ISSN 0869-5911, Petrology, 2006, Vol. 14, No. 5, pp. 515–527. © Pleiades Publishing, Inc., 2006.
Original Russian Text © G.Yu. Shvedenkov, V.V. Reverdatto, T.A. Bul'bak, N.A. Bryksina, 2006, published in Petrologiya, 2006, Vol. 14, No. 5, pp. 548–560.

Bimetasomatic Zoning in the CaO–MgO–SiO_2–H_2O–CO_2 System: Experiments with the Use of Natural Rock Samples

G. Yu. Shvedenkov†, V. V. Reverdatto, T. A. Bul'bak, and N. A. Bryksina

Institute of Mineralogy and Petrography, Siberian Division, Russian Academy of Sciences,
pr. Akademika Koptyuga 3, Novosibirsk, 630090 Russia
e-mail: rever@uiggm.nsc.ru

Received October 10, 2005

Abstract—Experiments reproducing the development of bimetasomatic zoning in the CaO–MgO–SiO_2–H_2O–CO_2 system were conducted at elevated *P–T* parameters with the use of samples of naturally occurring quartz–dolomite and calcite–serpentinite rocks. In order to maintain mass transfer exclusively via the diffusion-controlled mechanism, we used the method of the ensured compaction of the cylindrical sample surface with a thin-walled gold tube. In the course of the experiments, a single diopside zone ~2.5×10^{-5} m thick was obtained at the quartz–dolomite interface at $T = 600°C$, $P_{H_2O + CO_2} = 200$ MPa, and $X_{CO_2} = 0.5$ for 25–40 days and a succession of metasomatic zones at $T = 750°C$, $P_{H_2O + CO_2} = 300$ MPa, and $X_{CO_2} = 0.4$ for 48 days. The metasomatic zones were as follows (listed in order from quartz to dolomite): wollastonite || diopside || tremolite || calcite + forsterite; with the average width of the diopside zone equal to ~1.3×10^{-5} m and the analogous part of the wollastonite zone equal to ~2.6×10^{-5} m. Two zones (listed in order from calcite to serpentine) diopside and diopside–forsterite (the average widths of these zones were ~6×10^{-4} and ~8×10^{-4} m, respectively) were determined to develop at contact between serpentine and calcite during experiments that lasted 124 days at $T = 500°C$, $P_{H_2O + CO_2} = 200$ MPa, and $X_{CO_2} = 0.2$–0.4. In the former and latter situations, the growth rate of the zoning ranged between 3.1×10^{-12} and 1.2×10^{-11} m/s and between 5.6×10^{-11} and 7.5×10^{-11} m/s, respectively. The higher growth rate in the latter case can be explained by the higher water mole fraction in the fluid, with this water released during serpentinite decomposition in the experiments. The development of the only diopside zone in the experiments modeling the interaction of quartz and dolomite at $T = 600$–$650°C$ and $P_{H_2O + CO_2} = 200$ MPa is in conflict with theoretical considerations underlain by the Korzhinskii–Fisher–Joesten model. The interaction of quartz and dolomite in the CaO–MgO–SiO_2–CO_2–H_2O system at the P–T–X_{CO_2} parameters specified above should be attended by the origin of a number of reaction zones consisting of various proportions of talc, forsterite, tremolite, diopside, and calcite. The saturation of the fluid with respect to these minerals was likely not reached, and this resulted in the degeneration of the respective stability fields in the succession of zones. Conceivably, this was related to the insufficient rates of quartz and dolomite dissolution and the relatively low diffusion rates of the dissolved species in the low-permeable medium. In the experiments with interacting calcite and serpentine, the zoning calcite || diopside || diopside + forsterite || serpentine developed in its complete form, in agreement with the theory. Equilibrium was likely achieved in these experiments due to the higher diffusion coefficients.

DOI: 10.1134/S0869591106050067

INTRODUCTION

By studying uncompleted reaction metamorphic rocks, the researcher can obtain insight into the mechanisms of mineral transitions, but it remains thereby impossible to quantify the duration and kinetics of the reaction process. The duration of a reaction can be evaluated only from the results of experiments carried out with the use of specialized equipment. Experiments of this type were conducted mostly with the use of powders (see, for example, Zaraisky et al., 1981, 1986; Zaraisky, 1989, Dachs and Metz, 1988; Heinrich et al., 1986, 1989; Käse and Metz, 1980; Kridelbaugh, 1973; Lüttge and Metz, 1991; Schramke et al., 1987; Tanner et al., 1985), with only a few experimental studies conducted with the use of rock samples (Brady, 1979; Lüttge and Metz, 1993; Shvedenkov et al., 1996, 2002, 2005; Reverdatto and Shvedenkov, 2004). Lüttge and Metz (1993) have carried out a specialized experimental research of the reaction dolomite + 2 quartz = diopside + $2CO_2$ with the use of both powders and rock samples, with the participation of an H_2O–CO_2 fluid, at $X_{CO_2} = 0.9$. These experiments have demonstrated that

---

† Deceased.

the mechanism of the reaction (dissolution of the preexisting minerals–transportation of the dissolved material in the interstitial fluid–nucleation of newly formed phases) is roughly identical in both situations, but the growth rates of the diopside reaction rims at the boundaries of dolomite and quartz grains is much lower in the sample of the natural rock than in the powder. The former value was lower even when the mineral material in the experiments partly consisted of a powder and partly of a single crystal, as was demonstrated by the example of the reaction: 2 periclase + quartz = forsterite (Brady, 1979). The decrease in the growth rates of reaction rims is most likely related to the higher density of the rocks as compared to the powders and the decrease in the interstitial space in the former (and the corresponding hampering of mass transfer). It is also quite obvious that the growth rate should depend on the composition of the intergranular fluid. Lüttge and Metz (1991) examined the interaction of dolomite and quartz powders in the presence of a CO_2 fluid and experimentally demonstrated that the progress of this reaction over a time period of one year is as low as 1–3% in the absence of water. The growth rates of reaction rims in all of these experiments were controlled mostly by diffusion mass transfer (Lüttge and Metz, 1993; Milke et al., 2001; Milke and Heinrich, 2002).

Data obtained on metamorphic rocks suggest that dissolved species diffusing in the intergranular fluid and involved in the nucleation and growth of minerals have different migration characteristics. Mineral reactions in a rock are controlled by a mass balance with respect of all components (except volatiles) and proceed in a certain local volume. The minerals incorporating the less mobile component grow most closely to the source of this component: a dissolving mineral grain or an aggregate of grains. More mobile components migrate farther away from the source along the gradients of their chemical potentials. In the succession of migration characteristics, the most mobile components are alkalis, which are followed by Ca, Mg, Fe, Si, and the least mobile (the most inert) Al and Ti (Carmichael, 1969; Fisher, 1970, 1973, 1977, 1978; Fisher and Elliott, 1974). Chemical components participating in diffusion-controlled metasomatism are characterized by an approximately the same succession of mobility, as was first noted by Korzhinskii (1955).

As their integral kinetic parameter, the migration ability of components is controlled, first of all, by the dissolution rates of minerals and the diffusion coefficients (Walther and Orville, 1982; Walther and Wood, 1984; Wood and Walther, 1983). In turn, the latter depend on the properties of the fluid, its P–T parameters, and the sizes and charges of diffusing particles of the dissolved species, their interaction with other species and the boundaries of mineral grains, and the thicknesses and spatial coherence/incoherence of fluid films (see, for example, Lichtner, 1996; Steefel and MacQuarrie, 1996; Walther and Wood, 1984). The relative position of components in the succession of their mobility can change depending on the physical characteristics and composition of the system. This should obviously somehow affect the modal composition and succession of zones in the reaction zoning developing during the metamorphism of heterogeneous rocks, for example, the growth of corona textures. One of the reasons for changes in the succession of the relative mobility of components and, hence, also in the metamorphic zoning, can likely be variations in the fluid composition (CO_2/H_2O ratio and the concentrations of NaCl, SO_2, and other components at all other factors remaining the same). Another reason is an increase in the density of the mineral aggregate and a simultaneous decrease in the interstitial volume in the experiments with natural rocks as compared to the experiments with powders.

The theoretical analysis of the zoning is conducted based on the principles of irreversible thermodynamics, within the scope of the model for diffusion-controlled metasomatism developed by Korzhinskii, Fisher, and Joesten (Korzhinskii, 1955, 1982; Fisher, 1973, 1978; Franz and Mao, 1976, 1979; Foster, 1977, 1981; Joesten, 1977, 1986; Joesten and Fisher, 1988; Sheplev et al., 1991, 1992; Ashworth and Sheplev, 1997; Ashworth et al., 1998; Sheplev et al., 1998). This model is underlain by significant assumptions and simplifications and seems to be able to describe the development of diffusion-controlled metasomatism at a contact of two originally nonequilibrium materials only in application to relatively simple situations, which can be described within the framework of a stationary approximation. In order to fully approach the model to the naturally occurring processes evolving with time, it is necessary to significantly modernize the experimental study of the mineral transformations to obtain the kinetic characteristics of the growth of diffusion-controlled zonal structures. This fairly complicated task requires a significant volume of experimental data. This paper reports some results of such a research.

STARTING MATERIAL AND EXPERIMENTAL TECHNIQUES

The starting materials for the experiments in the $CaO–MgO–SiO_2–H_2O–CO_2$ system were two samples of quartz–dolomite and serpentine–calcite rocks. One of the samples, taken in the eastern part of the Arts-Bogdo Range in Mongolia, was agate with amygdules filled with dolomite. The dolomite had the following chemical composition (wt %) 29.74 CaO, 20.00 MgO, 2.71 FeO, 0.06 MnO, 46.58 CO_2, 0.27 SiO_2, 0.27 Al_2O_3, and 0.15 H_2O. The analytical total was equal to 99.78 wt %. Neither TiO_2 nor Fe_2O_3 were detected. The concentrations of water and carbon dioxide were determined by differential thermal analysis. The analyses can be readily recalculated to the formula of a low-Fe dolomite with a minor Ca excess: $Ca_{1.02}(Mg_{0.96}Fe_{0.02})[CO_3]_{2.04}$. The unit cell parameters of the mineral are a = 4.797 Å, c = 16.059 Å, and V =

320.1 Å^3 and correspond to virtually pure dolomite. The quartz contains a minor amount of aqueous inclusions (0.7 wt %), which decrepitate when heated to >650°C. The other sample, taken from metasomatically altered marbles at the Kotui River in the northern Siberian Platform, consists of serpentine in contact with calcite. The chemical composition of the serpentine is as follows (wt %): 43.36 SiO_2, 0.20 Cr_2O_3, 41.61 MgO, 0.83 FeO, 0.01 CaO, 0.03 Na_2O, 13.40 H_2O, analytical total equals 99.44. The chemical composition of the calcite is (wt %): 56.68 CaO, 0.81 MgO, 0.01 MnO, 0.04 Na_2O, 0.02 SiO_2, 42.94 CO_2, 100.05 total.

In order to maintain exclusively diffusion-controlled mass transfer during the experiments, the rock cylinders (which were cut out of the natural rock samples in direction perpendicular or parallel to the contact of the interacting minerals) 5 mm in diameter and 8–10 mm high were pressurized in welded gold ampoules under a pressure of 40 MPa at room temperature. Inasmuch as a metallic tube decreases in diameter when elongated, this ensured the obturation of the surface of the cylindrical sample. In order to maintain a constant strain of the obturation surface of the gold tube during the experiment, rings of EI 437B Cr–Ni alloy with outer grooves were welded to the butt ends of the tube. For this purpose, the metal was rolled into these grooves on both sides. In the course of the experiment, the outer fluid came from the end of the cylinder through the hole in the ring. The charged gold ampoule was welded into a platinum ampoule of greater diameter. Silver oxalate and water were additionally placed into the outer ampoule to produce a water–carbon dioxide mixture. The welded platinum ampoule was heated in a Tuttle tube reactor connected with a hydraulic press (Fig. 1), which enabled us to vary the pressure independently of heating. Pure water was utilized as a pressure medium. The pressure was monitored with a manometer (which was connected with the reactor via a bellows) accurate to ±2 MPa. During the experiment, the manometer and reactor were blocked by a hydraulically operated valve with a needle. The reactor was heated and quenched isobarically to prevent the depressurization of the platinum ampoule, particularly within the region of the highly explosive decomposition of silver oxalate and the passage of the fluid into the supercritical state. The outer platinum ampoule maintained an oxygen pressure in the fluid corresponding to the Ni–NiO buffer. The experiments were carried out at T = 500–700°C, P_{tot} = 200–300 MPa for 25–124 days. The experimental regime was reached in 40 min, and the quenching to T < 100°C lasted 15 min. The experimental temperature was measured by a capillary-armored Pt–Rh thermocouple that was inserted into the high-pressure vessel through a hole in the valve. The temperature was measured accurate to ±2°C and was maintained during the experiment accurate to ±6°C by the temperature controller. After the experiments, the cylindrical rock samples were embedded into epoxy resin and sawn through the centers parallel to the elongation. One of these halves was utilized to prepare a polished section for examining the minerals by X-ray diffraction and microprobe; and the other half was kept as a reference sample. The composition of the fluid phase after the experiments differed from the initial composition of the fluid, because water and carbon dioxide were released during the reactions. The amount of CO_2 was determined from the weight difference for the Pt ampoule cooled to <0°C before and after its puncturing with a needle and subsequent drying at 70°C to a constant weight. The first and second weight differences corresponded to the amounts of CO_2 and H_2O, respectively.

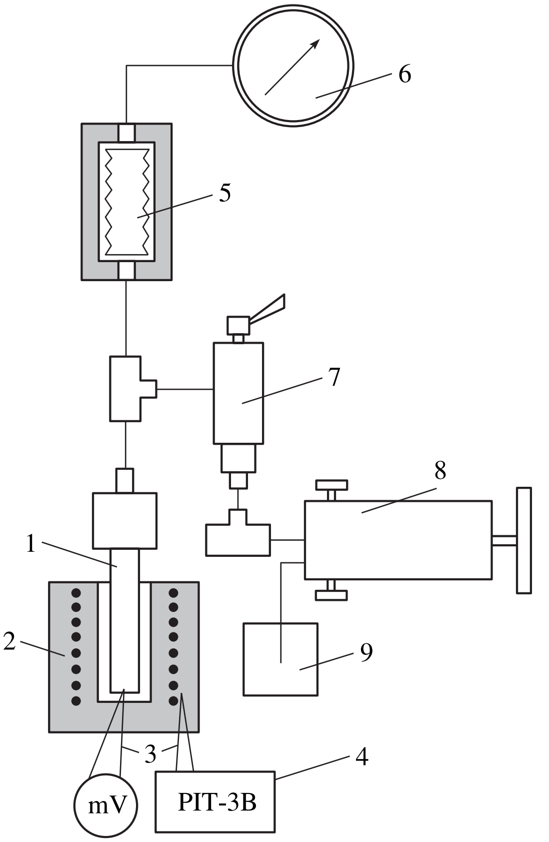

Fig. 1. Schematic representation of the experimental setup. (1) Reactor; (2) furnace; (3) thermocouples; (4) temperature controller; (5) bellows; (6) manometer; (7) valve; (8) hydraulic press; (9) vessel for solution.

RESULTS

Development of Bimetasomatic Zoning at a Quartz–Dolomite Interface

The experiments were conducted in the $CaO–MgO–SiO_2–H_2O–CO_2$ system at T = 600–750°C and $P_{H_2O+CO_2}$ = 200–300 MPa. This system was examined in detail with reference to the metamorphism of siliceous dolomites (Tracy and Frost, 1991). The mineral

Table 1. Results of experiments on the development of bimetasomatic zoning at a contact between quartz and dolomite

Experiment no.	T, °C	P, MPa	Duration, days	Initial X_{CO_2}	Final X_{CO_2}	Experimental products	Thicknesses of mineral zones
1	600	200	25	0.5	0.42	*Di*	*Di* (2.3×10^{-5})
2	600	200	40	0.5	0.48	*Di*	*Di* (3×10^{-5})
3	750	300	48	0.5	0.52	*Wo*, *Di*, *Tr*, *Fo*, *Mgs*	*Di* (1.2×10^{-5}) *Wo* (2.8×10^{-5})
4	750	300	48	0.5	0.46	*Wo*, *Di*, *Tr*, *Fo*, *Mgs*	*Di* (1.5×10^{-5}) *Wo* (2.5×10^{-5})
5	650	200	56	0	0.02	*Di*	*Di* (0.7×10^{-5})
6	650	200	56	0.5	0.55	*Di*	*Di* (0.4×10^{-5})
7*	650	200	56	0	0.06	*Di*	*Di* (0.9×10^{-5})

Note: Mineral symbols: *Di*—diopside, *Wo*—wollastonite; *Qtz*—quartz, *Tr*—tremolite, *Dol*—dolomite, *Fo*—forsterite, *Mgs*—magnesite.
* Experiment with 5% NaCl solution.

assemblages and equilibria corresponding to our experimental conditions were characterized in (Gottschalk and Metz, 1984; Käse and Metz, 1980; Lüttge and Metz, 1991, 1993; Tanner et al., 1985). The results of our experiments led us to establish (Table 1) that a single zone of diopside with an average thickness of 2.5×10^{-5} m was produced at T = 600°C, $P_{H_2O + CO_2}$ = 200 MPa, and X_{CO_2} = 0.02–0.55. The duration of the experiments (25–56 days) was likely still insufficient for a well-developed metasomatic zoning to be formed that included a succession of mineral assemblages with calcite, tremolite, diopside, forsterite, and other minerals. The reasons for the absence of these phases are discussed below. The reader can find a theoretical analysis of diverse variants of this zoning within the scope of the thermodynamics of irreversible processes in (Franz and Mao, 1976, 1979; Kuznetsova et al., 1992; Sheplev et al., 1998). The differences in the successions of mineral assemblages in this zoning were determined by the relative values of the chemical potentials of the diffusion compositions (CaO, MgO, and SiO_2) at constant pressure and temperature.

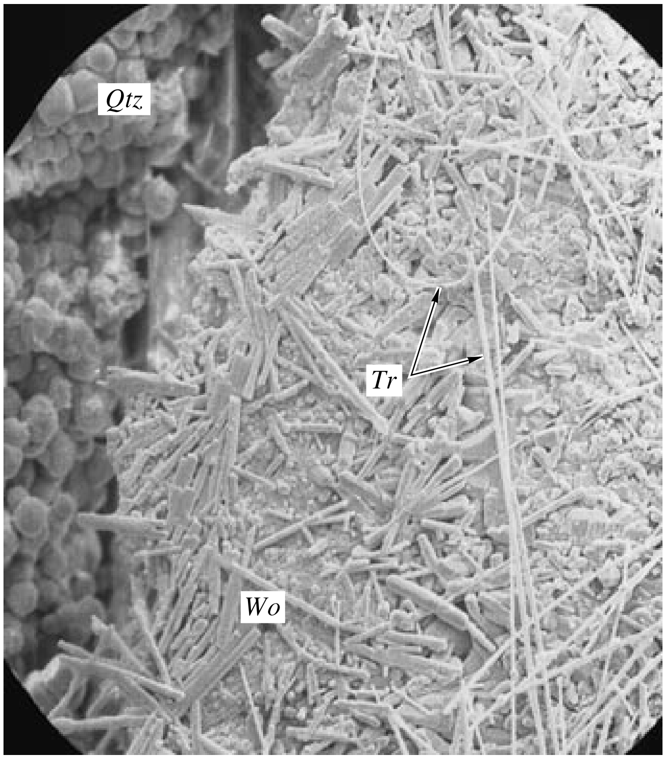

Fig. 2. Tremolite (*Tr*), diopside (*Di*), and wollastonite (*Wo*) produced at the contact between quartz (*Qtz*) and dolomite in the experiment lasting for 48 days (T = 750°C, P = 300 MPa, X_{CO_2} = 0.5). Electron microscopic image of a hand-sample, magnification ×2000.

When the temperature was increased to 750°C at $P_{H_2O + CO_2}$ = 300 MPa, a wollastonite zone was added to the only reaction zone of diopside produced in the experiment, because the experimental temperature was higher than that of the equilibrium calcite + quartz = wollastonite + CO_2 at $P_{H_2O + CO_2}$ = 300 MPa and $X_{CO_2} \approx 0.5$ (Gottschalk and Metz, 1984; Tracy ad Frost, 1991; Spear, 1993). Thus, the experiment was carried out under parameters at which wollastonite, forsterite with calcite, diopside with forsterite, and other minerals and assemblages are stable. As can be seen under a raster electron microscope, the following succession of zones was formed at the boundary between dolomite and quartz in the experiments at 750°C (the zones are listed in the direction from quartz to dolomite): "emptiness zone" ⟶ wollastonite ⟶ diopside ⟶ tremolite ⟶ calcite + forsterite. This succession is in general agreement with the succession modeled in experiments with powders (Zaraisky et al., 1986), except only the tremolite zone, for which it was hard to exactly pinpoint the relative position and determine the composition because of the fibrous character of the synthesized amphibole (Fig. 2). It is possible to propose a great vari-

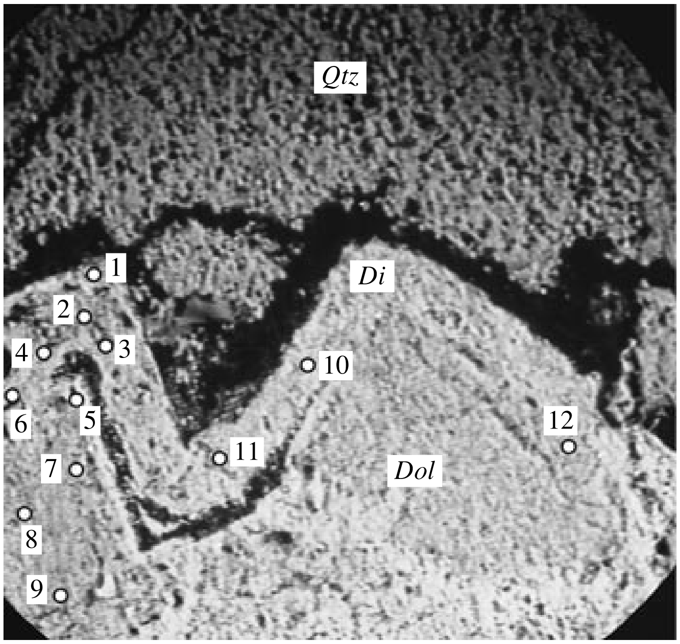

Fig. 3. Diopside (*Di*) zone that developed at the contact between dolomite (*Dol*) and quartz (*Qtz*) in experiment 6 (duration 56 days, $T = 650°C$, $P = 200$ MPa, $X_{CO_2} = 0.5$).

Electron microscopic image (JSM-35 electron microscope) of a thin section, magnification ×1100. Numbered circles are the sites of microprobe analyses (Table 2).

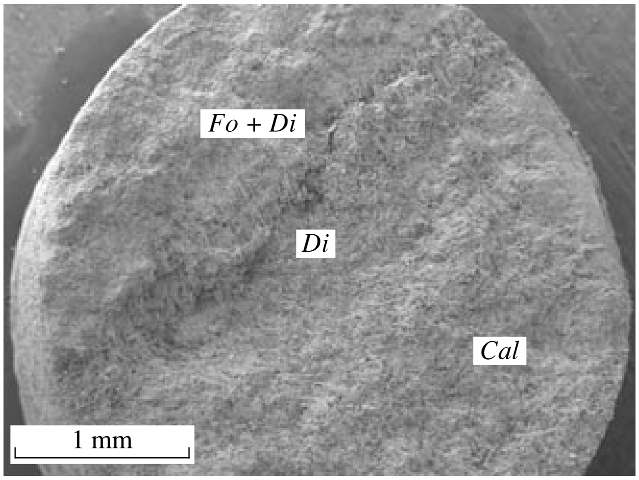

Fig. 4. Forsterite (*Fo*) + diopside (*Di*) and diopside zones that developed at the contact between serpentine and calcite (*Cal*) in an experiment modeling the development of metasomatic zoning (duration 124 days, $T = 500°C$, $P = 200$ MPa, $X_{CO_2} = 0.2$–0.4).

ety of reactions between minerals and fluid to account for the development of the zoning quartz || wollastonite || diopside || tremolite || calcite + forsterite || dolomite, but only the following of these reactions are independent (written without CO_2 and H_2O): 2 quartz + dolomite = diopside, 8 quartz + 5 dolomite = 3 calcite + tremolite, quartz + 2 dolomite = 2 calcite + forsterite, 11 quartz + 5 dolomite = 3 wollastonite + tremolite. The other possible reactions are linear combinations of these four reactions. The succession of mineral associations in the bimetasomatic zoning is determined, according to the theory, by the chemical potentials of the diffusing compositions (CaO, MgO, and SiO_2) at constant pressure and temperature.

Wollastonite and diopside form typical prismatic crystals, which can be readily distinguished based on the faceting of their tops. The elongated wollastonite crystals are ~10 μm long and <1 μm thick, whereas the diopside and forsterite crystallized as grains ≤1 μm. The hair-thin and sometimes curved tremolite fibers were in places as long as tens of micrometers. The primary contact between quartz and dolomite is dentate, with the "teeth" defined by rhombohedron apexes. The protruding tops of dolomite crystals are affected by more active bimetasomatic transformations than those in a flat contact (Fig. 3). The thicknesses of the newly formed mineral zones were evaluated under a scanning microscope with regard for microprobe analyses of the grains. Since the thicknesses vary along the original contact, Table 1 reports averaged values of various experiments. Summarizing all experimental data, the average thickness of the diopside zone can be estimated at 1.3×10^{-5} m and the average thickness of the wollastonite zone at 2.6×10^{-5} m.

Compared to the experiments with quartz and dolomite powders (Zaraisky et al., 1986; Zaraisky, 1989; Lüttge and Metz, 1993), bimetasomatic zoning developed more slowly in our experiments with compact rock samples. It is important to mention that the thickness of the metasomatic zoning in our experiment with a sample of a quartz–dolomite rock and 5% aqueous NaCl fluid (Table 1, experiment 7) increased insignificantly compared to the thickness of the zoning in the experiment with a salt-free fluid (Table 1, experiment 5). At the same time, the "crystallinity" of the zone and the sizes of diopside grain were larger in the experiment with NaCl than in experiments nos. 1, 2, 5, and 6. The analytical totals of components in microprobe analyses of the mineral aggregates produced in experiment no. 7 are higher than in the other experiments and approach 100 wt % (Table 2). The development of the "emptiness zone" 0.1–0.15 cm thick due to carbonate replacement implies that the porosity of the rock increased during the decarbonatization reaction. Analogous observations were made during similar experiments in (Lüttge and Metz, 1993).

Development of Bimetasomatic Zoning at a Serpentine–Calcite Interface

In our experiments 124 days long at $T = 500°C$, $P_{H_2O + CO_2} = 200$ MPa, and $X_{CO_2} = 0.2$–0.4, two zones were determined to develop at the contact between serpentine and calcite: diopside and diopside–forsterite

Table 2. Microprobe analyses (wt %) of mineral aggregates composing bimetasomatic zoning at the contact of quartz and dolomite

Analysis no.	CaO	Na_2O	MgO	SiO_2	Al_2O_3	FeO	MnO	Total	Mineral assemblage
Experiment 2									
1	22.78	0.55	16.58	51.14	0.00	3.38	0.21	94.73	*Di*
2	21.88	1.34	19.11	42.47	0.00	1.23	0.08	–	*Di + Dol*
3	30.17	0.74	15.56	29.74	0.00	1.10	0.13	–	*Di + Dol*
4	36.17	0.13	13.51	21.73	0.00	0.87	0.06	–	*Di + Dol*
5	31.27	0.42	11.66	34.63	0.03	2.59	0.21	–	*Di + Dol*
6	25.15	0.31	16.51	48.23	0.03	2.32	0.15	93.15	*Di*
7	23.08	0.59	18.22	52.79	0.22	2.84	0.19	97.77	*Di*
8	23.60	0.67	16.30	52.11	0.01	4.71	0.26	97.71	*Di*
9	21.40	0.72	17.70	54.47	0.16	3.27	0.24	98.08	*Di*
10	22.13	0.47	15.67	54.96	0.08	3.21	0.25	97.17	*Di*
11	22.23	0.81	18.67	51.81	0.04	3.44	0.19	97.31	*Di*
12	23.33	0.60	18.12	52.71	0.04	2.90	0.19	97.90	*Di*
13	0.16	0.02	0.10	101.59	0.09	0.03	0.00	102.02	*Qtz*
14	22.58	0.89	16.36	52.80	0.08	5.16	0.33	98.58	*Di*
15	23.49	0.76	16.59	54.17	0.02	4.17	0.20	99.49	*Di*
16	0.01	0.02	0.03	98.70	0.00	0.05	0.00	99.72	*Qtz*
17	31.01	0.03	19.68	0.01	0.00	1.15	0.03	–	*Dol*
Experiment 6									
1	23.26	0.82	18.21	47.33	0.02	4.47	0.34	94.44	*Di*
2	27.96	0.12	21.75	0.55	0.00	1.71	0.02	–	*Dol*
3	21.87	0.31	26.14	43.91	0.00	1.74	0.06	94.03	*Di*
4	26.10	0.14	17.10	51.45	0.00	0.93	0.02	95.75	*Di*
5	32.25	0.15	16.91	0.15	0.00	2.49	0.14	–	*Dol*
6	32.41	0.06	16.70	0.10	0.00	2.76	0.08	–	*Dol*
7	33.55	0.08	16.32	0.08	0.00	2.01	0.06	–	*Dol*
8	32.89	0.06	16.21	0.08	0.00	2.78	0.08	–	*Dol*
9	24.04	0.61	19.52	50.22	0.00	3.14	0.14	97.66	*Di*
10	24.11	0.23	15.82	55.28	0.00	1.26	0.02	96.73	*Di*
11	24.46	0.12	18.82	53.01	0.00	0.74	0.04	97.20	*Di*
12	26.51	0.11	16.99	50.65	0.00	0.60	0.00	94.86	*Di*
Experiment 7									
1	24.96	0.51	16.01	54.67	0.00	2.86	0.12	99.15	*Di*
2	23.38	0.94	12.50	53.19	0.03	6.86	0.44	97.33	*Di*
3	26.27	0.48	14.31	51.30	0.00	4.71	0.31	97.35	*Di*
4	21.56	0.32	23.86	52.78	0.00	1.16	0.02	99.71	*Di*
5	24.38	0.42	18.63	51.96	0.00	1.95	0.00	97.34	*Di*
6	24.99	0.58	19.20	53.12	0.13	2.28	0.16	100.46	*Di*

Note: See Table 1 for experimental conditions.

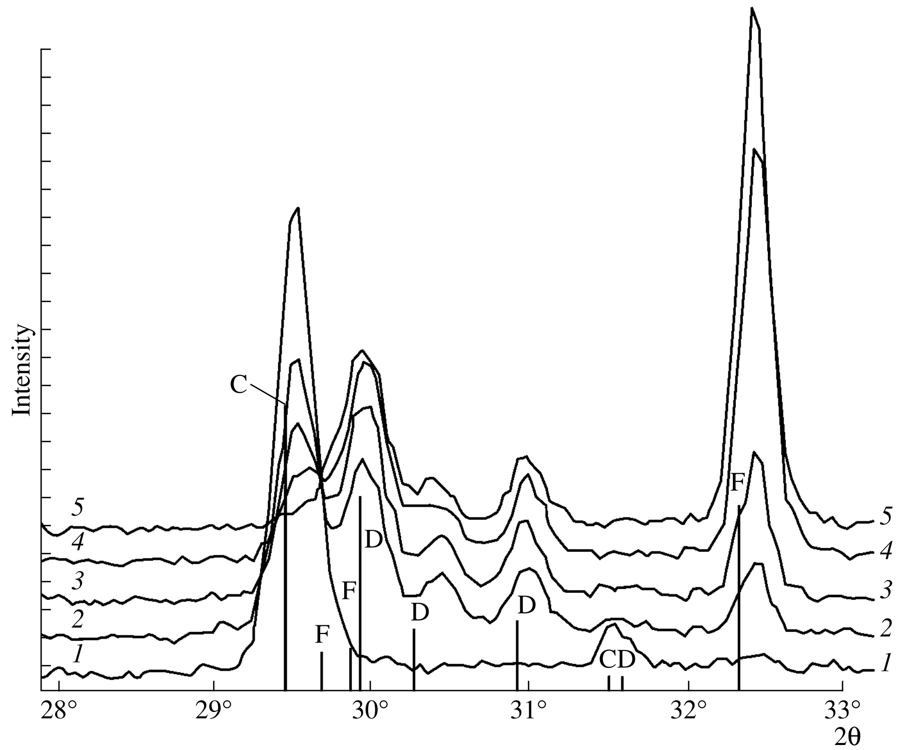

Fig. 5. Summarizing X-ray refractogram taken at the surface of the sample after the experiment (Bruker X-ray diffractometer). Sites of frame centers: (*1*) C || D boundary; (*2*) 10 μm before the C || D boundary; (*3*) 10 μm after the C || D boundary; (*4*) D || D + F boundary; (*5*) 10 μm before the optical D || D + F boundary. Intensities are given in relative units. Vertical bars indicate the position of the reference reflections of diopside (D), forsterite (F), and calcite (C). Counting time for one frame was 200 s. CuK_α anticathode. Analyst T.N. Drebushchak.

(Fig. 4). Diopside and forsterite in the zone closer to serpentine occur as prismatic elongated crystals up to 2–3 μm. The grain sizes in the granoblastic aggregate of the diopside zone was ≤1 μm. The thicknesses of these zones were 6×10^{-4} and 8×10^{-4} m, respectively, with deviations from the averages of $\pm 2 \times 10^{-5}$ m for both. The calcite–diopside boundary, i.e., the reaction front, was characterized by the release of CO_2 and the obvious decompaction of the material due to the increased porosity. Nevertheless, a sharp outer boundary was determined (on Bruker X-ray diffractometer equipped with a D8 DISCOVER GADDS counter for the surface scanning of samples over an area of no larger than ~1 mm in diameter) for the diopside zone within the range of 20 μm (reflections were integrated with a step of 0.02° over the angle of reflection 2θ) (Fig. 5).

THEORETICAL ANALYSIS OF ZONING

It is expedient to analyze the development of the zoning from the standpoint of the Korzhinskii–Fisher–Joesten model for diffusion-controlled metasomatism (Korzhinskii, 1955, 1982; Fisher, 1973, 1977; Joesten, 1977; Joesten and Fisher, 1988). The model was further developed in (Sheplev et al., 1991, 1998; Ashworth and Sheplev, 1997; Ashworth et al., 1998; and others). In compliance with this model, a succession of mineral layers should be formed at the contact of reacting media. In the $CaO(c)–MgO(m)–SiO_2(s)$ system containing two newly formed phases and consisting of one or two mineral layers, the following combinations are possible (Sheplev et al., 1991; Ashworth and Sheplev, 1997; Sheplev et al., 1998):

C || D || F || S
C || F || D + F || S
C || D + F || S
C || D + F || F || S
C || F || D || S
C || D || D + F || S
C || D + F || D || S,

where C is calcite, D is diopside, F is forsterite, and S is serpentine.

Let us select a single succession corresponding to the principle of the maximum production of entropy (Sheplev et al., 1991, 1998; Ashworth and Sheplev, 1997). For this purpose, we express the chemical compositions of minerals through the chemical composition of the reactants by the formula $A = N^T a$, where A = {C, D, F, S}, a = (c, m, s), the superscript T is a transposition symbol, and $N = \begin{pmatrix} 1100 \\ 0123 \\ 0212 \end{pmatrix}$.

The stoichiometric coefficients of a single independent reaction are (equal to) M = {–1, 1, 4, –3}, i.e., 1C + 3S = 1D + 4F.

Let us now consider the association of layers C || D || F || S and number the boundaries from left to right. The growth rate of mineral i at boundary k is denoted as V_{ki}. According to theoretical considerations (Sheplev et al., 1991; Ashworth and Sheplev, 1997; Sheplev et al., 1998), the growth rates of all minerals can be written as follows:

$$V_{1\mathrm{C}} = -1,$$

$$V_{1\mathrm{D}} = \frac{\frac{1}{L_\mathrm{c}}}{\frac{1}{L_\mathrm{c}} + \frac{1}{L_\mathrm{m}} + 4},$$

$$V_{2\mathrm{D}} = \frac{\frac{1}{L_\mathrm{m}} + 4}{\frac{1}{L_\mathrm{c}} + \frac{1}{L_\mathrm{m}} + 4},$$

$$V_{2\mathrm{F}} = -\frac{2\left(\frac{1}{L_\mathrm{m}} + 1\right)}{\frac{4}{L_\mathrm{m}} + 1},$$

$$V_{3\mathrm{F}} = \frac{6\left(\frac{3}{L_\mathrm{m}} + 1\right)}{\frac{4}{L_\mathrm{m}} + 1},$$

$$V_{3\mathrm{S}} = -3,$$

where $L_\mathrm{c} = \frac{L_{\mathrm{CaOCaO}}}{L_{\mathrm{SiO_2SiO_2}}}$, $L_\mathrm{m} = \frac{L_{\mathrm{MgOMgO}}}{L_{\mathrm{SiO_2SiO_2}}}$; and L_{CaOCaO}, L_{MgOMgO}, and $L_{\mathrm{SiO_2SiO_2}}$ are the Onsager coefficients. It can be concluded from these expressions for the rates that the first layer in the zoning extends at both of its boundaries (i.e., in both directions); and the second layer grows in one direction only, whereas its other side retreats (“dissolves”). A test of the occurrence of the first and second layers (Sheplev et al., 1991; Ashworth and Sheplev, 1997) indicates that this association exists throughout the whole ranges of the L_c and L_m parameters. According to the criterion of thermodynamic stability (Sheplev et al., 1991), the free energy G_{ik} of mineral i in layer k should be lower than or equal to the free energy of this mineral G_{if} in the equilibrium fluid

$$G_{ik} \le G_{if} = N^T\overline{\mu_k},$$

that is

$$\frac{dG_{if}}{dx} \ge 0,$$

where x is the space coordinate across the zoning. In other words, this means that the function $N^T\bar{\mu}_k$ should not decrease away from a layer devoid of mineral i toward a layer containing this mineral. Our numerical calculations of this function indicate that no stability criterion is met by this zoning.

The following expressions were obtained for the growth rates of minerals at the first and second boundaries in the layer succession C || D + F || S:

$$V_{1\mathrm{C}} = -1,$$

$$V_{1\mathrm{D}} = \frac{\frac{1}{L_\mathrm{c}}\left(\frac{4}{L_\mathrm{m}} + 1\right)}{\frac{4}{L_\mathrm{c}L_\mathrm{m}} + \frac{1}{L_\mathrm{c}} + \frac{9}{L_\mathrm{m}}},$$

$$V_{1\mathrm{F}} = -\frac{\frac{2}{L_\mathrm{c}}\left(\frac{1}{L_\mathrm{m}} + 1\right)}{\frac{4}{L_\mathrm{c}L_\mathrm{m}} + \frac{1}{L_\mathrm{c}} + \frac{9}{L_\mathrm{m}}},$$

$$V_{2\mathrm{D}} = \frac{\frac{9}{L_\mathrm{m}}}{\frac{4}{L_\mathrm{c}L_\mathrm{m}} + \frac{1}{L_\mathrm{c}} + \frac{9}{L_\mathrm{m}}},$$

$$V_{2\mathrm{F}} = \frac{6\left(\frac{3}{L_\mathrm{c}L_\mathrm{m}} + \frac{1}{L_\mathrm{c}} + \frac{6}{L_\mathrm{m}}\right)}{\frac{4}{L_\mathrm{c}L_\mathrm{m}} + \frac{1}{L_\mathrm{c}} + \frac{9}{L_\mathrm{m}}},$$

$$V_{1\mathrm{S}} = -3.$$

At any values of the Onsager coefficients, $V_{1\mathrm{D}} > 0$ and $V_{1\mathrm{F}} < 0$. Since the growth rates of these minerals at the same boundary cannot have different signs, this succession should be rejected from further consideration. Analogous tests were carried out for the following successions of layers:

C || F || D + F || S,
C || D + F || F || S,
C || F || D || S,
C || D + F || D || S.

None of them has met the existence conditions of zoning (Sheplev et al., 1991).

Let us now examine the succession of layers C || D || D + F || S. Denoting the growth rate of mineral i at the left- and right-hand boundaries of layer k by W_{ki}^{left} and W_{ki}^{right}, we obtain for them

$$W_{1D}^{\text{left}} = \frac{\frac{1}{L_c}}{\frac{1}{L_c} + \frac{1}{L_m} + 4},$$

$$W_{1D}^{\text{right}} = \frac{\frac{1}{L_c}\left(\frac{1}{L_m} + 1\right)\left(\frac{12}{L_m^2 L_c} + \frac{19}{L_m L_c} + \frac{27}{L_m^2} + \frac{36}{L_m} + \frac{4}{L_c}\right)}{\left(\frac{4}{L_c L_m} + \frac{1}{L_c} + \frac{9}{L_m}\right)\left(\frac{1}{L_c} + \frac{1}{L_m} + 4\right)\left(\frac{3}{L_c L_m} + \frac{1}{L_c} + \frac{6}{L_m}\right)},$$

$$W_{2D}^{\text{left}} = \frac{\frac{3}{L_c L_m}\left(\frac{1}{L_m} + 1\right)}{\left(\frac{4}{L_c L_m} + \frac{1}{L_c} + \frac{9}{L_m}\right)\left(\frac{3}{L_c L_m} + \frac{1}{L_c} + \frac{6}{L_m}\right)},$$

$$W_{2F}^{\text{left}} = -\frac{\frac{2}{L_c}\left(\frac{1}{L_m} + 1\right)}{\left(\frac{4}{L_c L_m} + \frac{1}{L_c} + \frac{9}{L_m}\right)},$$

$$W_{2D}^{\text{right}} = \frac{\frac{9}{L_m}}{\left(\frac{4}{L_c L_m} + \frac{1}{L_c} + \frac{9}{L_m}\right)},$$

$$W_{2F}^{\text{right}} = \frac{6\left(\frac{3}{L_m L_c} + \frac{6}{L_m} + \frac{1}{L_c}\right)}{\left(\frac{4}{L_c L_m} + \frac{1}{L_c} + \frac{9}{L_m}\right)}.$$

Inasmuch as W_{ki}^{left} and W_{ki}^{right} have the same sign for any k and the growth rates of the first and second layers are not negative, all requirements needed for this zoning to form are satisfied at any values of the Onsager parameters. Furthermore, this succession also meets the stability criterion (Sheplev et al., 1991; Ashworth and Sheplev, 1997). As can be seen in Table 3, which presents the calculation results of the G_{if} function for L_c = 1 and L_m = 1, the function $N^T\bar{\mu}_k$ does not diminish away from the layer devoid of mineral i, toward a layer containing this mineral, i.e., the succession C || D || D + F || S is thermodynamically stable throughout the whole range of the Onsager coefficients. For comparison, Table 4 also presents the results of analogous calculations for the succession C || D || F || S. These data indicate that this succession does not satisfy the stability criterion.

Table 3. Values of the dG_{if}/dx function for the succession of layers **C||D||D + F||S** at $L_s = L_m = L_c = 1$

C	**D**	**F**	**S**	k
–0.833	0	0.667	1.167	1
–0.643	0	0	0.214	2

Note: Here and in Table 4, G_{if} is the free energy of mineral i (i = **C**, **D**, **F**, **S**) in the fluid; x is the space coordinate across the zoning, k is the layer number.

Table 4. Values of the dG_{if}/dx function for the succession of layers **C||D||F||S** at $L_s = L_m = L_c = 1$

C	**D**	**F**	**S**	k
–0.833	0	0.667	1.167	1
0	1.8	0	0.6	2

Hence, of the possible layer successions existing at any values of the Onsager coefficients, the stability criterion (Sheplev et al., 1991; Ashworth and Sheplev, 1997) is satisfied by the only succession C || D || D + F || S, which was reproduced experimentally.

ESTIMATION OF THE GROWTH RATES OF BIMETASOMATIC ZONING

Knowing the thicknesses of the grown zones and the duration of their growth, one can quantify the growth rates of the zoning. In the first experiment, in which zoning developed at a dolomite–quartz interface, the only zone of diopside ~2.5×10^{-5} m thick grew for 25–56 days at T = 600–650°C and $P_{H_2O + CO_2}$ = 200 MPa. At T = 750°C and $P_{H_2O + CO_2}$ = 300 MPa, the succession of zones Q || W || D || T || C + F || Dol, where Q is Qtz, W is wollastonite, D is diopside, T is tremolite, C is calcite, F is forsterite, and Dol is dolomite, was produced for 48 days. The thickness of the diopside zone was 1.3×10^{-5} m, and the wollastonite zone was 2.6×10^{-5} m thick. In the other experiment, a succession of zones C || D || D + F || S developed between calcite and serpentine at T = 500°C and $P_{H_2O + CO_2}$ = 200 MPa for 124 days. In this succession, the diopside zone is 6×10^{-4} m thick (on average), and the diopside–forsterite zone is 8×10^{-4} m thick. These data allowed us to calculate the growth rates of bimetasomatic zones. In the first experiment, the reaction rates ranged between 3.1×10^{-12} and 1.2×10^{-11} m/s, and the analogous values for the second experiment are 5.6×10^{-11} to 7.5×10^{-11} m/s.

The expansion of bimetasomatic zoning is essentially controlled by diffusion and determined by the characteristic parameters $w = \frac{x}{\sqrt{t}}$, where x is the distance, and t is the time (Korzhinskii, 1982). Knowing the evaluated x (in meters) and t (in seconds), one can readily calculate w. According to the results of the first experiment, w varies from 6.4×10^{-9} to 1.7×10^{-8} m/s$^{1/2}$, and the analogous value for the second experiment are 1.8×10^{-7} and 2.4×10^{-7} m/s$^{1/2}$. It follows that zoning grew more quickly in the second experiment.

In order to characterize the growth of metasomatic zoning, Zaraisky (1989) made use of the expression $b = \frac{w^2}{2}$, where b is a "constant of zone boundary movement." This expression can be deduced from the relation $w = \frac{x}{\sqrt{t}} = \sqrt{2D_i\frac{\Delta C_i}{\Delta\rho_i}}$, where D_i is the diffusion coefficient, ΔC_i is the concentration change in the pore solution, and $\Delta\rho_i$ is the change of the concentration in the solid phase at the zone boundary (Korzhinskii, 1982). D_i has the meaning of the "effective" diffusion coefficient of composition i in the pore solution with regard to the tortuosity of channels in the porous medium (Zaraisky et al., 1986; Zaraisky, 1989; Dagan, 1989). If the value of w is known, the variations of b can be calculated. From the results of the first experiment (zoning formed at a quartz–dolomite contact), the value of b is approximately assayed to vary within the range of 2×10^{-17} to 1.4×10^{-16} m^2/s; and the analogous estimates for the second experiment (zoning between calcite and serpentine) are 1.6×10^{-14} to 2.9×10^{-14} m^2/s. Obviously, the "constant of zone boundary movement" b is much higher in the latter situation than in the former, and this can be explained by the more active mass transfer due to the elevated water mole fraction in the fluid released during serpentine decomposition in the experiment. The parameter b involves not only mass transfer but also chemical interactions. However, the latter are faster processes than diffusion, and thus, the overall velocity of the boundaries during the growth of the zoning is evidently controlled by diffusion. To calculate the concentration coefficient for Fick's diffusion equation, one should know, along with w, also the concentration of the component in the solution and solid phase on both sides of the metasomatic zone boundary (Korzhinskii, 1982; Zaraisky et al., 1986; Zaraisky, 1989). These parameters were not evaluated within the framework of our research.

CONCLUSIONS

When the processes forming metamorphic rocks and controlling their evolution are studied, much information can be derived from studying mineral relics and reaction textures preserved in these rocks. Among these relics and textures, much attention attract textures produced by diffusion-controlled bimetasomatism at the contacts of heterogeneous originally nonequilibrated rocks or minerals. These textures are the intermediate products of subsolidus mineral transformations en route to the final equilibrium. A model of their genesis was developed within the scope of irreversible thermodynamics in (Fisher, 1973, 1977, 1978; Fisher and Elliott, 1974; Franz and Mao, 1976, 1979; Joesten, 1977, 1986; Ashworth and Sheplev, 1997; Ashworth et al., 1998; Sheplev et al., 1991, 1992, 1998). In this model, a metamorphic rock is regarded as a continual substance with statistically interpreted movements of the particles of the matter. The model is based on the assumption of local thermodynamic equilibrium (Korzhinskii, 1955), which makes it possible to use the Gibbs–Duhem equilibrium together with equations for chemical reactions and Fick's diffusion equations. The model assumes that neither the P–T parameters of a closed system nor its number of phases and chemical components vary; the volume of the solid phases is much greater than the volume of the intergranular fluid; the diffusion flows of components depend on their concentrations and can be expressed through the corresponding gradients of chemical potentials; the concentrations of components in the fluid do not vary (are almost constant) with time and, thus, mass transfer proceeds in a quasistationary regime; all reaction zones are formed concurrently and grow automodelly; a balance of chemical components takes place at zone boundaries; no reactions proceed between the fluid and minerals within all zones; etc. It is usually also assumed that the number of the minerals is greater by one than the number of the components, and, hence, only one reaction can be written for the participating minerals. If the number of the minerals is greater than the number of the components by two or more, the overall reaction is presumed to be a combination of a number of concurrent reactions, etc. The mathematical formulation of the model is a closed system of homogeneous linear differential equations with boundary conditions of the third type and constraints in the form of inequalities. The information derived from the equations is quite extensive: it is possible to calculate the number of the reaction zones–layers, the relative number of phases in each zone, the succession of the zones, their relative thicknesses, etc.

Our experiments on the interaction of serpentine with calcite for 124 days at $T = 500°C$, $P_{H_2O + CO_2} = 200$ MPa, and $X_{CO_2} = 0.5$ have demonstrated the origin of zoning whose succession of zones does not contradict the aforementioned theoretical model. At the same time, our experiments on the interaction of quartz with dolomite for 25–56 days at $T = 600$–$650°C$, $P_{H_2O + CO_2} = 200$ MPa, and $X_{CO_2} = 0.02$–0.55 produced a single zone of diopside, which is at variance with the theoretical prediction in (Franz and Mao, 1976, 1979; Kuznetsova et al., 1992; Sheplev et al., 1998) within the framework of the Korzhinskii–Fisher–Joesten model. The interaction of quartz and dolomite in the CaO–MgO–SiO$_2$–

CO$_2$–H$_2$O system at the aforementioned P–T–X_{CO_2} parameters should result in a number of reaction zones that contain various combinations of talc, forsterite, tremolite, diopside, and calcite. The diversity of the successions of mineral assemblages in the zoning is predetermined by the relative values of the chemical potentials of the diffusing components at constant P, T, and X_{CO_2}. The duration of our experiment (25–56 days) was likely insufficient for the development of metasomatic zoning that could include, along with diopside, also other minerals, and no stationary conditions of diffusion-controlled mass transfer seem to be achieved in the experiment. A very important condition of zoning growth is the saturation of the fluid with respect to all minerals stable within the boundaries of the developing zone (Fisher, 1973, 1977, 1978; Fisher and Elliott, 1974; Franz and Mao, 1976, 1979; Sheplev et al., 1991, 1992, 1998; Kuznetsova et al., 1992). The transitions between zones are controlled by the variations in the chemical potentials of components and depend on the concentrations of the latter in the fluid. If a single diopside zone grows at a contact between dolomite and quartz, the condition of fluid saturation with components was satisfied for diopside alone. The saturation of the fluid with respect to talc, forsterite, calcite, and tremolite was not reached during the experiment, and this resulted in the degeneration of the respective stability fields, so that no aforementioned minerals were formed in the zoning. Conceivably, this was caused by the insufficient dissolution rates of quartz and dolomite and the relatively low diffusion rates of the dissolved species in the low-permeable medium. In the experiments on the interaction between calcite and serpentine, the C || D || D + F || S zoning was produced in complete agreement with the theory. Equilibrium was likely achieved in this situation also thanks to the higher diffusion coefficients of the components.

Some of our experimental results were consistent with the theory (the Korzhinskii–Fisher–Joesten model), whereas others were in conflict with it. Obviously, studies in this field should be continued, and if the metasomatic zoning patterns produced in future experiments are inconsistent with those predicted theoretically (for example, some phases and/or zones are absent or appear, or the changes in the thicknesses of certain zones are out of proportion, i.e., are not automodel, etc), then factors responsible for these deviations and not accounted for in the theory should be identified. Such factors may involve, for example, variations in the concentrations of components in the fluid with time, changes in the growth and dissolution conditions of minerals in the course of the experiments, variations in the rock permeability and the mobility of components, etc.

ACKNOWLEDGMENTS

The authors thank G.P. Zaraisky (Institute of Experimental Mineralogy, Russian Academy of Sciences) and R. Milke (Mineralogisch–Petrographisches Institut, Basel Universität, Switzerland) for constructive criticism that led us to improve the manuscript. This study was financially supported by grants from the President of the Russian Federation (RF NSH-225.2003.05 and NSH-4922.2006.5), the Russian Foundation for Basic Research (project nos. 03-05-65076, 04-05-64358, 04-05-64347, and 05-05-64057), CRDF REC-008 grants (NO-008-XI), YI-CG-08-06 for the independent states of the former Soviet Union.

REFERENCES

1. J. R. Ashworth and V. S. Sheplev, “Diffusion Modelling of Metamorphic Layered Coronas with Stability Criterion and Consideration of Affinity,” Geochim. Cosmochim. Acta **61**, 3671–3689 (1997).
2. J. R. Ashworth, V. S. Sheplev, N. A. Bryxina, et al., “Diffusion-Controlled Corona Reaction and Overstepping in a Garnet Granulite, Yenisey Ridge, Siberia,” J. Metamorph. Geol. **16**, 231–246 (1998).
3. J. B. Brady, “Intergranular Diffusion in Quartz–Periclase Reaction Couples,” Ann. Rept. Geophys. Lab. Carnegie Inst. Yearbook **78**, 577–580 (1979).
4. D. M. Carmichael, “On the Mechanism of Prograde Metamorphic Reactions in Quartz-Bearing Pelitic Rocks,” Contrib. Mineral. Petrol. **20**, 244–267 (1969).
5. E. Dachs and P. Metz, “The Mechanism of the Reaction 1 Tremolite + 3 Calcite + 2 Quartz = 5 Diopside + 3 CO$_2$ + 1 H$_2$O: Results of Powder Experiments,” Contrib. Mineral. Petrol. **100**, 542–551 (1988).
6. G. Dagan, *Flow and Transport in Porous Formations* (Springer, Berlin-Heidelberg, 1989).
7. G. W. Fisher and D. Elliott, “Criteria for Quasi-Steady Diffusion and Local Equilibrium in Metamorphism,” in *Geochemical Transport and Kinetics*, Ed. by A. W. Hofmann et al., Carnegie Inst. Wash. Publ. **634**, 231–241 (1974).
8. G. W. Fisher, “Nonequilibrium Thermodynamics as a Model for Diffusion-Controlled Metamorphic Processes,” Am. J. Sci. **273**, 897–924 (1973).
9. G. W. Fisher, “Rate Laws in Metamorphism,” Geochim. Cosmochim. Acta **42**, 1035–1050 (1978).
10. G. W. Fisher, “The Application of Ionic Equilibria to Metamorphic Differentiation: An Example,” Contrib. Mineral. Petrol. **29**, 91–103 (1970).
11. G. W. Fisher, “Nonequilibrium Thermodynamics in Metamorphism,” in *Thermodynamics in Geology*, Ed. by D. G. Fraser, NATO Adv. St. Inst. Ser. C. (Reidel, Dordrecht, 1977), Vol. 30, pp. 381–403.
12. C. T. Foster, “A Thermodynamic Model of Mineral Segregations in the Lower Sillimanite Zone near Rangeley, Meine,” Am. Mineral. **66**, 260–277 (1981).
13. C. T. Foster, “Mass Transfer in Sillimanite-Bearing Pelitic Schists near Rangeley, Meine,” Am. Mineral. **62**, 727–746 (1977).

14. J. D. Franz and H. K. Mao, "Bimetasomatism Resulting from Intergranular Diffusion. II. Prediction of Multimineralic Zone Sequences," Am. J. Sci. **279**, 302–323 (1979).
15. J. D. Franz and H. K. Mao, "Bimetasomatism Resulting from Intergranular Diffusion: I. A Theoretical Model for Monomineralic Reaction Zone Sequences," Am. J. Sci. **276**, 817–840 (1976).
16. M. Gottschalk and P. Metz, "Konsistente Gleichgewichtsdaten für Reaktionen in Metamorphen Kieseligen Dolomiten," Forts. Mineral. **62**, 78–79 (1984).
17. W. Heinrich, P. Metz, and M. Gottschalk, "Experimental Investigation of the Kinetics of the Reaction: 1 Tremolite + 11 Dolomite = 8 Forsterite + 13 Calcite + 9 CO_2 + 1 H_2O," Contrib. Mineral. Petrol. **102**, 163–173 (1989).
18. W. Heinrich, P. Metz, and W. Bayh, "Experimental Investigation of the Mechanism of the Reaction: 1 Tremolite + 11 Dolomite = 8 Forsterite + 3 Calcite + 9 CO_2 + 1 H_2O. A SEM Study," Contrib. Mineral. Petrol. **93**, 215–221 (1986).
19. R. Joesten and G. Fisher, "Kinetics of Diffusion-Controlled Mineral Growth in the Christmas Mountains (Texas) Contact Aureole," Geol. Soc. Am. Bull. **100**, 714–732 (1988).
20. R. Joesten, "Evolution of Mineral Assemblage Zoning in Diffusion Metasomatism," Geochim. Cosmochim. Acta **41**, 649–670 (1977).
21. R. Joesten, "The Role of Magmatic Reaction, Diffusion and Annealing in the Evolution of Coronitic Microstructure in Troctolitic Gabbro from Risör, Norway," Mineral. Mag. **50**, 441–467 (1986).
22. H.-R. Käse and P. Metz, "Experimental Investigation of the Metamorphism of Siliceous Dolomites: IV. Equilibrium Data of the Reaction: 1 Diopside + 3 Dolomite = 2 Forsterite + 4 Calcite + 2 CO_2," Contrib. Mineral. Petrol. **73**, 151–159 (1980).
23. D. S. Korzhinskii, "Outline of Metasomatic Processes," in *Main Problems in the Concept of Magmatogenic Ore Deposits*, Ed. by A. G. Betekhtin (AN SSSR, Moscow, 1955), pp. 335–456 [in Russian].
24. D. S. Korzhinskii, *Theory of Metasomatic Zoning* (Nauka, Moscow, 1982) [in Russian].
25. S. J. Kridelbaugh, "The Kinetics of the Reaction: Calcite + Quartz = Wollastonite + Carbon Dioxide at Elevated Temperatures and Pressures," Am. J. Sci. **273**, 757–777 (1973).
26. R. P. Kuznetsova, V. S. Sheplev, and V. Yu. Kolobov, "Analysis of the Growth of Zoned Mineral Segregations and Determination of Mass-Transfer Characteristics during Metamorphism. IV. Study of the System SiO_2–MgO–CaO," Geol. Geofiz. **33** (9), 52–61 (1992).
27. P. C. Lichtner, "Continuum Formulation of Multicomponent–Multiphase Reactive Transport," in *Reactive Transport in Porous Media*, Ed. by P. C. Lichtner, C. I. Steefel, and E. H. Oelkers, Rev. Mineral. **34**, 1–81 (1996).
28. A. Lüttge and P. Metz, "Mechanism and Kinetics of the Reaction: 1 Dolomite + 2 Quartz = 1 Diopside + 2 CO_2 Investigated by Powder Experiments," in *Quantitative Methods in Petrology. An issue in honor of H.J. Greenwood*, Ed by T. M. Gordon and R. F. Martin, Can. Mineral. **29**, 803–821 (1991).
29. A. Lüttge and P. Metz, "Mechanism and Kinetics of the Reaction: 1 Dolomite + 2 Quartz = 1 Diopside + 2 CO_2: a Comparison of Rock-Sample and Powder Experiments," Contrib. Mineral. Petrol. **115**, 155–164 (1993).
30. R. Milke and W. Heinrich, "Diffusion-Controlled Growth of Wollastonite Rims Between Quartz and Calcite: Comparison between Nature and Experiment," J. Metamorph. Geol. **20**, 467–480 (2002).
31. R. Milke, M. Wiedenbeck, and W. Heinrich, "Grain Boundary Diffusion of Si, Mg, and O in Enstatite Reaction Rims: a SIMS Study Using Isotopically Doped Reactants," Contrib. Mineral. Petrol. **142**, 15–26 (2001).
32. V. V. Reverdatto and G. Yu. Shvedenkov, "Experimental Determination of the Rates of Metamorphic Reactions," in *Proceedings of the 10th International Symposium on Experimental Mineralogy, Petrology, and Geochemistry, Frankfurt, Germany, 2004* (Frankfurt, 2004), Lithos **73**, Suppl. 1–2, S92 (2004).
33. J. A. Schramke, D. M. Kerrick, and A. C. Lasaga, "The Reaction Muscovite + Quartz = Andalusite + K-Feldspar + Water. Part 1. Growth Kinetics and Mechanism," Am. J. Sci. **287**, 517–559 (1987).
34. V. S. Sheplev, R. P. Kuznetsova, and V. Yu. Kolobov, "Analysis of the Growth of Zoned Mineral Segregations and the Determination of Mass-Transfer Characteristics during Metamorphism. III. Model of Stationary Diffusion," Geol. Geofiz. **33** (6), 49–57 (1992).
35. V. S. Sheplev, V. Yu. Kolobov, R. P. Kuznetsova, and V. V. Reverdatto, "Analysis of the Growth of Zoned Mineral Segregations and Determination of Mass-Transfer Characteristics during Metamorphism. I. Theoretical Model in a Stationary Approximation," Geol. Geofiz. **32** (12), 3–16 (1991).
36. V. S. Sheplev, V. Yu. Kolobov, and R. P. Kuznetsova, "Analysis of Growth of Zonated Mineral Associations," in *Theophrastus' Contributions*, Ed. by J. L. Bowman (Theophrastus, Athens, 1998), Vol. 2, pp. 223–247.
37. G. Yu. Shvedenkov, N. A. Bryksina, and V. V. Reverdatto, "Experimental and Theoretical Modeling of Bimetasomatic Zonality at the Calcite/Serpentine Contact during Rock Metamorphism at 500°C and 200 MPa," Dokl. Akad. Nauk **387**, 245–249 (2002) [Dokl. Earth Sci. **387**, 981–984 (2002)].
38. G. Yu. Shvedenkov, V. V. Reverdatto, and T. A. Bul'bak, "Experimental Modeling of the Formation of Zoned Textures in Siliceous Dolomites," in *Proceedings of International (10th All-Russia) Petrographic Conference Petrography of 21th Century. Metamorphism, Cosmic, Experimental and General Problmes of Petrology, Apatity, Russia, 2005*, Ed. by F. P. Mitrofanov and Zh. A. Fedotov (Kol'sk. Nauchnogo Ts. RAN, Apatity, 2005), Vol. 4, pp. 263–265 [in Russian].
39. G. Yu. Shvedenkov, V. Yu. Kolobov, V. V. Reverdatto, and V. S. Sheplev, "Determination of Ca and Mg Diffusion Coefficients from the Experimental Reproduction of Bimetasomatic Zonality in Quartz–Dolomite Rock Specimens," Dokl. Akad. Nauk **348**, 240–244 (1996) [Dokl. Earth. Sci. **384**, 633–637 (1996).

40. F. S. Spear, *Metamorphic Phase Equilibria and Pressure–Temperature–Time Paths* (Book Crafters, Chelsea, 1993).
41. C. I. Steefel and K. T. B. MacQuarrie "Approaches to Modeling of Reactive Transport in Porous Media," in *Reactive Transport in Porous Media*, Ed. by P. C. Lichtner, C. I. Steefel, and E. H. Oelkers, Rev. Mineral **34**, 83–129 (1996).
42. S. R. Tanner, D. M. Kerrick, and A. C. Lasaga, "Experimental Kinetic Study of the Reaction: Calcite + Quartz = Wollastonite + Carbon Dioxide, from 1 to 3 Kilobars and 500 to 850°C," Am. J. Sci. **285**, 577–620 (1985).
43. R. J. Tracy and B. R. Frost, "Phase Equilibria and Thermobarometry of Calcareous, Ultramafic and Mafic Rocks, and Iron Formations," in *Contact metamorphism*, Ed. by D. Kerrick, Rev. Mineral. **26**, 207–289 (1991).
44. J. V. Walther and B. J. Wood, "Rate and Mechanism in Prograde Metamorphism," Contrib. Mineral. Petrol. **88**, 246–259 (1984).
45. J. V. Walther and P. M. Orville, "Rates of Metamorphism and Volatile Production and Transport in Regional Metamorphism," Contrib. Mineral. Petrol. **79**, 252–257 (1982).
46. B. J. Wood and J. V. Walther, "Rates of Hydrothermal Reactions," Science **222**, 413–415 (1983).
47. G. P. Zaraisky, *Zoning and Conditions of Formation of Metasomatic Rocks* (Nauka, Moscow, 1989) [in Russian].
48. G. P. Zaraisky, V. A. Zharikov, F. M. Stoyanovskaya, and V. N. Balashov, *Experimental Study of Bimetasomatic Skarn Formation* (Nauka, Moscow, 1986) [in Russian].
49. G. P. Zaraisky, Yu. B. Shapovalov, and O. N. Belyaevskaya, *Experimental Study of Acid Metasomatism* (Nauka, Moscow, 1981) [in Russian].