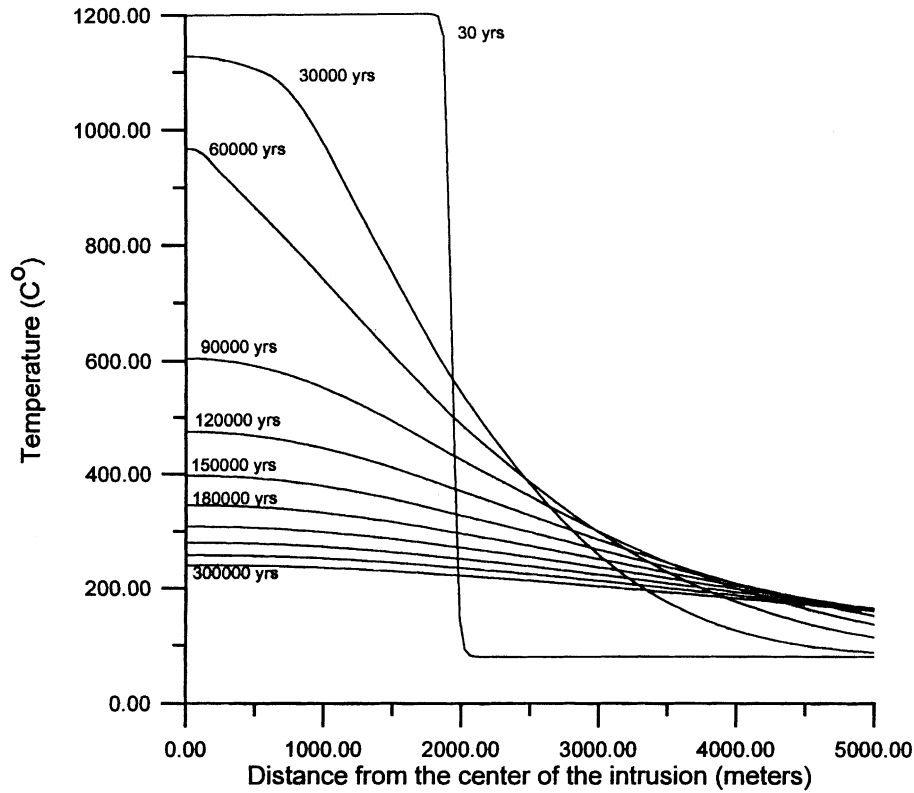


Fig. 2. Temperature dynamics of a cylindrical intrusion. The radius of the intrusion is 1950 meters. The model includes crystallization heat and a change in thermal conductivity due to a phase transition

gives a very good approximation of the observed DIM. Mathematically, therefore, the problem does not have a unique solution with this particular set of observed data.

However, the mean value theorem (e.g. *Bronshstein and Semendyayev, 1979*) allows us to extract an effective reaction rate. Adapted to our case, the mean value theorem would be reformulated as: for given distance from the intrusion contact, there is a mean value of temperature ( $T^*$ ) such that:

$$k_0 \cdot \exp\left(\frac{-E}{RT(t)}\right) = k_0 \cdot \exp\left(\frac{-E}{RT^*}\right)$$

Thus, the effective rate may be defined:

$$k_{eff} = k_0 \cdot \exp\left(\frac{-E}{RT^*}\right)$$

The effective rate is the main factor responsible for the position of steep change in a composition profile (Fig. 2). Different combinations of  $E$  and  $k_0$  affect the slope and curvatures of that change. As a result, we may reasonably assume that the effective rate is approximately the same for all our calculations (Fig. 2). This

assumption enable us to write an equation for the mean temperature using two sets of  $E$  and  $k_0$ .

$$k'_0 \cdot \exp\left(\frac{-E'}{RT^*}\right) = k''_0 \cdot \exp\left(\frac{-E''}{RT^*}\right).$$

The mean temperature is slightly lower than the maximum temperature. For example, where the strongest changes in TiO<sub>2</sub> occur, the calculated mean temperature is about 470 °C. At this temperature, all combinations of  $E$  and  $k_0$ , in good approximation with the observed DIM, are located along the line:

$$k_0 \cdot \exp\left(\frac{-E}{RT^*}\right) = 10^{-12}.$$

The effective rate of the metamorphism in the aureole of the Kharlovo massif turns out to be about  $10^{-12} \text{ sec}^{-1}$  for metamorphic reactions involving biotite.

The rate obtained enables an *in situ* effective diffusion coefficient to be estimated. Like the effective metamorphic rate, the effective diffusion coefficient is not a material property. It reflects how fast the reacting components were transferred from one location to another and is a cumulative reflection of actual transport mechanisms. For instance, in nature, transport in non-equilibrium, porous media is highly complex (e.g. Bolton et al., 1999) and may be described mathematically with many simplifying assumptions in a few cases. However, for dynamics, how fast a substance is transferred, is of a greater importance than by which mechanism. This «speed» may be formalized as the effective diffusion coefficient, since transport of components is governed by a diffusion-like equation.

The effective diffusion coefficient may be calculated using the scales of the material transport involved in metamorphic reactions, and the effective rate of metamorphism. As previously evaluated by mass-balance calculations, mass transfer of major components for the biotite-forming reaction was limited to very small volumes (microsites) of the order of  $0.01 \text{ mm}^3$ . Such scales of mass transfer indicate that diffusion is main limiting factor for mass exchange during contact metamorphism (Balashov VN, personal communication). A characteristic distance of mass transfer in the metamorphic reaction may therefore be estimated at 0.23 mm. This is the distance the components were transported during diffusion-controlled metamorphic reactions (scale of mass transfer). In our case, it is the radius of a sphere with  $0.01 \text{ mm}^3$  volume. In order to provide transport of components from this distance and to maintain the reaction rate, the effective diffusion coefficient may be estimated as  $5.29 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ .

## Discussion and conclusions

As regards the effective rate of overall reaction calculated by inverse modeling, the estimates obtained can hardly be compared with those available in the literature due to a strong dependence on a kinetic model. In these models, the rates of metamorphic reactions are usually considered under conditions of close contact between all reactants and products. In practice, transport of reacting minerals may be slower than the overall reaction rate, making it necessary to consider the constraints imposed by transport on the metamorphic process, an argument beyond

the scope of our study. For example, understanding of the rates of material transport during reactions requires knowing the velocities of grain boundary film flow and the thicknesses of grain boundary films involved in specific metamorphic processes. Nevertheless, the calculated estimates are in value interval between the approximate rates of contact metamorphism obtained using a simple heating model (*Walther and Wood, 1984*) and the maximum average rate of regional metamorphism computed by *Walther and Orville (1982)* in the relevant temperature range.

As regards the effective diffusion coefficient, this value may be compared with recent experimental results, on diffusion through bulk mineral grains and grain-boundary diffusion in or near the relevant temperature range. This value is somewhat lower than the estimates of the diffusion coefficients for components in solid phases obtained by experimental data for the respective PT-parameters (*Balashov, 1995*) and are quite close to experimentally-derived grain-boundary diffusion coefficients in mineral aggregates (*Farver and Yund, 1995, 1996*). Although the effective diffusion coefficient is less precisely estimated in our models, partly due to uncertainty in the time scale of the reaction, it is a good indication that the results compare well with experimental data and are consistent with solid-state diffusion, especially through grain boundaries. It is also in a good agreement with grain-boundary diffusion, which may enhance the effective diffusion coefficients over those in bulk grains (*Joesten, 1991*). The values obtained fall well within the interval of effective diffusion coefficients estimated using the diffusion metasomatism model for metamorphic nodules and coronary micro-textures (*Joesten and Fisher, 1998; Ashworth et al., 1998*).

Thus, in terms of the overall process, our study seems to be adequate and will certainly facilitate the choice of specific isograds for further study. Theoretically, the method described in the paper can be used to determine the relationship between time, temperature and mineral composition changes for a wide range of contact metamorphic reactions. The approach is, perhaps, a unique tool for the determination of the kinetic parameters of metamorphism, and could be utilized for a better understanding of the processes occurring in texture-homogeneous rocks, in which chemical reactions often reach completion, making it impossible to establish the ratio between reactant and product minerals.

### Acknowledgements

We would like to thank *T. Rivers, D. Pattison* and *D. Lentz* for organizing an excellent Special Session in Metamorphic Petrology in honour of *R. Kretz* in Ottawa, in May 1997, where these results were presented by the first author. The paper has benefited from comments by *V. N. Balashov, V. S. Sheplev,* and *V. V. Khlestov*. The paper was considerably improved following constructive reviews by *R. Abart* and an anonymous reviewer. Financial support was provided by the Russian Foundation for Basic Research (grant 00-05-65386) to IIL, Department of Energy (grant DOE) to AAT.

### References

- Ashworth JR (1986)* The role of magmatic reaction, diffusion and annealing in the evolution of coronitic microstructure in troctolitic gabbro from Risor, Norway: a discussion. *Mineral Mag* 50: 469–473

- Ashworth JR, Sheplev VS (1997) Diffusion modelling of metamorphic layered coronas with stability criterion and consideration of affinity. *Geochim Cosmochim Acta* 61: 3671–3689
- Ashworth JR, Sheplev VS, Bryxina NA, Kolobov Vyu, Reverdatto VV (1998) Diffusion-controlled corona reaction and overstepping of equilibrium in a garnet granulite, Yenisey Ridge, Siberia. *J Metamorph Geol* 16(2): 231–246
- Atherton MP (1980) The occurrence and implications of chloritoid in a contact aureole andalusite schist from Ardara, County Donegal. *J Earth Sci R Dubl Soc* 3: 101–109
- Balashov VN (1995) Diffusion of electrolytes in hydrothermal systems: free solution and porous media. In: *Shmulovich KI, Yardley BWD, Gonchar GG* (eds) *Fluids in the crust: equilibrium and transport properties*. Chapman & Hall, London, pp 215–251
- Balashov VN, Yardley BWD (1998) Modeling metamorphic fluid flow with reaction-compaction-permeability feedbacks. *Am J Sci* 298(6): 441–470
- Bolton EW, Lasaga AC, Rye DM (1999) Long-term flow/chemistry feedback in a porous medium with heterogeneous permeability: kinetic control of dissolution and precipitation. *Am J Sci* 299: 1–68
- Bronshtein IN, Semendyayev KA (1979) *Handbook of mathematics*. Verlag Harri Deutsch, 973 pp
- Carlson WD, Johnson CD (1991) Coronal reaction textures in garnet amphibolites of the Llano Uplift. *Am Mineral* 76: 756–772
- Carmichael DM (1969) On the mechanisms of prograde metamorphic reactions in quartz-bearing pelitic rocks. *Contrib Mineral Petrol* 20: 244–267
- Carlsaw HS, Jaeger JC (1959) *Conduction of heat in solids*. Oxford Press, Oxford, p 510
- Clayton JL, Bostick NH (1986) Temperature effects on kerogen and on molecular and isotopic composition of organic matter in Pierre Shale near an igneous dike. *Org Geochem* 10: 135–143
- Eugster HP (1970) Thermal and ionic equilibria among muscovite, K-feldspar and aluminosilicate assemblages. *Fortschr Mineral* 47: 106–123
- Farver JR, Yund RA (1995) Grain boundary diffusion of oxygen, potassium and calcium in natural and hot-pressed feldspar aggregates. *Contrib Mineral Petrol* 118: 340–355
- Farver JR, Yund RA (1996) Volume and grain boundary diffusion of calcium in natural and hot-pressed aggregates. *Contrib Mineral Petrol* 123: 77–91
- Ferry JM (1983) Applications of the reaction progress variable in metamorphic petrology. *J Petrol* 24: 343–376
- Ferry JM (1984) A biotite isograd in south-central Maine, USA: mineral reactions, fluid transfer. *J Petrol* 25: 871–893
- Fisher GW (1970) The application of ionic equilibria to metamorphic differentiation: an example. *Contrib Mineral Petrol* 29: 91–103
- Fitts DD (1962) Nonequilibrium thermodynamics: a phenomenological theory of irreversible processes in fluid systems. McGraw-Hill, New York, p 173
- Foster CT Jr (1977) Mass transfer in sillimanite-bearing pelitic schists near Rangeley, Maine. *Am Mineral* 62: 727–746
- Foster CT Jr (1981) A thermodynamic model of mineral segregations in the lower sillimanite zone near Rangeley, Maine. *Am Mineral* 66: 260–277
- Helgeson HC (1968) Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions I. Thermodynamic relations. *Geochim Cosmochim Acta* 32: 853–877
- Jaeger JC (1968) Cooling and solidification of igneous rocks. In: *Hess HH, Poldervaart A* (eds) *Basalts. The Poldervaart treatise on rocks of basaltic composition*. Interscience Publisher, New York London Sidney, pp 503–536

- Joesten R* (1974) Local equilibrium and metasomatic growth of calc-silicate nodules from a contact aureole, Christmas Mountains, Big Bend region, Texas. *Am J Sci* 274: 876–901
- Joesten R* (1977) Evolution of mineral assemblage zoning in diffusion metasomatism. *Geochim Cosmochim Acta* 41: 649–670
- Joesten R* (1991) Grain-boundary diffusion kinetics in silicate and oxide minerals. In: *Ganguly J* (ed) *Diffusion, atomic ordering and mass transport*. Springer, New York, pp 345–395
- Joesten R, Fisher G* (1988) Kinetics of diffusion-controlled mineral growth in the Christmas Mountains (Texas) contact aureole. *Geol Soc Am Bull* 100: 714–732
- Lasaga AC* (1983) Geospeedometry: an extension of geothermometry In: *Saxena SK* (ed) *Kinetics and equilibrium in mineral reactions*. Advances in physical geochemistry. Springer, New York, pp 81–114
- Lasaga AC* (1986) Metamorphic reaction rate laws and development of isograds. *Mineral Mag* 50: 359–373
- Lasaga AC, Rye DM* (1993) Fluid flow and chemical reaction kinetics in metamorphic systems. *Am J Sci* 293: 361–404
- Likhanov II* (1989) Low-grade biotite isograd within the contact aureole of Kharlovo gabbro massif. *Soviet Geol Geophys* 30: 40–48
- Likhanov II* (1990) Epidote consuming reaction at low-temperature contact metamorphism of metapelites (in Russian). *Zap Vses Mineral Obschest* 119: 40–48
- Likhanov II, Ten AA* (1994) Use of contact metamorphism temperatures to determine whether traprock sills were intruded concurrently or at different times. *Dokl Acad Sci USSR: Earth Science Sections* 322(1): 117–121
- Likhanov II, Reverdatto VV, Memmi I* (1994) Short-range mobilization of elements in the biotite zone of contact aureole of the Kharlovo gabbro intrusion (Russia). *Eur J Mineral* 6: 133–144
- Likhanov II, Reverdatto VV, Memmi I* (1995) The origin of arfvedsonite in metabasites from the contact aureole of the Kharlovo gabbro intrusion (Russia). *Eur J Mineral* 7: 379–389
- Likhanov II, Ten AA, Reverdatto VV, Solotchina EP* (1996) Low-grade metamorphism of clays at the contacts with andesite necks in Turkmenia (in Russian). *Dokl Akad Nauk* 346: 91–94
- Likhanov II, Reverdatto VV, Memmi I* (1997) Mineral reaction mechanisms and kinetics in the matrix during metamorphism. Annual Joint Meeting of the VSG and MinSoc of Great Britain, Cambridge, UK, January 6–9, 1997. *J Conf Abstr* 2(1): 49
- Likhanov II, Ten AA, Reverdatto VV, Ananiev VA, Memmi I* (1999) Kinetics of diffusion-controlled mineral reactions in the matrix in the Kharlovo (South Siberia, Russia) contact aureole. Research report of University of Minnesota and Supercomputer Institute, pp 1–42
- Menard T, Spear FS* (1996) Interpretation of plagioclase zonation in calcic pelitic schists, south Strafford, Vermont, and the effects on thermobarometry. *Can Mineral* 34: 133–146
- Miyashiro A* (1958) Regional metamorphism of the Gosaisyo-Takanuki district in the Central Abakuma Plateau. *J Fac Sci Univ Tokyo* 11: 211–229
- Nelder JA, Mead R* (1965) A simplex method for function minimisation. *Computer J* 7: 308–313
- Prigogine I* (1961) *Introduction to thermodynamics of irreversible processes*, 2<sup>nd</sup> ed. Interscience, New York, p 119
- Reverdatto VV, Melenevskij VN* (1983) Magmatic heat as a factor of hydrocarbon generation; the case of the basaltic sills (in Russian). *Geologiya i Geofizika* 6: 15–24

- Reverdatto VV, Sharapov VN, Lavrent'ev YuG, Pokachalova OS* (1974) Investigation in isochemical contact metamorphism. *Contrib Mineral Petrol* 48: 287–299
- Reverdatto VV, Anoshin GN, Vasilenko VB* (1978) Behavior of U, Th, Au, Fe and P at contact metamorphism of metapelites (in Russian). *Dokl Acad Nauk* 260: 426–429
- Rice JM, Ferry JM* (1982) Buffering, infiltration, and the control of intensive variables during metamorphism. In: *Ferry JM* (ed) *Characterization of metamorphism through mineral equilibria*. Mineralogical Society of America, pp 263–326
- Rubie DC, Thompson AB* (1985) Kinetics of metamorphic reactions at elevated temperatures and pressures: an appraisal of available experimental data. In: *Thompson AB, Rubie DC* (eds) *Advances in physical geochemistry. Kinetics, textures and deformation*. Springer, Berlin Heidelberg New York Tokyo, pp 27–49
- Sanford RF* (1980) Textures and mechanisms of metamorphic reactions in the Cockeysville marble near Texas, Maryland. *Am Mineral* 65: 654–669
- Skelton ADL, Bickle MJ, Graham CM* (1997) Fluid-flux and reaction rate from advective-diffusive coronation of mafic sill margins in the Dalradian, southwest Scottish Highlands. *Earth Planet Sci Lett* 146: 527–539
- Vidale R* (1969) Metasomatism in a chemical gradient and formation of calc-silicate bands. *Am J Sci* 267: 857–887
- Walther JW* (1983) Description and interpretation of metasomatic phase relations at high pressures and temperatures. 2. Metasomatic reactions between quartz and dolomite at Campolungo, Switzerland. *Am J Sci* 283-A: 459–485
- Walther JW, Orville PM* (1982) Rates of metamorphism and volatile production and transport in regional metamorphism. *Contrib Mineral Petrol* 79: 252–257
- Walther JW, Wood BJ* (1984) Rate and mechanism in prograde metamorphism. *Contrib Mineral Petrol* 88: 246–259
- Wilson CR, Smith D* (1985) A numerical study of mineral zoning formed during the cooling of finite volume grains. *J Geophys Res* 90 (B12): 10351–10358
- Yardley BWD* (1977) The nature and significance of the mechanism of sillimanite growth in the Connemara schists, Ireland. *Contrib Mineral Petrol* 65: 53–58
- Yardley BWD* (1989) *An introduction to metamorphic petrology*. Longmans, Harlow, p 248

Authors' addresses: *I. I. Likhanov, V. V. Reverdatto, V. A. Ananiev*, Institute of Mineralogy and Petrography, Koptyug Ave. 3, Novosibirsk, 630090, Russia; *A. A. Ten*, Department of Geology and Geophysics and Supercomputer Institute, University of Minnesota, 1200 Washington Avenue, South Minneapolis, MN 55415-1227, USA; *I. Memmi*, Dipartimento di Scienze della Terra, Università di Siena, Via Laterina 8, I-53100, Siena, Italy