# Short-range mobilization of elements in the biotite zone of contact aureole of the Kharlovo gabbro massif (Russia)

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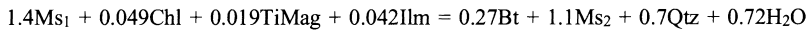
# Short-range mobilization of elements in the biotite zone of contact aureole of the Kharlovo gabbro intrusion (Russia)

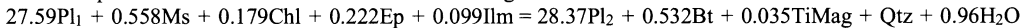Igor I. LIKHANOV[1], Vladimir V. REVERDATTO[1]
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**Abstract:** Biotite formation occurred at 400-430° in the contact aureole of the Kharlovo gabbro massif, according to the reaction :
$1.4Ms_1 + 0.049Chl + 0.019TiMag + 0.042Ilm = 0.27Bt + 1.1Ms_2 + 0.7Qtz + 0.72H_2O$
whereas epidote breakdown occurred at 450° according to the reaction:
$27.59Pl_1 + 0.558Ms + 0.179Chl + 0.222Ep + 0.099Ilm = 28.37Pl_2 + 0.532Bt + 0.035TiMag + Qtz + 0.96H_2O$
Mass balance and compositional variation in the outer part of the contact aureole shows that mass transfer of the main petrogenetic components was confined to small domains of a few hundredths of $mm^3$ in chlorite-biotite-mica and epidote-plagioclase-titanomagnetite aggregates. The chemical homogeneity of the environment was practically unaffected by the thermal metamorphism.

**Key-words**: biotite, epidote, low-grade contact metamorphism, mineral reactions, mass balance, Altay, Russia.

## Introduction

One of the problems of metamorphic petrology is the behaviour of matter at different levels of organization: from beds and layers to mineral grains, aggregates and segregates. Textural study of metamorphic reactions, together with calculation of volumes affected by matter exchange, may be a useful approach, especially when low temperatures and short times prevent the attainment of large-scale equilibrium. Variations in thermodynamic conditions are recorded by phase transitions, structures, textures and rock or mineral zoning. Mass transfer may be of further interest in connection with the quantitative treatment of metamorphic ore formation.

This problem is discussed for two low-temperature metamorphic reactions occurring in metapelites from the contact aureole of the Kharlovo gabbro massif.

## Geological setting and whole-rock chemistry

The study area is the contact aureole of the Kharlovo gabbro massif at the north-west foot of the Altay mountain range in Siberia, close to the village of Kharlovo, on the bank of the Charysh river. The gabbro massif crops out over a circular area of about 12 $km^2$. The intrusion (Fig. 1) comprises concentric bands of alternating ore-bearing (titanomagnetite) and ore-free layers, forming a "funnel-shaped" structure (Sakovych, 1969). The massif comprises two different magmatic phases which were later injected by various dyke swarms.
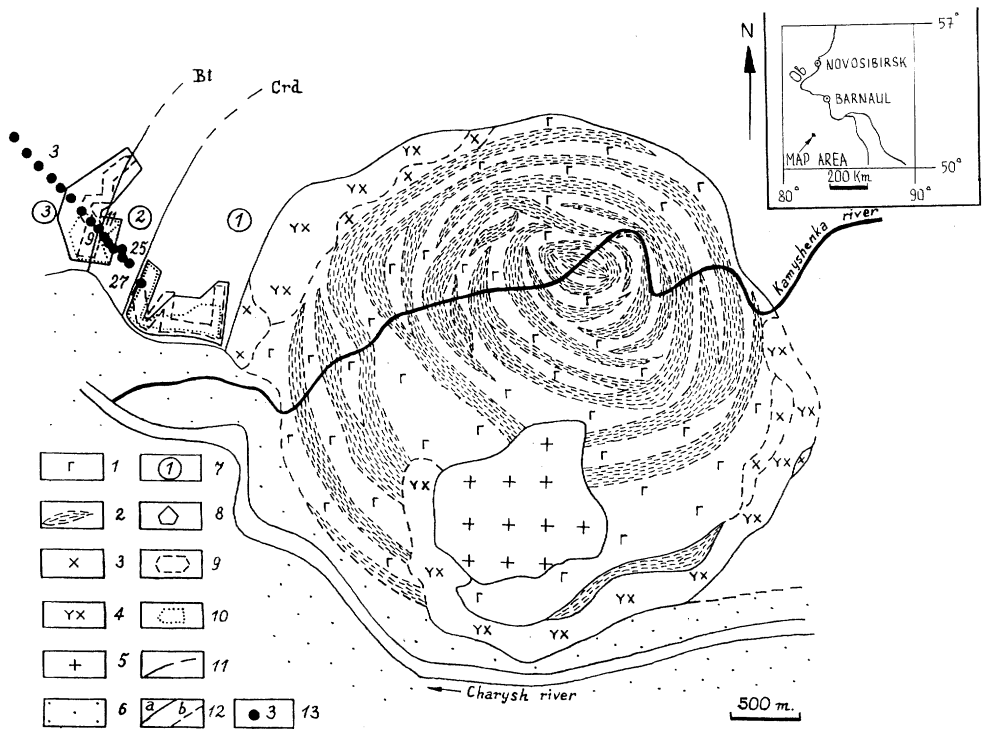
Fig. 1. The Kharlovo gabbro massif and a fragment of the western part of the contact aureole.
1 - leucogabbro; 2 - titanomagnetite melanogabbro; 3 - diorite; 4 - syenite-diorite; 5 -granodiorite; 6 - alluvium; 7 - metamorphic zones: 1 - inner, middle and spotted hornfelses zones; 2 - outer biotite zone; 3 - unaltered country rocks; contours of sampling areas: 8 - for study of rare earth and trace element distributions, 9 - F, 10 - U, Th, Au, Fe, P; 11 - positions of isograds; 12 - geological boundaries: mapped (a) and deduced from magnetic survey data (b); 13 - sample location.

More than 90% of the intrusive body is composed of rocks of the first magmatic phase: a dark olivine-titanomagnetite gabbro alternating with bands of ore-free leucocratic gabbro in the core, surrounded by a fine-grained diorite and syenodiorite shell. During the last phase, medium-grained granodiorites formed and now cross-cut the gabbro as small stocks. Finally, several dyke swarms, ranging from diabase to granite-porphyries, were injected through the massif.

K-Ar ages of the Kharlovo gabbro are about 420-430 Ma (Sakovych, 1969). The two intrusive phases were closely spaced in time and allow us to consider them together as an Early Devonian igneous complex. Probably the dry gabbro plutonic body was the principal heat source of the contact metamorphism.

The contact with the country rocks is sharp and discordant. The country rocks consist of psammitic rocks regionally metamorphosed to greenschist facies conditions. The rocks enclosing the massif to the west are homogeneous metapelites (Table 1).

A geochemical study carried out by Reverdatto (1973) and Reverdatto et al. (1974) on country and contact metamorphic rocks revealed the isochemical nature of the contact metamorphism, based on comparison of the mean values, contents and dispersion of major, rare earth and trace elements between hornfels and unaltered schists. Similar patterns were found for rare and trace elements, including U, Th, P, Au, F (Reverdatto et al., 1976, 1978; Kolobov et al., 1986). Variable contents were detected only for FeO and

Table 1. Selected whole-rock compositions of rocks from country rock schist (sample 3), outer biotite zone (samples 9, 11, 25) and spotted hornfels zone (sample 27).

| Samp.N | 3 | 9 | 11 | 25 | 27 |
|---|---|---|---|---|---|
| $SiO_2$ | 65.70 | 67.80 | 66.10 | 66.80 | 60.30 |
| $TiO_2$ | 0.80 | 0.80 | 0.79 | 0.64 | 0.97 |
| $Al_2O_3$ | 13.00 | 12.80 | 15.00 | 13.90 | 19.20 |
| $Fe_2O_3$ | 6.20 | 6.10 | 6.10 | 5.66 | 7.48 |
| MnO | 0.10 | 0.07 | 0.06 | 0.13 | 0.09 |
| MgO | 2.44 | 2.44 | 2.60 | 2.04 | 3.54 |
| CaO | 1.91 | 2.13 | 1.06 | 0.76 | 0.87 |
| $Na_2O$ | 3.13 | 3.22 | 3.65 | 3.48 | 3.10 |
| $K_2O$ | 1.30 | 1.22 | 1.60 | 2.21 | 2.87 |
| $P_2O_5$ | 0.21 | 0.20 | 0.20 | 0.23 | 0.26 |
| L.O.I. | 4.46 | 3.05 | 3.03 | 3.25 | 1.04 |
| $H_2O$ | 0.37 | 0.20 | 0.37 | 0.25 | 0.12 |
| Tot. | 99.62 | 100.04 | 100.56 | 99.35 | 100.53 |

Position of samples shown in Fig. 1.

$H_2O$, and can be explained by variations in $H_2O$ and $O_2$ fugacity during metamorphism.

## Mineral zones and isograds

The thermal effects of the gabbro pluton on the country rocks are first perceptible through the appearance of fine biotite flakes in chlorite-muscovite-plagioclase-quartz-ilmenite-magnetite-epidote schists. The rocks preserve most of their pre-contact metamorphic features, such as clastic grains, relict psammitic texture and schistosity. Typical low-grade biotite-bearing hornfelsic schists are micro- or fine-grained banded rocks, grey or dark-grey in colour with relict psammitic and fragmentary newlyformed lepidogranoblastic textures. The lepidogranoblastic fine-grained matrix consists of recrystallized aggregates of muscovite-biotite-chlorite-quartz-albite with epidote, carbonate and ore mineral admixtures. These low-grade biotite-bearing hornfelsic schists differ from the country rocks by virtue of their more compact structure, darker colour and biotite content. The contact aureole, as defined by the biotite isograd, extends 1.2 km to the west of the massif (Fig. 1). It exhibits distinct zonation due to changes in hornfels structure and mineral associations. The following sequence of mineral associations (most frequent minerals underlined; mineral abbreviations according to Kretz, 1983) is observed within the aureole moving towards the pluton :
1) Chl + Ms + Pl + Qtz + Ilm + Mag + Ep + Hem ± Cal (country rocks),
2) Bt + Ms + Chl + Pl + Qtz + Mag ± Ep (outer biotite zone),
3) Crd + Bt + Ms + Qtz + Pl + Mag (spotted hornfels zone),
4) Crd + Bt + Pl + Qtz + And ± Mag (middle zone),
5) Crd + Bt + Pl + Kfs + Qtz + And ± Mag (inner zone),
6) Crd + Bt + Spn + Sil + Pl + Kfs + Mag (quartz-free segregations in inner zone).

Thicknesses are about 400 m for the biotite zone, (i.e. association 2); 300 m in the spotted hornfels zone (association 3); 400 m in the middle zone (association 4); 50 m in the inner zone (association 5). Spinel-cordierite-sillimanite-bearing quartz-free aggregates occur locally in the inner zone within 10 m of the contact. The genesis of these aggregates reflects the compositional heterogeneity of the protolith.

## Methods of investigation

The following methods were used : 1) bulk chemical analysis of rocks and minerals (Tables 1, 2, 4); 2) calculation of modal mineral composition (Table 3) on the basis of whole-rock chemistry (Ferry, 1984); 3) calculation of chemical reactions in hornfels and comparison with volume relations in the rocks; 4) estimation of the minimum volume involved in the redistribution of chemical components followed by mass balance and analysis of mass transfer.
1) Whole-rock chemical analyses (Table 1) were performed in the chemical laboratory of the Institute of Geology, Siberian Branch of the Academy of Science of Russia, Novosibirsk by I.M. Phominykh. Mineral compositions were determined using a CAMEBAX-micro automated electron microprobe at the Institute of Mineralogy and Petrography, Novosibirsk (Table 2). Chemical analysis of the phases in fine-grained and interlayered aggregates were performed with an EDAX energy dispersive system attached to a PHILIPS 515 SEM at the Earth Science Department of Siena University, Italy (Table 4). Analytical conditions were : 15 kV and 20 μA emis-

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Table 2. Average composition and structural formulae for minerals from country rock schists (c.s.), outer biotite zone (b.z.) and spotted hornfels zone (h.z.).

| | Muscovite | | | Chlorite | Bt | Crd | Epidote | | | | Plagioclase | | | | Ilm | TMag |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Zone | c.s | b.z | h.z | c.s | h.z | h.z | c.s. | c.s. | h.z. | h.z. | c.s. | c.s. | h.z. | h.z. | c.s | c.s |
| N | 7 | 6 | 4 | 7 | 4 | 3 | $5_{core}$ | $5_{rim}$ | $4_{core}$ | $4_{rim}$ | $4_{core}$ | $4_{rim}$ | 4 | 4 | 3 | 3 |
| $SiO_2$ | 49.69 | 48.52 | 48.94 | 27.24 | 37.74 | 48.94 | 40.98 | 39.54 | 38.73 | 39.34 | 69.76 | 70.79 | 69.13 | 69.26 | - | - |
| $TiO_2$ | 0.12 | 0.36 | - | - | 3.18 | - | 0.01 | 0.03 | 0.05 | 0.21 | - | - | - | - | 55.16 | 7.52 |
| $Al_2O_3$ | 27.75 | 34.57 | 35.22 | 20.12 | 18.94 | 30.97 | 23.38 | 22.70 | 22.97 | 22.57 | 19.37 | 19.49 | 19.83 | 21.05 | - | 0.24 |
| FeO | 3.21 | 1.60 | 0.53 | 23.91 | 21.70 | 9.71 | 12.44 | 13.74 | 12.71 | 13.15 | - | - | - | - | 40.28 | 77.04 |
| MgO | 2.17 | 1.22 | 0.61 | 15.28 | 6.53 | 7.89 | 0.13 | 0.05 | 0.16 | 0.08 | - | - | - | - | 0.23 | 3.76 |
| MnO | - | - | - | - | - | - | 0.11 | 0.08 | 0.10 | 0.19 | - | - | - | - | - | 0.79 |
| CaO | - | - | - | - | - | - | 20.07 | 21.27 | 21.34 | 21.50 | 0.11 | 0.15 | 0.21 | 0.82 | - | - |
| $Na_2O$ | 0.27 | 0.25 | 0.55 | - | 0.03 | - | 0.02 | 0.03 | 0.05 | 0.03 | 10.56 | 10.43 | 9.95 | 9.81 | 0.87 | - |
| $K_2O$ | 8.93 | 9.97 | 10.64 | 0.06 | 9.76 | - | - | 0.01 | 0.01 | 0.01 | 0.05 | 0.07 | 0.09 | 0.17 | - | - |
| Sum | 92.14 | 96.49 | 96.34 | 86.61 | 94.93 | 97.52 | 97.15 | 97.44 | 96.10 | 97.07 | 99.85 | 100.92 | 99.20 | 101.11 | 96.54 | 89.35 |
| Si | 3.41 | 3.17 | 3.19 | 2.87 | 2.69 | 5.11 | 6.59 | 6.43 | 6.37 | 6.42 | 3.03 | 3.04 | 3.02 | 2.98 | - | - |
| Ti | 0.01 | 0.02 | - | - | 0.19 | - | - | - | 0.01 | 0.02 | - | - | - | - | 1.06 | 0.20 |
| Al | 2.24 | 2.66 | 2.71 | 2.50 | 1.73 | 3.80 | 4.43 | 4.35 | 4.45 | 4.33 | 0.99 | 0.99 | 1.02 | 1.07 | - | 0.01 |
| Fe | 0.18 | 0.09 | 0.03 | 2.11 | 1.41 | 0.85 | 1.67 | 1.87 | 1.75 | 1.79 | - | - | - | - | 0.86 | 3.34 |
| Mg | 0.22 | 0.12 | 0.06 | 2.40 | 0.75 | 1.23 | 0.03 | 0.01 | 0.04 | 0.02 | - | - | - | - | 0.01 | 0.20 |
| Mn | - | - | - | - | - | - | 0.01 | 0.01 | 0.01 | 0.02 | - | - | - | - | - | 0.02 |
| Ca | - | - | - | - | - | - | 3.46 | 3.71 | 3.76 | 3.76 | 0.01 | 0.01 | 0.01 | 0.04 | - | - |
| Na | 0.04 | 0.03 | 0.07 | - | 0.01 | - | - | 0.01 | 0.02 | 0.01 | 0.89 | 0.87 | 0.84 | 0.82 | 0.04 | - |
| K | 0.78 | 0.83 | 0.88 | 0.01 | 0.96 | - | - | - | - | - | - | - | 0.01 | 0.01 | - | - |

All Fe as FeO. N = Number of averaged spot analyses. Epidote, cations per 25 oxygen atoms; cordierite, cations per 18 oxygen atoms; chlorite, cations per 14 oxygen atoms; biotite and muscovite, cations per 11 oxygen atoms; plagioclase, cations per 8 oxygen atoms; titanomagnetite, cations per 4 oxygen atoms; ilmenite, cations per 3 oxygen atoms. Chemical analysis of chlorites and biotites from outer biotite zone are shown in Table 4.

Table 3. Calculated mineral abundances for selected country rocks and for rocks of the outer parts of the Kharlovo aureole.

| Samp.N | Content, mole/cm³ | | | | Content, vol.% | | | | |
|---|---|---|---|---|---|---|---|---|---|
|  | 3 | 11 | 25 | 27 | 3 | 9 | 11 | 25 | 27 |
| Muscovite | 0.939 | 0.740 | 0.676 | 0.676 | 4.220 | 3.680 | 3.960 | 3.220 | 4.500 |
| Chlorite | 0.355 | 0.260 | 0.165 | - | 1.600 | 1.450 | 1.390 | 0.790 | - |
| Biotite | - | 0.083 | 0.744 | 1.484 | - | 0.520 | 0.440 | 3.550 | 9.880 |
| Epidote | 0.253 | 0.102 | 0.060 | - | 1.140 | 0.780 | 0.540 | 0.290 | - |
| Plagioclase | 3.110 | 4.960 | 3.800 | 3.130 | 13.980 | 14.730 | 26.540 | 18.150 | 20.570 |
| Quartz | 16.850 | 11.670 | 15.180 | 8.980 | 75.770 | 75.920 | 62.450 | 72.510 | 59.790 |
| Magnetite | 0.565 | 0.870 | 0.309 | 0.092 | 2.540 | 2.310 | 4.660 | 1.480 | 0.610 |
| Ilmenite | 0.167 | - | - | - | 0.750 | 0.600 | - | - | - |
| Cordierite | - | - | - | 0.664 | - | - | - | - | 4.420 |

Positions of samples shown in Fig. 1.

sion current, spot size 500 Å. Natural minerals were used as standards.

2) Because of the small grain size and complex intergrowths, the modes of minerals (Table 3) were calculated from their average composition in a sample and the sample's whole-rock chemical composition (Table 1). For each sample :

$$i/Al = (\Sigma a_{i,j} n_j / \Sigma a_{Al,j} n_j) \qquad (1)$$

where $i/Al$ is the whole-rock atomic ratio of an element with respect to Al, $n_j$ is the number of moles of each mineral species $j$ in a sample and $a_{i,j}$ is the number of atoms of $i$ per standard formula unit of mineral $j$ (from data such as those given in Tables 2 and 4). The volume of rock considered was arbitrarily taken as 1000 cm³

$$\Sigma \bar{V}_j n_j = 1000 \qquad (2)$$

where $\bar{V}_j$ is the molar volume of $j$. Values of $n_j$ were calculated for samples by solving Eqs (1) and (2); moles of mineral $j$ were recalculated as volumes (modes) using molar volume data for minerals from Karpov *et al.* (1976).

3) To test the reliability of equation (1), a volume of reacting phases was estimated by the following relationships: $V'_j = n_j \bar{V}_j$, where n is the number of moles of mineral $j$ from the reaction equation. The ratio of the mineral volumes of phases is estimated in relation to the volume of one of the newly formed minerals ($V'_j/V_{Bt}$ in Table 5). These volume ratios were compared with variations in phase contents calculated by whole rock chemistry ($\Delta V_j / \Delta V_{Bt}$ in Table 5).

4) The balance of petrogenetic components was estimated for small aggregates, where a var-iation in mineral content occurred as a result of reaction at constant volume. We compared the number of component moles in such aggregates before and after the reaction. This enabled us to determine the character of the mineral transfor-mations and amounts of mass-transfer (Table 6).

## Mineral chemistry

The average compositions and structural formulae of the main minerals appear in Table 2. Muscovite, widespread in the country rocks and hornfelses, has a celadonite content - expressed as $(Mg + Fe/(Mg + Fe + Al^{VI}))$ - decreasing from 0.2 (unaltered country rocks) to 0.04 (hornfels zone) and is intermediate in terms of the mus-covite-ferrimuscovite-phengite solid solution (Kanehira & Banno, 1960).

The arrow in Fig. 2 shows the compositional trend of muscovite with increasing metamorphic grade.

Chlorite, ubiquitous in the country rocks, abruptly declines in quantity at the biotite-in iso-grad and completely disappears in the spotted hornfelses (Table 3). Its composition varies little: from Fe-clinochlore to Fe-Al-clinochlore (Bayl-iss, 1975; Bailey, 1980).

Biotite grows exclusively from chlorite, replac-ing it along grain boundaries, fractures and cleav-age planes (Fig. 3). SEM-EDS analyses of chlorites, biotites and their aggregates are shown in Table 4. The compositions compare well with

Table 4. Chemical data and calculated cation contents for samples 11 and 9, assuming (a) to be chlorite, (b) a 2:1 chlorite/biotite mixed-layer, (c) a 1:1 chlorite/biotite mixed-layer, and (d) biotite.

| | | 11 | | | | 9 | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | a | b | c | d | a | b | c | d |
| | $SiO_2$ | 29.65 | 29.11 | 34.99 | 34.49 | 25.65 | 33.06 | 33.71 | 36.17 |
| | $TiO_2$ | 0.31 | 1.49 | 1.44 | 3.01 | 0.04 | 2.77 | 3.06 | 2.56 |
| | $Al_2O_3$ | 20.62 | 18.64 | 18.69 | 17.35 | 23.35 | 20.90 | 20.83 | 20.59 |
| | FeO | 19.48 | 20.06 | 19.92 | 20.95 | 23.44 | 21.18 | 20.78 | 18.09 |
| | MgO | 15.79 | 14.68 | 11.70 | 8.44 | 14.98 | 15.09 | 14.08 | 10.21 |
| | MnO | 0.28 | 0.31 | 0.28 | 0.13 | 0.08 | - | - | - |
| | CaO | 0.16 | 0.04 | 0.25 | 0.08 | - | - | - | - |
| | $Na_2O$ | 0.13 | 0.04 | 0.51 | 0.18 | - | 0.13 | - | 0.03 |
| | $K_2O$ | 0.54 | 2.70 | 3.64 | 9.31 | 0.12 | 2.77 | 3.86 | 9.00 |
| | Tot | 86.96 | 87.07 | 91.42 | 93.96 | 87.66 | 95.90 | 96.32 | 96.65 |
| "talc" layer { | Si | 3.03 | 2.82 | 3.07 | 2.70 | 2.67 | 2.88 | 2.82 | 2.68 |
| | Al | 0.97 | 1.18 | 0.93 | 1.30 | 1.33 | 1.12 | 1.18 | 1.32 |
| | Al | 0.76 | 0.57 | 0.66 | 0.30 | 0.77 | 0.67 | 0.57 | 0.48 |
| | Ti | 0.02 | 0.11 | 0.09 | 0.18 | - | 0.18 | 0.19 | 0.14 |
| | Fe | 0.84 | 0.98 | 0.97 | 1.37 | 1.02 | 0.92 | 0.96 | 1.12 |
| | Mn | 0.02 | 0.03 | 0.02 | 0.01 | 0.01 | - | - | - |
| | Mg | 1.21 | 1.27 | 1.02 | 0.98 | 1.16 | 1.18 | 1.15 | 1.13 |
| | OH | 2.00 | 2.00 | 2.00 | 2.00 | | | | 2.00 |
| "brucite" or cation layer | | | | | | 2.00 | 2.00 | 2.00 | |
| { | Al | 0.76 | 0.38 | 0.34 | - | 0.76 | 0.45 | 0.30 | - |
| | Mg | 1.20 | 0.85 | 0.51 | - | 1.16 | 0.78 | 0.60 | - |
| | Fe | 0.83 | 0.65 | 0.49 | - | 1.02 | 0.62 | 0.49 | - |
| } | OH | 6.00 | 4.00 | 3.00 | - | 6.00 | 4.00 | 3.00 | - |
| | K | 0.07 | 0.33 | 0.41 | 0.93 | 0.02 | 0.31 | 0.41 | 0.85 |
| | Na | 0.03 | 0.01 | 0.09 | 0.03 | - | 0.02 | - | - |
| { | Ca | 0.02 | - | 0.02 | 0.01 | - | - | - | - |

Al, Fe and Mg distributed in equal proportions between "talc" and "brucite" layers, Mn in "talc" only. (OH)$^-$ content assumed. FeO = Fe$_{Total}$.

Table 5. Comparison of observed mineral volume ratios with values calculated from the biotite-forming reaction (1).

| Mineral | $V_j.10^{-3}mm^3$ | | $V_j$ (vol.%) | | $\Delta V_j$ | $\dfrac{\Delta V_j}{\Delta V_{Bt}}$ | $V'_j$ | $\dfrac{V'_j}{V'_{Bt}}$ |
|---|---|---|---|---|---|---|---|---|
| | 3 | 9 | 3 | 9 | | | | |
| Chlorite | 0.190 | 0.170 | 1.600 | 1.450 | -0.150 | 0.290 | 10.200 | 0.240 |
| Biotite | - | 0.060 | - | 0.520 | +0.520 | 1.000 | 41.660 | 1.000 |
| Muscovite | 0.500 | 0.440 | 4.220 | 3.680 | -0.540 | 1.040 | 42.210 | 1.010 |
| Magnetite | 0.300 | 0.270 | 2.540 | 2.310 | -0.230 | 0.440 | 0.080 | 0.002 |
| Ilmenite | 0.090 | 0.070 | 0.750 | 0.600 | -0.150 | 0.290 | 1.330 | 0.030 |
| Quartz | 8.900 | 9.010 | 75.770 | 75.920 | +0.150 | 0.290 | 15.880 | 0.380 |

$V_j$ = a volume of mineral j, where j is chlorite, biotite, muscovite, magnetite, ilmenite, quartz in a rock volume of 0.01 mm$^3$, $V'_j$ = mineral volume calculated from reaction equation. $\Delta V_j$ = changes in mineral volumes as a result of the biotite-forming reaction.

Table 6. The balance of petrogenetic components before (sample 3) and after (sample 9) the biotite formation reaction.

| | 3 | | | | | | | 9 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | N | nSiO₂ | nTiO₂ | nAl₂O₃ | nFeO | nMgO | nK₂O | N | nSiO₂ | nTiO₂ | nAl₂O₃ | nFeO | nMgO | nK₂O |
| Chlorite | 0.09 | 0.26 | - | 0.23 | 0.19 | 0.22 | - | 0.08 | 0.21 | - | 0.23 | 0.16 | 0.19 | - |
| Biotite | - | - | - | - | - | - | - | 0.04 | 0.11 | 0.01 | 0.07 | 0.04 | 0.05 | 0.03 |
| Muscovite | 0.36 | 1.23 | - | 0.81 | 0.06 | 0.08 | 0.28 | 0.31 | 0.98 | 0.01 | 0.82 | 0.03 | 0.04 | 0.26 |
| Magnetite | 0.67 | - | 0.13 | 0.01 | 1.57 | 0.13 | - | 0.61 | - | 0.12 | 0.01 | 1.43 | 0.12 | - |
| Ilmenite | 0.28 | - | 0.30 | - | 0.24 | - | - | 0.22 | - | 0.23 | - | 0.19 | - | - |
| Quartz | 39.22 | 39.22 | - | - | - | - | - | 39.71 | 39.71 | - | - | - | - | - |
| Tot | | 40.71 | 0.43 | 1.05 | 2.06 | 0.43 | 0.28 | | 41.01 | 0.37 | 1.13 | 1.85 | 0.40 | 0.29 |

$N = V_j / \bar{V}_j$ - molar quantity of minerals (in moles) in volume of rock = 0.01 mm³, $n_k = N n_{k,i}$ - molar quantity of petrogenetic components in mineral j, where k is $SiO_2$, $TiO_2$, $Al_2O_3$, FeO, MgO and $K_2O$ ($n_k \cdot 10^{-8}$ moles).

the 2:1 and 1:1 chlorite/biotite interstratifications described by Maresch et al. (1985). Atomic proportions (atoms per formula unit, a.f.u.) of various elements vs. K are shown in Fig. 4; whereas the Si content is practically constant, the K increase (from 0.07 to 0.93 a.f.u.) is accompanied by decreasing octahedral cations (Mg + Fe + $Al^{VI}$) (from 5.59 to 2.65 a.f.u.) and a parallel increase in the (Fe/(Fe + Mg)) ratio (from 0.41 to 0.58). The (Fe/(Fe + Mg)) ratio of the biotite ranges from 0.5 in spotted hornfels to 0.7-0.75 in the inner zone of the contact aureole (Reverdatto, 1967).
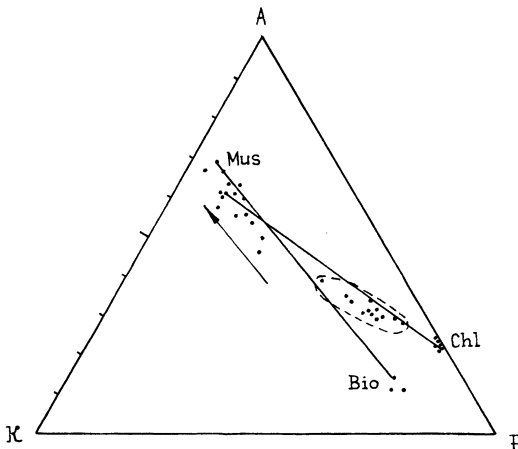


Fig. 2. A'KF diagram showing compositions of minerals (dots) and rocks (dots with dashed outline). Tie-lines joining Ms₁-Chl and Ms₂-Bt are shown as solid lines. The arrow shows the compositional trend of muscovite with increasing metamorphic grade.
A' = $Al_2O_3$-$K_2O$-$Na_2O$; F = FeO + MgO + MnO; K = $K_2O$.

The plagioclase in the country rocks is unzoned with a (Ca/(Ca + Na)) ratio of 0.004 to 0.01. Near the biotite isograd - where epidote breakdown occurs - the (Ca/(Ca + Na)) ratio increases to 0.05 and reverse zoning is observed. The (Ca/(Ca + Na)) ratio finally increases up to 0.14-0.15 in cordierite-bearing spotted hornfels, as in the Ballachulish aureole (Pattison & Harte, 1991). Andesine remains stable in the massive hornfels of the inner zone.

Epidote occurs as small (up to 0.2 mm), rare, rounded or irregular grains. In the country rocks it is usually zoned, with rims enriched in Fe and Ca and depleted in Al relative to the core. Near the biotite-in isograd and in the outer biotite zone, the epidote grains are no longer zoned but appear corroded (Fig. 5), partially replaced by magnetite and recrystallized into aggregates of smaller prismatic crystals. The unzoned epidote is a chemically homogeneous pistacite (Ps = Fe/(Fe + Al) = 0.22-0.33) having the highest pistacite content (up to 33%) when associated with two ore phases (ilmenite and titanomagnetite). Moving further towards the contact, epidote disappears completely in the spotted hornfels zone.

Cordierite occurs in spotted hornfels as small porphyroblasts in the lepidogranoblastic matrix. In the massive hornfels, cordierite forms irregularly twinned polygonal grains or aggregates of smaller subgrains having honeycomb-like extinction. The (Fe/(Fe + Mg)) ratio of the mineral ranges from 0.22-0.40 in spotted hornfels to 0.44-0.50 in the inner zone of the contact aureole.

Ore phases - mainly ilmenite and titanomagnetite - are common as fine grains. Approaching the contact, the Ti content in magnetite increases
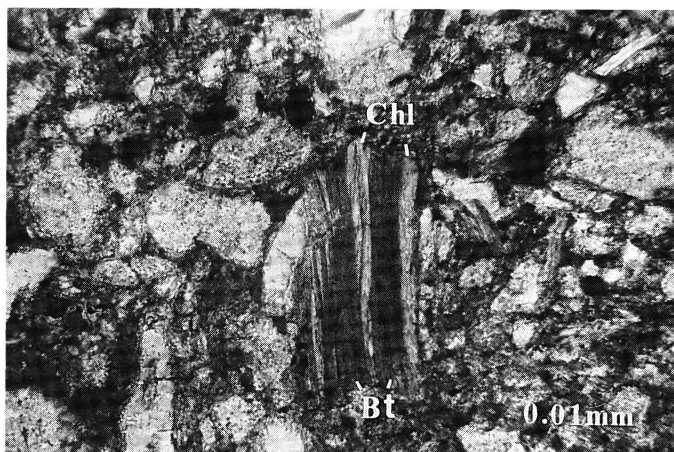
Fig. 3. Chlorite-biotite aggregate in chlorite-mica matrix. Sample 9. Polished section, plane light.

from 0.10 to 0.28 a.f.u. Less magnetite is observed in the hornfelses of the inner zones of the aureole; hematite disappears in the biotite zone.

The (Fe/(Fe + Mg)) ratio of cordierite and biotite generally increases with increasing temperature, due to reaction with magnetite, the modal content of which decreases towards the contact with the gabbro massif (Reverdatto, 1967).
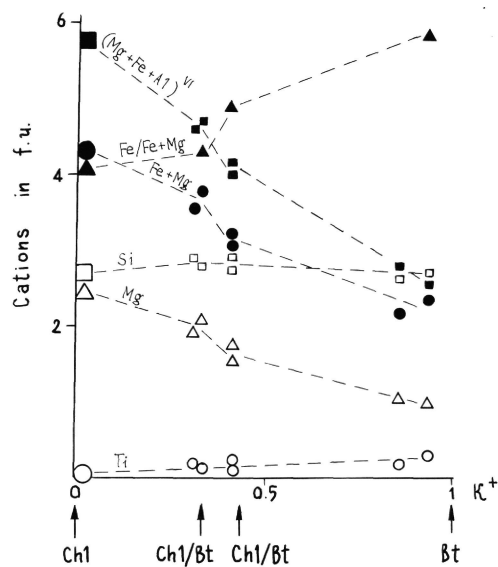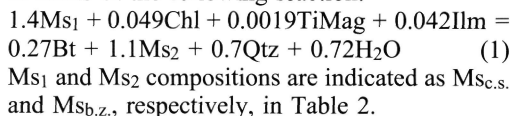


Fig. 4. Cations in f.u. *vs.* K content for chlorite, biotite, 1:1 and 2:1 chlorite/biotite mixed-layer interstratifications.

## Mineral reactions and mass balance

The reactions producing biotite in metapelites, though discussed by many authors (Ernst, 1963; Mather, 1970; Korikovsky, 1973; Ono, 1977; Carmignani *et al.* 1982; Ferry, 1984; Miyashiro & Shido, 1985; Wang *et al.*, 1985), have rarely been studied in contact metamorphic rocks (Tilley, 1924; Rastall, 1910; Pitcher & Sinha, 1958; Pattison, 1987; Pattison & Harte, 1991; Pattison & Tracy, 1991). In these studies the reactions were generally postulated without precise information on mineral composition.

The appearance of biotite in the contact aureole of the Kharlovo massif, in the system $SiO_2$-$TiO_2$-$Al_2O_3$-FeO-MgO-$K_2O$-$H_2O$ and on the basis of analytical mineral data, may be written in terms of the following reaction:

$$1.4Ms_1 + 0.049Chl + 0.0019TiMag + 0.042Ilm = 0.27Bt + 1.1Ms_2 + 0.7Qtz + 0.72H_2O \qquad (1)$$

$Ms_1$ and $Ms_2$ compositions are indicated as $Ms_{c.s.}$ and $Ms_{b.z.}$, respectively, in Table 2.

This reaction appears on the A'KF diagram (Fig. 2) as the intersection of the more phengitic muscovite-chlorite with the less phengitic muscovite-biotite tie-line. The reaction is confirmed by mineral abundances in thin section, where the formation of biotite is accompanied by decreasing contents of chlorite, muscovite and ore minerals in parallel with changing white mica composition.

Table 5 reports modal abundances under biotite-out (specimen 3) and biotite-in (specimen 9)
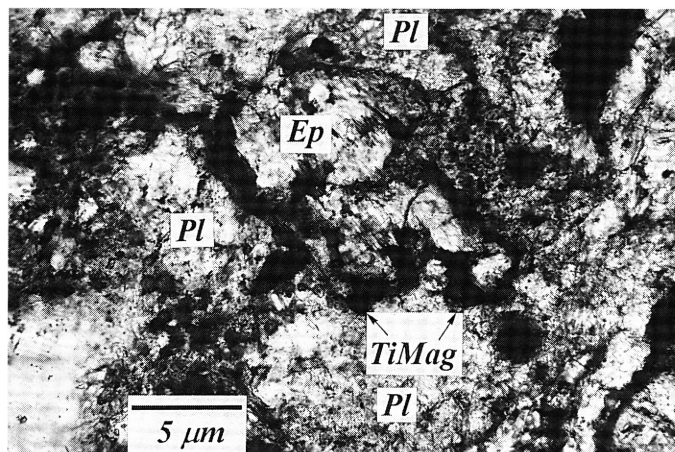
Fig. 5. Epidote grain partially replaced by magnetite. Sample 17. Polished section, plane light.

conditions. These data closely match values calculated using molar volumes from Karpov *et al.* (1976), after testing the internal consistency according to Ferry (1984). Minor discrepancies may be due to minor differences in whole-rock composition and to errors in the calculation of the molar volume of minerals with variable composition. The balance of petrogenetic components was estimated for fine chlorite-biotite-mica segregations. Mass balance analysis (Table 6) showed that the reaction volume in the rock is of the order of 0.01 mm$^3$ (the boundary of the chlorite-biotite aggregate with other minerals) (Likhanov, 1989). This reaction volume, although it is a minimum estimate for mass transfer, does not preclude a larger reaction volume; in fact, although the contribution to mineral growth was mostly from the nearest neighbours (Reverdatto & Kolobov, 1987), the actual volume in which chemical exchange occurred may have been greater. The newly forming minerals may also have received substances from more distant dissolving minerals.
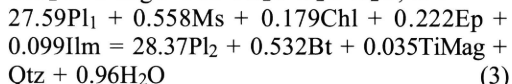
The temperature of the regional metamorphism in the country rocks (calculated by the chlorite-muscovite and muscovite-plagioclase geothermometers; Kotov, 1986) was 350-380°C. The temperature of thermal metamorphism within the biotite zone near the biotite-in isograd was 400-430°C, according to the muscovite-biotite geothermometer (Perchuk, 1970).

The cordierite-forming reaction may be written in the system $SiO_2$-$Al_2O_3$-$TiO_2$-FeO-MgO-$K_2O$-$H_2O$ as:

$0.438Chl + 0.583Ms + 0.132TiMag + Qtz + 0.096Ilm = 0.45Crd + 0.654Bt + 1.61H_2O$ (2)
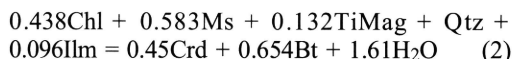
Cordierite porphyroblasts occur mostly in layers with high modal biotite and low modal muscovite, typically forming small knots (about 1 mm in diameter). According to the muscovite-biotite geothermometer (Hoish, 1989) and cordierite-biotite geobarometer (Perchuk *et al.*, 1983) and in agreement with experimental data (Seifert, 1970), cordierite formation is estimated to have occurred at T = 470-480°C and P = 1-1.5 kbar.

Many authors regard the plagioclase-epidote equilibrium as a metamorphic indicator (Ramberg, 1952; Waard, 1959; Rutland, 1962). In particular, Rambaldi (1973) and Crawford (1966) studied some mineral reactions involving epidote and plagioclase in metamorphic schists, but did not consider measured mineral compositions and reactant/product volume ratios. The epidote consuming reaction in the contact aureole of the Kharlovo massif, in the system $SiO_2$-$Al_2O_3$-$TiO_2$-FeO-MgO-CaO-$Na_2O$-$K_2O$-$H_2O$, is :

$27.59Pl_1 + 0.558Ms + 0.179Chl + 0.222Ep + 0.099Ilm = 28.37Pl_2 + 0.532Bt + 0.035TiMag + Qtz + 0.96H_2O$ (3)

Epidote breakdown took place at T = 450°C (according to the muscovite-chlorite and muscovite-biotite geothermometers). The volume in which the epidote was consumed was estimated as follows. First, the average volume ($V_{Ep}$) of unaltered grains in the country rocks, assumed to be a sphere, was determined to be $9.10^{-4}$ mm$^3$. Given the molar volume ($\bar{V}_{Ep}$) and the content of Ca in epidote ($X_{Ca,Ep}$), the quantity of epidote
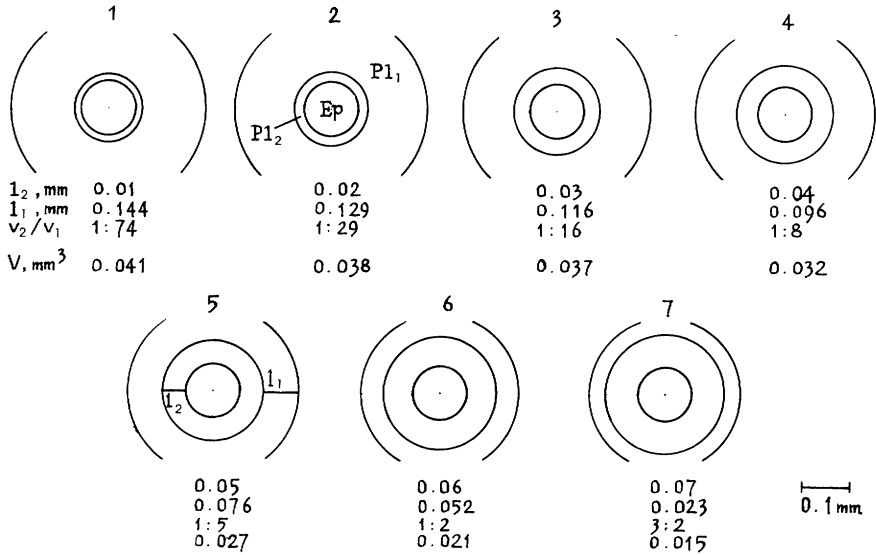
Fig. 6. Various calculated possibilities for volumes for redistribution of Ca around the epidote grain (sample 25). $l_1$ - plagioclase envelope with an anorthite component of $X_{An} = 1.1\%$, $l_2$ - plagioclase envelope with a higher anorthite content of $X_{An} = 4.4\%$, $v_2/v_1$ - volume ratios of plagioclase with $X_{An} = 4.4\%$ to plagioclase with $X_{An} = 1.1\%$; $V, mm^3$ - the volume in which Ca redistribution took place as a result of the epidote-consuming reaction.

and moles of Ca were calculated with the formulae $n_{Ep} = V_{Ep}/\bar{V}_{Ep}$ and $n_{Ca,Ep} = n_{Ep}.X_{Ca,Ep}$, respectively. The volume in which Ca redistribution between reacting phases as a result of reaction (3) took place was estimated on the basis of microstructural relations between epidote and plagioclase. In the country rock, epidote is associated with plagioclase ($Pl_1$) characterized by a $(Ca/(Ca + Na))$ ratio of 0.01. Inside the biotite zone, where epidote breakdown occurred, newly formed plagioclase ($Pl_2$) with a $(Ca/(Ca + Na))$ ratio of 0.05 grew between albite and epidote (Fig. 6). As all Ca was redistributed from epidote to plagioclase, the volume and extent of Pl growth can be estimated from the anorthite content, providing $n_{Ca,Ep} = n_{Ca,Pl1} + n_{Ca,Pl2}$. The calculated thicknesses of $Pl_1$ and $Pl_2$ rims around epidote are shown in Fig. 6. In sample 25, $Pl_2$ was found to have a thickness of 0.04-0.05 mm when the ratio of $Pl_2$ to $Pl_1$ volume was 1/8 - 1/5 (versions 4 and 5 in Fig. 6). This agrees with the petrography. Therefore, the volume in which Ca redistribution took place is 0.032-0.027 mm$^3$. A still lower volume is required for the redistribution of Al, Fe and Si from epidote to other phases.

The volume ratios of phases participating in reaction (3) compare quite well with the real distribution of minerals in the rocks (Likhanov, 1990). Mass balance shows that the scale of redistribution of the main petrogenetic components, (Si, Al, Fe, Mg, Na, Ca and K) among reacting phases was limited for epidote-plagioclase-titanomagnetite segregations to 0.03 mm$^3$ or less. Minor variations in alkali and aluminum contents are related to previous heterogeneity in the rock composition and to error in the estimation of phase/modal compositions.

## Discussion

Epidote-consuming and biotite-forming reactions were studied in the contact aureole of the Kharlovo gabbro intrusion. Reaction volumes for these processes are of the order of 0.01-0.03 mm$^3$. Diffusional flow and concentration gradients were so short-ranged that they did not lead to appreciable matter redistribution within the rock. This small reaction volume and limited diffusion may have been due to the short period of thermal metamorphism, so that local equilibria could only occur within small chlorite-biotite-mica and epidote-plagioclase-titanomagnetite

segregations. Short-range redistribution of elements occurs during low-temperature contact metamorphism; greater reaction volumes of the order of several cm³ are involved during regional metamorphic events (Reverdatto & Kolobov, 1987). Factors such as temperature, fluid pressure and deformation affect reaction volume size.

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