ISSN 1028-334X, Doklady Earth Sciences, 2019, Vol. 488, Part 2, pp. 1173–1177. © Pleiades Publishing, Ltd., 2019.
Russian Text © The Author(s), 2019, published in Doklady Akademii Nauk, 2019, Vol. 488, No. 4.

GEOCHEMISTRY

Inverse Modeling for Evaluation of the Kinetic Parameters of Metamorphic Reactions in Texture-Homogenous Rocks

I. I. Likhanov*

Presented by Academician V.V. Reverdatto July 8, 2018

Received September 17, 2018

Abstract—To obtain the kinetic parameters of diffusion-controlled mineral reactions in texture-homogenous rocks, a new approach is proposed. The method is based on comparison of the modeling concepts of the thermal field evolution to the observed variations in the chemical composition of minerals within the contact aureole of the Kharlovo gabbro massif. The effective rate of mineral reactions involving biotite ($\sim 10^{-12}$ s^{-1}) and the effective coefficient of diffusion (5.29×10^{-16} cm^2/s at $T = 475$°C) are determined. The results of theoretical modeling are in agreement with the data on the rates of reactions of contact metamorphism, as well as with the empirical estimates of the coefficients of diffusion at grain boundaries in mineral aggregates and segregations under the corresponding *PT* parameters.

DOI: 10.1134/S1028334X19100064

Mineral transformations occurring under metamorphism are controlled by the following kinetic stages: the dissolution of the grains of early minerals, diffusion mass transfer within the interglanular volume, and the generation of new phases [1]. Evaluation of the mass transfer parameters is a complicated problem linked to experimental studies [2]. As applied to metamorphic reactions, the experiments were few in number because of great technical difficulties; hence, the modeling approaches were developed to study the kinetic features of mineral transformation. The occurrence of relic phases and reaction products in zonal reactive microtextures (symplektites, kelyphytes, coronites, etc.) allow one to reconstruct quantitatively the processes of metamorphism using the tools of nonequilibrium thermodynamics [3]. The application of this approach to the characterization of mass transfer parameters in fine-grained texture-homogeneous rocks becomes complicated since often no relics of the initial phases are found owing to the completion of mineral reactions. In this case, the reactions might be characterized exclusively on the basis of the change of mutually exclusive paragenesises before and after certain isograds [4]. Some of the generalized characteristics of mass transfer were obtained by solving the dynamics problems of the known time and *PT* parameters based on the geological surveys of the textures and structures of the rocks, as well as of the zonality in rocks and minerals [1, 2].

Despite the progress in obtaining the quantitative characteristics of mass transfer using the available modeling approaches, some of the problems in mineral transformations within texture-homogenous rocks are still unresolved and require further study. In view of this, an attempt was made to develop a new procedure to determine the kinetic parameters of mass transfer in texture-homogenous rocks and to compare the results of computer simulation and the data of experiments on the kinetics of solid-phase transformations.

This approach is based on comparison of the modeling concepts of the evolution of temperature to the observed changes in the chemical composition of minerals in the rocks. The contact aureole is from the Kharlovo massif in the northwestern foothills of the Altai Mountains (Fig. 1) [5]. The massif of stocklike "cylindrical" shape of ~1950 m radius is mainly constituted of Middle Paleozoic gabbro. The rocks enclosing the massif are represented by sandy–schist Cambrian deposits of the Altai series metamorphosed under the conditions of a facies of green schists. The hornfels aureole registered by the biotite isograd is as wide as 1.2 km. The degree of metamorphism increases from the enclosing ricks to the intrusive contact, and the following changes in the mineral paragenesises are seen:

Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia
**e-mail: likh@igm.nsc.ru*

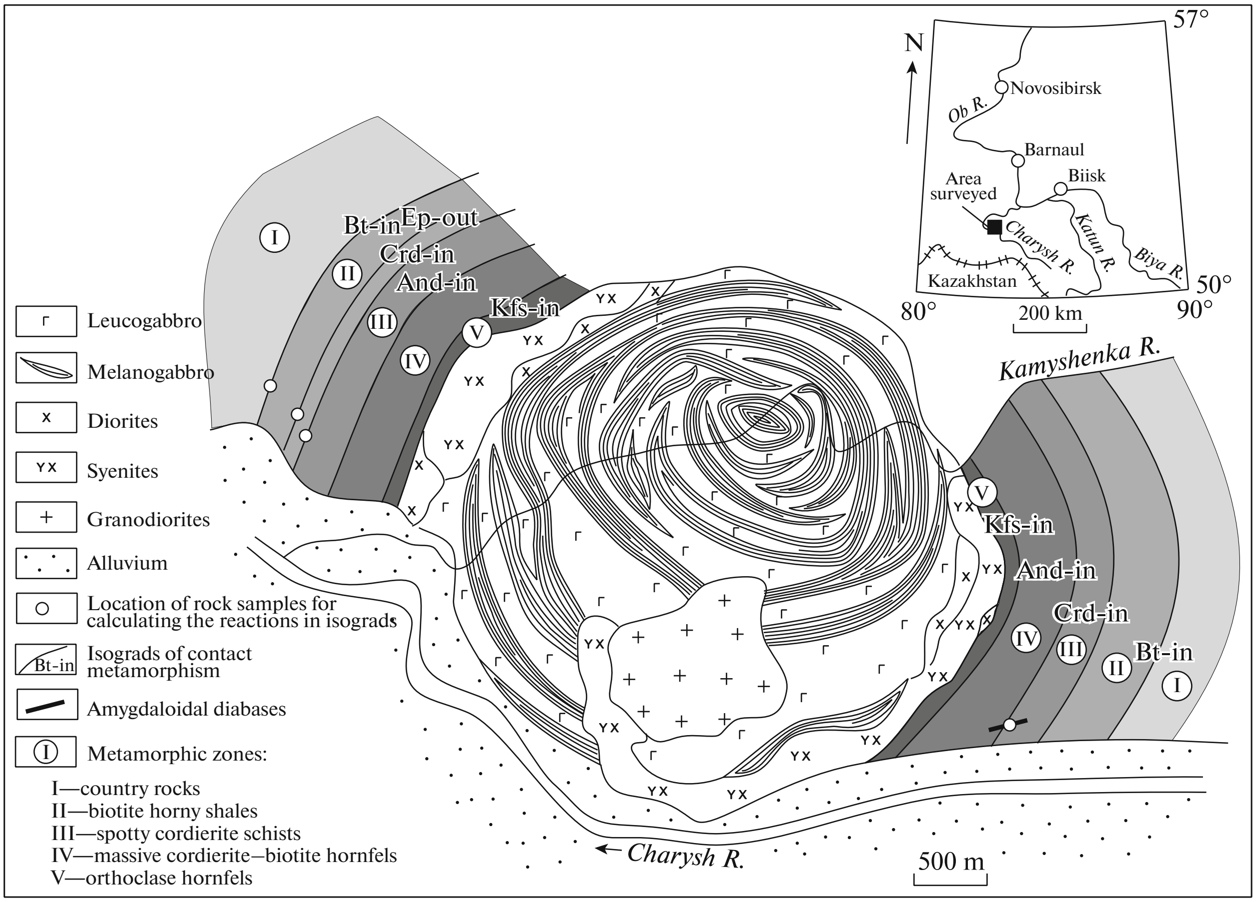

Fig. 1. Kharlovo gabbro massif and fragments of the western and eastern parts of the contact aureole.

(I) Chl + Ms + Pl + Qtz + Ilm + Ep + Mgt (enclosing rocks);

(II) Bt + Chl + Ms + Pl + Qtz + Mgt ± Ep (biotite schists);

(III) Crd + Bt + Ms + Pl + Qtz + Mgt (“spotted” cordierite hornfels);

(IV) Crd + Bt + Pl + Qtz + And ± Mgt (massive cordierite–biotite hornfels);

(V) Crd + Bt + Pl + Kfs ± And ± Qtz ± Mgt (orthoclase hornfels);

(VI) Crd + Bt + Pl + Kfs + Sil + Spl ± Mgt (quartz-free separations) (Fig. 1).

According to geothermobarometry, the temperature of regional metamorphism amounted to 250–380°C; the contact metamorphism occurred within a wide range of temperatures (400–600°C) at $P = 0.5$–1 kbar [6].

Modeling concepts were based upon the hypothesis of the exponential temperature dependence of the rate of metamorphic transformations. To accomplish this, the mineral reactions with biotite were selected for biotite occurring in all the zones of the contact aureole and the increase in TiO_2 content correlated well with the distance to the intrusive contact (Fig. 2a) and, respectively, with the growth in temperature [4]. After the transformations and appropriate scaling, the concentration profile of TiO_2 content in biotite was converted into the degree of incompleteness of the reaction (RID; Fig. 2b). This dimensionless parameter may be treated as the concentration [7] and amounts to 1 for nontransformed rocks (preintrusive stage) and to zero for rocks in the equilibrium state at the P–T parameters of thermal metamorphism. In view of the configuration of the profile observed (Fig. 2b) and the temperature dependence of the reaction rate, it was assumed that the dynamics of biotite formation conformed to a first-order reaction:

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

where E is the activation energy, R is the gas constant, T is absolute temperature, k_0 is frequency factor, t is time, and r is distance. This approach is applied to the description of zonality in minerals [7].

The thermal evolution around a magma body of cylindrical shape was obtained by solving the system of differential equations for conductive heat transfer including the heat conductivity and latent heat of crystallization. Analytical expressions for drawing the evolution of a thermal field are presented in [8, 9].

To solve the equation of thermal balance, the Crank–Nicolson finite difference method was used. The values of parameters applied in developing the model are shown in Table 1. Figure 3a presents the thermal profiles for various times for a cylindrical intrusive body of 1950 m radius testifying to relatively high temperatures in the contact zone over 150 000 years.

The kinetic parameters of metamorphic reactions (E and k_0) were determined on the basis of the thermal characteristics of the rocks, the geometry of the intrusive body, and the converted profile of the alteration of biotite composition expressed as the degree of incompleteness of the reaction. The problem was resolved by fitting reduced to variation of the E and k_0 values to minimize the difference between the measured and calculated RID values [10].

This minimum was determined using the simplex method [11]. Each of the steps consisted in solving the direct problem and comparing it to the observed profile of variations.

In view of the essential nonlinearity of Eq. (1), the E and k_0 values are found to be interdependent and make the inverse problem ambiguous. The solutions obtained for the inverse problem are equivalent along the $k_0\exp(-E/RT) = \text{const}$ line.

There is an infinite set of E and k_0 combinations lying in the line noted and resulting in solutions close to the observed TiO_2 profile in the case of substitution into Eq. (1). Figure 2b presents two possible solutions of considerably differing parameters. Despite the quite wide scattering of kinetic parameters, the model profile of the degree of reaction incompleteness coincides with the data on determining TiO_2 within the analytical errors and modeling miscalculations, which prevents a preference for one solution or another. However, using the mean value theorem [12], the rate of metamorphic transformation may be determined in terms of the effective rate of a reaction instead of finding the E and k_0 values. Here, the effective rate should be a factor controlling the location of inclinations in the composition profiles. Various combinations of E and k_0 values result in different inclinations and curvatures of these graphs.

The effective rate is expressed as

$$k_{\text{eff}} = k_0 \exp\left(\frac{-E}{RT^*}\right), \tag{2}$$

where T^* is the effective temperature.

Since the effective rate is the same for both sets of kinetic parameters, the intersection point of the rates in Fig. 3b determines the effective temperature and, hence, the rate. The condition of the intersection of the curves is

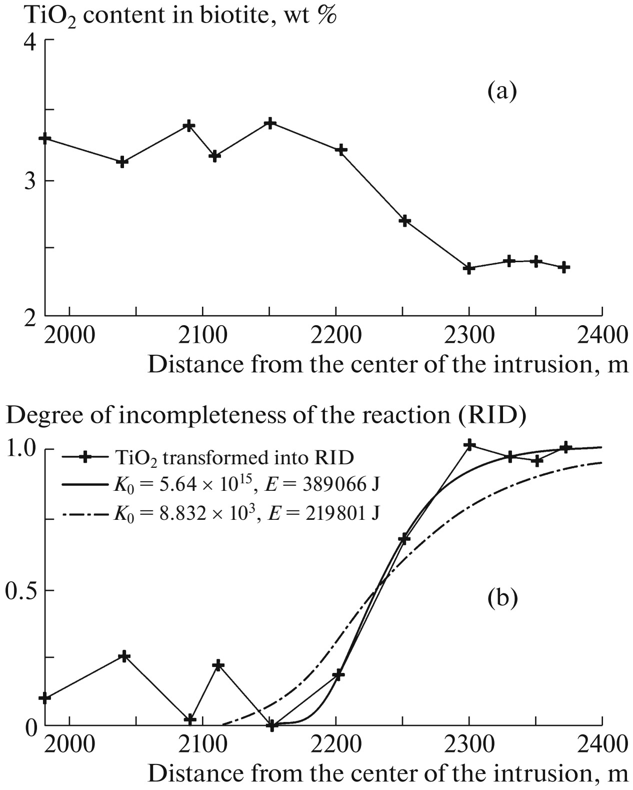

Fig. 2. (a) Observed concentration profile of the TiO_2 content in biotite and (b) calculated model profiles of various E and k_0 parameters.

$$k_{0,1} \exp\left(\frac{-E_1}{RT^*}\right) = k_{0,2} \exp\left(\frac{-E_2}{RT^*}\right), \tag{3}$$

where the additional lower indices 1 and 2 note the first and second set of parameters, respectively. Thus, the effective temperature is calculated as

$$T^* = \frac{E_2 - E_1}{R^* \ln\left(\dfrac{k_{0,2}}{k_{0,1}}\right)}. \tag{4}$$

The coincidence of the profiles of quite widely scattered kinetic parameters point to the occurrence of reactions at the average temperature of ~475°C (Fig. 3b). At this temperature, all the combinations of the E and k_0 values show good approximation to the observed profile and fit into the following line:

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

Thus, the effective rate of metamorphic reactions involving biotite in the contact aureole of the Kharlovo massif amounted to $\sim 10^{-12}$ s^{-1}.

One must note that these values are not exact for the time variability of temperatures. These are just the reference temperatures and rates at which the most

Table 1. Thermomechanical parameters applied in developing the model

Symbol	Symbol explanation	Value	Units
c_p^{add}	Additive heat capacity	2.52×10^6	J m^{-3} K
Q	Latent heat of crystallization	1.05×10^9	J m^{-3}
χ_{liquidus}	Heat conductivity of melt	1	J m^{-3} s^{-1}
χ_{solidus}	Heat conductivity of gabbro	2.03	J m^{-3} s^{-1}
χ_{country}	Heat conductivity of metapelites	2.27	J m^{-3} s^{-1}
$T_{\mathrm{intrusion}}$	Initial temperature of melt	1473 (1200)	K(°C)
T_{liquidus}	Temperature of melt	1373 (1100)	K(°C)
T_{solidus}	Solidification temperature	1323 (950)	K(°C)
$T_{\mathrm{background}}$	Temperature of country rocks before magma intrusion	353 (80)	K(°C)

pronounced transformations in rocks should take place.

The effective coefficients of diffusion were obtained using the values of the effective reaction rate and the extent of mass transfer provided that the substance transfer was controlled by diffusion. This parameter represents the quickness of the transfer of a considerable amount of matter. Previously, the volumes within which the metamorphic reactions involving biotite occurred were estimated as equal to ~0.01 mm^3 [5]. In this case, the extent of matter redistribution (the radius of the sphere of the volume obtained) amounted to ~0.23 mm. To realize the transfer of a substance to a distance as such, the effective coefficient of diffusion should amount to 5.29×10^{-16} cm^2/s at $T = 475$°C.

The estimates obtained for the effective rate of metamorphic reactions involving biotite are comparable to the data on the advance rate of the front of metamorphism when forming the spotted and massif hornfels in the Kharlovo contact aureole [13], as well as to the estimates of reaction rates under the contact metamorphism given in the review by Baxter [2]. The results of theoretical modeling are in agreement with the range of effective coefficients of diffusion evaluated using the model of diffusion metasomatosis for texture-heterogeneous rocks [1, 3, 14], as well as with the experimental data on the coefficients of diffusion over the grain boundaries within mineral aggregates at the corresponding *PT* parameters [15].

Most likely, the system in these instances was close for the rapid (pore–fluidal) diffusion transfer and redistribution of matter conforming to the regularities of solid-phase transfer over the grain boundaries. In terms of the process as such, the approach presented is evidently the only tool for determining the effective kinetic parameters in texture-homogenous rocks.

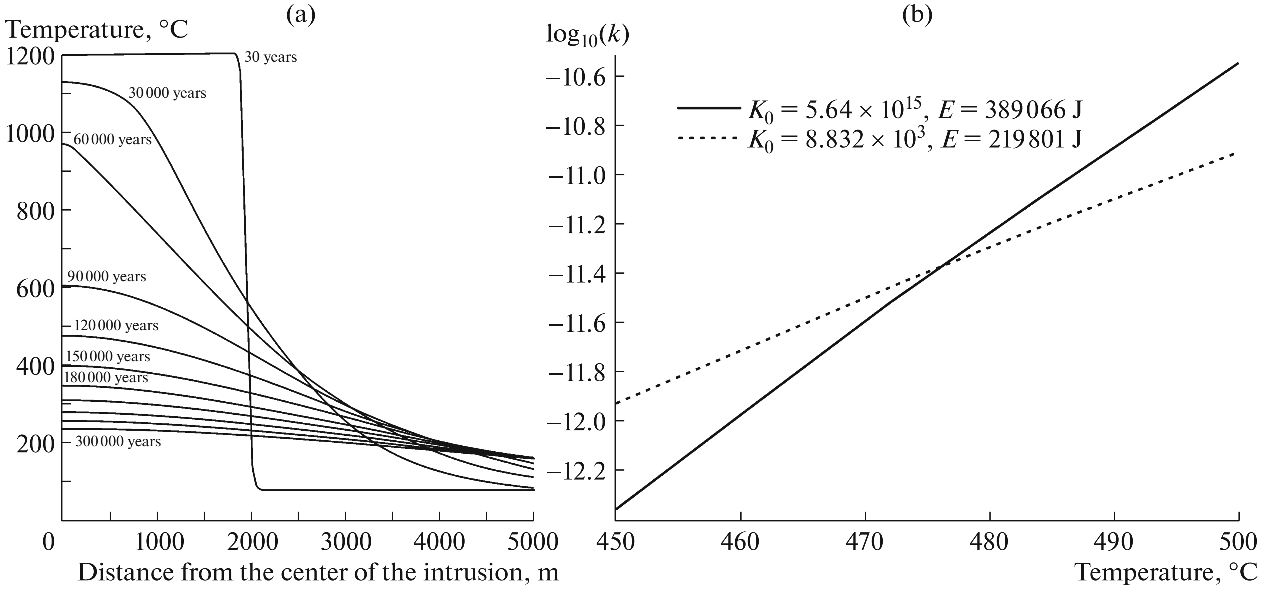

Fig. 3. (a) Thermal isochrones for a cooling-down cylindrical basite intrusion of 1950-m radius and (b) temperature dependence of the reaction rate (k) for the two sets of calculated kinetic parameters (E and k_0).

FUNDING

This study was supported by the Russian Foundation for Basic Research, project no. 18–05–00152.

REFERENCES

1. G. W. Fisher, Geochim. Cosmochim. Acta **42**, 1035–1050 (1978).
2. E. F. Baxter, Geol. Soc. London Spec. Publ. **220**, 183–202 (2003).
3. R. Joesten and G. Fisher, Geol. Soc. Am. Bull. **100**, 714–732 (1988).
4. V. V. Reverdatto, I. I. Likhanov, O. P. Polyanskii, V. S. Sheplev, and V. Yu. Kolobov, *Metamorphism: Nature and Models* (Siberian Branch RAS, Novosibirsk, 2017) [in Russian].
5. I. I. Likhanov, V. V. Reverdatto, and I. Memmi, Eur. J. Mineral **6**, 133–144 (1994).
6. I. I. Likhanov, V. V. Reverdatto, and I. Memmi, Eur. J. Mineral **7**, 379–389 (1995).
7. E. W. Bolton, A. C. Lasaga, and D. M. Rye, Am. J. Sci. **299**, 1–68 (1999).
8. I. I. Likhanov and A. A. Ten, Dokl. Akad. Nauk SSSR **321** (5), 1044–1048 (1991).
9. I. I. Likhanov, A. A. Ten, V. V. Reverdatto, and E. P. Solotchina, Dokl. Earth Sci. **346** (1), 78–82 (1996).
10. I. I. Likhanov, A. A. Ten, V. V. Reverdatto, V. A. Ananiev, and I. Memmi, Mineral. Petrol. **71**, 51–65 (2001).
11. J. A. Nelder and R. Mead, Comput. J. **7**, 308–313 (1965).
12. I. N. Bronshtein and K. A. Semendyayev, *Handbook of Mathematics* (Verlag Harri Deutsch, Berlin, 1979).
13. V. V. Reverdatto, A. V. Babichev, I. I. Likhanov, and O. P. Polyanskii, Dokl. Earth Sci. **480** (4), 750–753 (2018).
14. I. I. Likhanov, Geol. Soc. London Spec. Publ. **478**, 89–115 (2018). https://doi.org/10.1144/SP478.11
15. V. N. Balashov and B. W. D. Yardley, Am. J. Sci. **298**, 441–470 (1998).

Translated by A. Rylova