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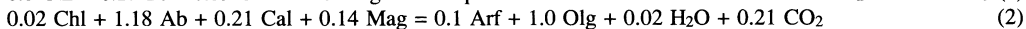
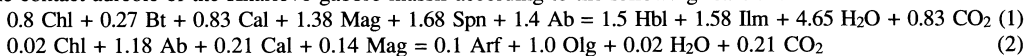
The origin of arfvedsonite in metabasites from the contact aureole of the Kharlovo gabbro intrusion (Russia)

IGOR I. LIKHANOV¹⁾, VLADIMIR V. REVERDATTO¹⁾ and ISABELLA MEMMI²⁾

¹⁾ Institute of Mineralogy and Petrography, Siberian Branch of Russian Academy of Sciences, 630090, Novosibirsk, Russia

²⁾ Dipartimento di Scienze della Terra, Università di Siena, Via delle Cerchia 3, 53100 Siena, Italy

Abstract : Hornblende and arfvedsonite were formed at $T = 525\text{-}550^\circ\text{C}$ and $P = 1\text{-}1.5$ kbar in the middle part of the contact aureole of the Kharlovo gabbro massif according to the following reactions:



A rare combination of heterogeneous rock composition, PT-parameters and thermal metamorphism of short duration led to the formation of arfvedsonite in metabasites. Arfvedsonite formed under local saturation of pore solution by Si, Na and Fe in a very small volume as a result of a local metasomatic reaction. These reactions were controlled mainly by sodium and silicon leaching during incongruent dissolution of acid plagioclase. Mass balance analysis and the variation of composition and amount of coexisting mineral show that the transfer of the main petrogenetic components was limited to volumes as small as $0.06\text{-}0.1 \text{ mm}^3$.

Key-words: arfvedsonite, hornblende, contact metamorphism, mass balance of metamorphic reactions, Kharlovo (Russia).

Introduction

During studies of mineral transformations in metamorphic rocks, a knowledge of the rock volumes in which chemical reactions occur provides useful information. Low-temperature contact metamorphic reactions in metapelites have been previously studied in the contact aureole of the Kharlovo gabbro massif and the scale of local equilibria domains was obtained (Likhanov *et al.*, 1994). The present paper deals with the formation of amphiboles in the Kharlovo massif aureole. In the metabasites from the middle part of this aureole, arfvedsonite, a relatively uncommon amphibole, was observed. Arfvedsonite is

never formed by the isochemical metamorphism of normal rocks, as it requires rocks initially rich in Fe, Si and Na and depleted in Al. In all the well-known occurrences, arfvedsonite appears to have formed through hydrothermal-metasomatic processes that supplied Na and Fe. This can account for its formation in the quartzites of the Krivoy district (the Ukrainian shield), in the ultrabasic rocks of the Bazhenov massif (Urals) and in the gneisses of the exocontact aureole of the Kave alkaline granites of the Kola Peninsula (Chukhrov, 1981). Arfvedsonite is metastable in normal metabasites. Robinson *et al.* (1971) reported the only known occurrence of arfvedsonite in metamorphic rocks from the Wabush Iron For-

mation (Labrador); there, Mg-arfvedsonite and cummingtonite occur as intimately intergrown subhedral grains, both exhibiting several orientations of exsolution lamellae.

Numerous reactions have been suggested to explain metabasite mineral associations (Loomis, 1966; Griffin & Heier, 1973; Miller, 1974; Kuniyoshi & Liou, 1976; Ferry *et al.*, 1987; Russ-Nabelek, 1989; Beard, 1990; Grant & Frost, 1990; Manning & Bird, 1991; Shive *et al.*, 1991), even though not always confirmed by compositional data or experimental studies.

In the present paper the hornblende and arfvedsonite-forming reactions are reported. They were calculated based on real compositions of minerals and taken as the basis for mass balance and scales of mass transfer during contact metamorphism.

Geological setting

The study area is part of the contact aureole of the Kharlovo gabbro intrusive body, at the north-west foot of the Altay mountain range in south Siberia, close to the village of Kharlovo, on the bank of the Charysh river (Reverdatto, 1967, 1970; Likhanov, 1989, 1990). The gabbro massif crops out over a circular area of about 12 km². The massif consists of two different magmatic phases that were later injected by various dyke swarms. More than 90 % of the volume is the result of the first magmatic phase: concentric bands of alternating dark olivine-titanomagnetite

gabbro and ore-free leucocratic gabbro form a "funnel-shaped" structure (Sakovych, 1969). During the latter phase, medium-grained granodiorite formed a small stock which cross-cut the gabbro. Part of the south-eastern contact aureole is shown in Fig. 1. The schematic map of the massif, its geographic position and mineralogical and petrographic data were reported by Likhanov *et al.* (1994).

K-Ar ages of the gabbro intrusion are 420-430 Ma (Sakovych, 1969). The two intrusive phases were closely spaced in time and may be considered together as an Early Devonian igneous complex.

The contact with the country rocks is sharp and discordant. The country rocks consist of psammitic sediments interbedded with rare, thin beds of basic lavas and tuff layers, that were regionally metamorphosed to greenschist facies conditions during the Cambrian-Ordovician Caledonian orogeny. Metapsammities consist of chlorite, muscovite, albite and quartz, with sporadic epidote, calcite and ore minerals. The country rocks adjacent to the gabbro pluton are recrystallized to hornfels (Reverdatto, 1967; Likhanov *et al.*, 1994).

Geochemical studies (Reverdatto, 1973; Reverdatto *et al.*, 1974; 1976; 1978) on country and contact metamorphic rocks indicate that the contact metamorphism was isochemical. The contact aureole, as defined by the biotite-in isograd, extends 1.1-1.3 km to the east of massif (Fig.1) with distinct zonation due to changing

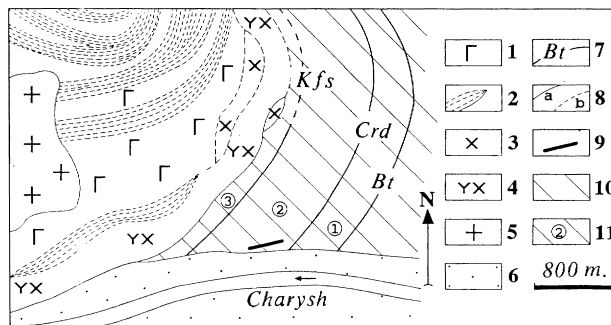


Fig.1. Part of the south-eastern contact aureole of the Kharlovo gabbro intrusion. Key: 1 - leucogabbro; 2 - titanomagnetitic melanogabbro; 3 - diorite; 4 - quartz syenite-diorite; 5 - plagiogranite and granodiorite; 6 - alluvium; 7 - isograds; 8 - geological boundaries mapped (a) and deduced from magnetic survey data (b); 9 - thin platy body of amygdaloidal diabase; 10 - country schists regionally metamorphosed under greenschist-facies conditions; 11 - metamorphic zones of contact aureole: 1 - outer biotite zone, 2 - spotted hornfels and middle zones, 3 - inner zone.

hornfels structure and mineral associations. Mineral assemblages (abbreviations according to Kretz, 1983), from lower to higher temperature, are:

- 1) Chl + Ms + Pl + Qtz + Ilm + Mag + Ep \pm Hem \pm Cal (country rocks),
- 2) Bt + Ms + Chl + Pl + Qtz + Mag \pm 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 \pm Mag (inner zone),
- 6) Crd + Bt + Spl + Sil + Pl + Kfs + Mag (thin, quartz-free segregations in the inner zone).

Methods of investigation

Rock compositions were determined by X-ray fluorescence, with a "VRA-20" energy dispersive spectrometer and mineral compositions by a "Camebax-micro" electron microprobe in the Institute of Mineralogy and Petrography, Novosibirsk (Table 1). Chemical analyses of the fine-grained phases were performed by EDAX 9100/70 energy dispersive system attached to a PHILIPS 515 SEM at the Siena University (Tables 1, 2).

Chemical reactions were calculated using real compositions and were taken as the basis for mass balance and scales of mass transfer during contact metamorphism. The volumes of reacting phases were estimated by the equation: $V_j = n_j \bar{V}_j$,

Table 1. Average compositions and cation proportions of minerals from metabasites.

	Chl1	Chl2	Hbl	Arf	Ab	Olg	Lbr	Ilm	Spn	Mag	Cal	Bt
SiO ₂	31.03	35.38	40.87	48.77	67.35	62.81	52.73	-	29.03	-	-	35.85
TiO ₂	-	-	3.26	1.84	-	-	-	47.68	40.21	6.38	-	4.74
Al ₂ O ₃	11.48	9.58	9.85	1.22	20.20	23.80	29.64	0.20	0.56	-	-	11.03
FeO	24.89	25.09	23.20	32.95	0.27	0.26	0.45	50.35	0.66	86.61	0.5	25.53
MnO	0.13	0.11	0.31	0.72	-	-	-	-	0.05	-	0.74	0.11
MgO	18.87	15.97	6.79	1.90	-	-	-	0.04	0.03	-	-	11.08
CaO	0.10	0.35	10.29	2.28	1.27	5.03	12.09	-	26.75	-	56.81	0.34
Na ₂ O	0.21	0.05	2.70	7.54	9.82	8.84	4.59	-	0.08	-	-	0.22
K ₂ O	0.03	0.01	0.86	1.38	0.53	0.17	-	-	0.04	-	-	8.26
Sum.	86.73	86.54	98.13	98.60	99.44	100.91	99.49	98.26	97.31	92.99	58.05	96.43
Si	3.30	3.76	6.32	7.69	2.97	2.77	2.40	-	0.97	-	-	2.77
Ti	-	-	0.38	0.22	-	-	-	0.94	1.01	0.19	-	0.28
Al	1.44	1.20	1.80	0.23	1.05	1.24	1.59	-	-	-	-	1.00
Fe ³⁺	-	-	0.23	0.53	-	-	-	-	-	1.31	-	-
Fe ²⁺	2.21	2.23	2.77	3.82	0.01	0.01	0.02	1.11	-	1.65	0.02	1.65
Mn	0.01	0.01	0.04	0.10	-	-	-	-	-	-	0.03	0.01
Mg	2.99	2.53	1.57	0.45	-	-	-	-	-	-	-	1.28
Ca	0.01	0.04	1.71	0.39	0.06	0.24	0.59	-	0.96	-	1.01	0.03
Na	0.04	0.01	0.81	2.31	0.84	0.76	0.41	-	-	-	-	0.03
K	-	-	0.17	0.28	0.03	0.01	-	-	-	-	-	0.81

Arfvedsonite analysis normalized to 16 cations, hornblende normalized to 15eNK cations; chlorite cations per 14 oxygen atoms; biotite, cations per 11 oxygen atoms; plagioclases, cations per 8 oxygen atoms; sphene, cations per 5 oxygen atoms; magnetite, cations per 4 oxygen atoms and ilmenite, cations per 3 oxygen atoms. All Fe as FeO. Fe³⁺ in magnetite was recalculated according to Carmichael (1967), and in amphiboles according to Robinson *et al.* (1982) and Schumacher (1991). Chl₁ is chlorite from matrix, Chl₂ is chlorite from amygdules.

Table 2. Chemical compositions and structural formulae of hornblende and arfvedsonite in the profile of Fig. 4.

	Arfvedsonite				Hornblende					Arfvedsonite		
	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	49.21	48.95	47.09	47.23	40.84	40.38	40.51	41.26	40.26	47.22	47.79	47.49
TiO ₂	1.55	2.21	2.30	2.79	3.26	3.90	2.85	3.55	4.07	2.27	2.52	2.73
Al ₂ O ₃	0.87	1.36	1.53	1.19	10.19	9.04	10.83	10.09	11.26	1.31	1.36	1.72
FeO	31.19	33.32	31.60	33.38	23.52	24.61	22.46	22.04	22.38	31.99	33.94	32.38
MnO	0.80	0.88	1.30	1.22	0.47	0.55	0.39	0.43	0.46	1.25	1.36	1.17
MgO	3.66	1.08	1.73	0.56	5.85	5.48	7.28	7.48	6.74	1.40	0.74	1.91
CaO	0.98	2.30	2.04	1.51	10.33	10.07	10.51	9.91	9.94	1.58	2.41	2.36
Na ₂ O	8.99	7.16	8.37	8.19	3.06	3.31	3.18	3.27	3.04	8.40	7.55	7.45
K ₂ O	1.48	1.41	1.30	1.30	0.82	0.92	0.66	0.75	0.60	1.34	1.34	1.24
Sum.	98.72	98.67	97.25	97.37	98.35	98.26	98.66	98.79	98.74	97.77	99.01	98.45
Si	7.572	7.631	7.474	7.582	6.314	6.311	6.168	6.254	6.104	7.551	7.581	7.520
Al ^{IV}	0.158	0.25	0.286	0.225	1.687	1.665	1.832	1.746	1.896	0.247	0.254	0.321
sum (T)	7.729	7.887	7.761	7.807	8.000	7.976	8.000	8.000	8.000	7.798	7.836	7.841
Al ^{VI}	0.000	0.000	0.000	0.000	0.170	0.000	0.111	0.056	0.116	0.000	0.000	0.000
Ti	0.179	0.26	0.275	0.337	0.379	0.458	0.326	0.405	0.464	0.273	0.301	0.325
Fe ³⁺	1.313	0.707	1.055	0.753	0.257	0.238	0.573	0.556	0.613	0.983	0.575	0.527
Mg	0.840	0.251	0.409	0.134	1.348	1.277	1.652	1.690	1.523	0.334	0.175	0.451
Fe ²⁺	2.701	3.646	3.140	3.728	2.784	2.978	2.287	2.238	2.224	3.295	3.928	3.761
Mn	0.104	0.116	0.175	0.166	0.062	0.073	0.050	0.055	0.059	0.169	0.183	0.157
Ca	0.162	0.384	0.347	0.260	1.711	1.686	1.714	1.609	1.615	0.271	0.410	0.400
Na(M ₄)	1.701	1.636	1.599	1.622	0.289	0.290	0.286	0.391	0.386	1.675	1.429	1.379
sum(M ₄)	7.000	7.000	7.000	7.000	7.000	7.000	7.000	7.000	7.000	7.000	7.000	7.000
Na(A)	0.980	0.832	0.976	0.927	0.628	0.713	0.653	0.570	0.508	0.929	0.893	0.909
K	0.291	0.281	0.263	0.266	0.162	0.183	0.128	0.145	0.116	0.273	0.271	0.250
sum(A)	1.271	1.113	1.239	1.193	0.790	0.896	0.781	0.715	0.624	1.202	1.164	1.159
Sum	16.000	16.000	16.000	16.000	15.790	15.872	15.871	15.715	15.624	16.000	16.000	16.000
wt%Fe ₂ O ₃	11.34	1.15	8.83	6.23	2.21	2.03	5.00	4.87	5.37	8.17	4.82	4.42
wt%FeO	20.99	32.29	23.65	27.77	21.53	22.79	17.96	17.65	17.54	24.64	29.61	28.40
wt%H ₂ O	1.95	1.88	1.89	1.87	1.94	1.92	1.97	1.98	1.98	1.88	1.89	1.89
Full Total	101.81	100.67	100.03	99.86	100.50	100.38	101.14	101.25	101.27	99.45	101.38	100.79

Normalization and Fe³⁺ recalculation as in Table 1.

where n_j is the number of moles and \bar{V}_j is the molar volume of mineral j . Values of molar volumes were taken from Karpov *et al.* (1976) and Karzhavin (1991). The ratio of the mineral volumes of phases to the volume of newly formed arfvedsonite was also estimated ($V'_{ji}V'_{Arf}$ in Table 4). These volume ratios were compared

with volume ratios ($V_{ji}V_{arf}$) of phase contents calculated by quantitative-mineralogical determinations in thin sections (Table 3).

The scales of mass transfer of petrogenetic components as a result of the arfvedsonite formation reaction were estimated as follows. With knowledge of the molar volume (\bar{V}_j) and content

Table 3. Comparison of observed mineral volume ratios with values calculated from the arfvedsonite-forming reaction equation.

	V_j, cm^3	V_j/V_{Arf}	$V_j \cdot 10^{-8} \text{cm}^3$	V_j/V_{Arf}
Albite	118.12	4.24	3.26	4.53
Oligoclase	100.30	3.59	2.72	3.78
Arfvedsonite	27.89	1.00	0.72	1.00
Calcite	7.75	0.28	0.18	0.25

V_j - a volume of mineral j , where j is albite, oligoclase, arfvedsonite and calcite in a rock volume of 0.06 mm^3 ; V'_j - mineral volume calculated from the reaction equation.

of component i in phase j ($X_{i,j}$), it is possible to determine the quantity of mineral j (moles) and the amount of component i by using the relations $n_j = V_j/\bar{V}_j$ and $n_{i,j} = n_j X_{i,j}$. The balance of petrogenetic components was estimated for small microdomains of the rock, assuming practically constant volume. A number of the component moles in such microdomains both before and after the beginning of the reaction was compared, which gave us informations about the character of the mineral transformations and mass-transfer scales (Table 4).

Petrography of metabasites

Rare, basic effusive rocks occur as amygdaloidal diabases. They are massive and greenish to dark-grey in colour, with non-uniformly distributed amygdules that are less than 2 mm in diameter and are filled with calcite and chlorite. Calcite occurs in the interior of the amygdules, chlorite at the edge. The texture of the rock is microporphyritic and intersertal. The diabases are composed of plagioclase, chlorite, calcite, sphene

and ore minerals, and rarely biotite. Chemical compositions of the rocks are graphically shown in Fig. 2.

We studied in detail the diabase body (60-80 cm thick) that underwent thermal metamorphism in the middle part of the contact aureole (the zone of cordierite-biotite hornfels).

The following zoning was clearly distinguished: (1) at both sides of the body there are symmetrical zones of endocontact aphanitic diabases, about 10-15 cm thick, in which amygdules are absent; and (2) in the central part fine-grained amygdaloidal diabases, that are 40-50 cm thick. These are clearly distinguishable by their spotted texture and they contain up to 15 vol. % of amygdules.

Mineral compositions and PT-conditions of metamorphism

The average compositions and cation proportions of the main metabasite minerals are given in Table 1.

Table 4. The balance of petrogenetic components before and after the arfvedsonite-forming reaction.

	$n_j \cdot 10^{-10}$	Before reaction				after reaction			
		n_{SiO_2}	$n_{\text{Al}_2\text{O}_3}$	$n_{\text{Na}_2\text{O}}$	n_{CaO}	n_{SiO_2}	$n_{\text{Al}_2\text{O}_3}$	$n_{\text{Na}_2\text{O}}$	n_{CaO}
Albite	0.033	0.098	0.035	0.028	0.002				
Calcite	0.005	-	-	-	0.005				
Oligoclase	0.027	-	-	-	-	0.075	0.033	0.021	0.006
Arfvedsonite	0.003	-	-	-	-	0.020	0.001	0.006	0.001
Sum		0.098	0.035	0.028	0.007	0.095	0.034	0.027	0.007

$n_j = V_j / \bar{V}_j$ - a molar quantity of minerals (in moles) in a rock volume of 0.06 mm^3 ; $n_{i,j} = n_j X_{i,j}$ - a molar quantity of petrogenetic components in mineral j , where i is SiO_2 , Al_2O_3 , CaO and Na_2O ($n_{i,j} \cdot 10^{-8}$ moles).

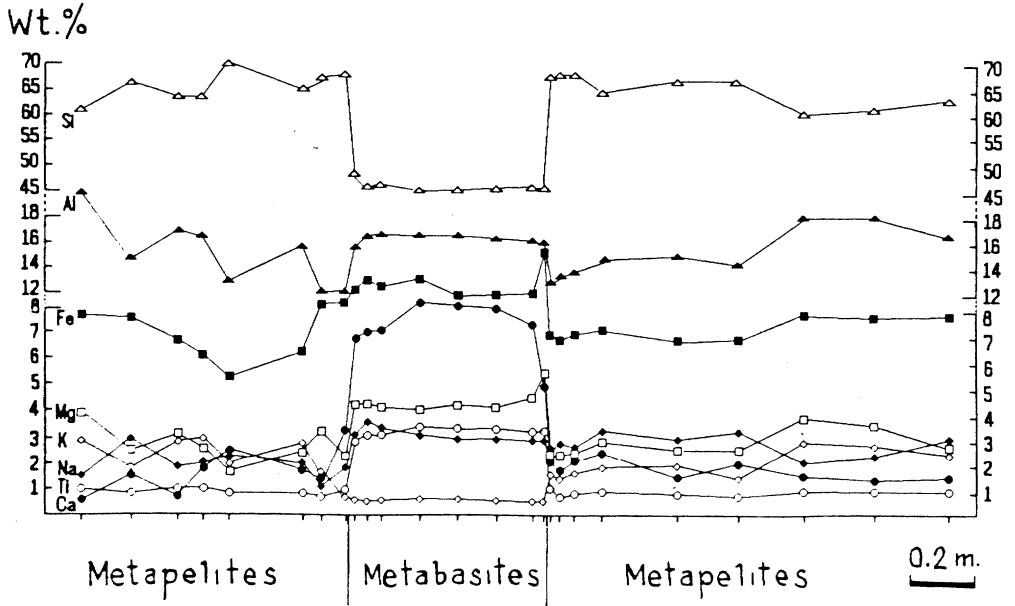


Fig. 2. Whole-rock chemical composition profile located across the diabase body and surrounding metapelites. Sample location on the profile is on the abscissa; chemical component contents of the rocks (in wt %) are on the ordinate.

Chlorite (Chl), one of the most abundant minerals of the diabase, has a nearly constant composition: Al/(Al + Mg + Fe) ratio ranges from 0.22 in the matrix to 0.20 in the amygdules; Fe/(Fe + Mg) ratio varies from 0.47 in the amygdules to 0.43 in the matrix. According to Bayliss's (1975) classification, the chlorite belongs to the Fe-clinocllore group.

Plagioclase makes up 40-50 vol.% of the rock. It forms microlites or small phenocrysts up to several millimeters in size and is usually complexly zoned (Fig. 3a). The phenocrysts and microlites are magmatic labradorite (Lbr) with anorthite content of 57-59%, that are rimmed by a thin, optically distinct layer (3 mm) of albitic plagioclase, (4-9% An). Near the calcite-chlorite amygdules, albite (Ab) rims are locally replaced by oligoclase (Olg). These domains of the most recent plagioclase (18-25% An) form fine irregular spots and spongy fragments 2.5 mm in size (Fig. 3b).

The contact metamorphism gave rise to hornblende (Hbl) in the central part of the diabase body; small rod- and needle-like crystals up to 0.2 mm in length were formed. According to Leake's (1978) classification, the amphibole ($6.25 < Si < 6.5$; $Mg/(Mg + Fe^{2+}) = 0.35$;

$Fe^{3+} > Al^{VI}$; $(Na + K)_A = 0.89$; $Ti = 0.38$) is a magnesian hastingsitic hornblende.

In the vicinity of calcite-chlorite amygdules, hornblende grains are commonly rimmed by an alkali-amphibole that may form bladed and needle-like crystals varying from several micrometers to a few hundredths of a mm in size. In thin section, the amphibole is deep-blue and almost opaque. Pleochroism is characterized by z (dark blue) $> y$ (blue) $> x$ (dark brown); $n_z = 1.703 \pm 0.003$, $n_y = 1.701 \pm 0.003$, $n_x = 1.697 \pm 0.003$. Its chemical composition ($Si > 7.5$; $Fe^{2+}/(Fe + Mg) = 0.92$; $Mn_C = 0.15$; $Fe^{3+}/(Fe^{3+} + Al) > 0.5$; $(Na + K)_A = 1.15$; $Na_B = 1.46$) classifies it as arfvedsonite (Leake, 1978), in agreement with X-ray analysis data. A concentration profile through a hornblende grain rimmed by arfvedsonite (Fig. 4) was obtained by microprobe and SEM-EDS and the analyses are reported in Table 2. We can observe that the transition in chemical composition from hornblende to arfvedsonite is sharp, with no intermediate types. We can also observe from the arfvedsonite structural formulae that T-site sums are always lower than 8 and A-site sums are always higher than 1. Because of the lack of structural evidence, it is not clear whether this discrepancy is due to ana-

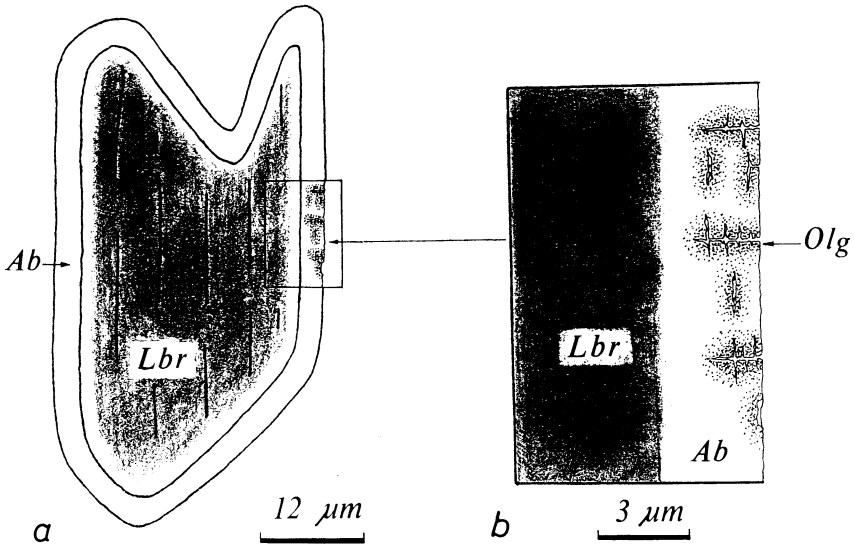


Fig. 3 a) Sketch of zoned plagioclase grain near calcite-chlorite amygdule; b) enlarged insert showing albite locally replaced by oligoclase (dotted area) near cracks.

lytical error or, alternatively, to the occurrence of some four-coordinate Ti, as reported by Oberti *et al.* (1992) for richterites within lamproites.

Biotite (Bt) forms fine flakes in the matrix that are up to 5 mm in length. The mineral varies in colour from orange-brown to red-brown as TiO₂ content increases up to 4.74 weight %. Its

Fe²⁺/(Fe²⁺ + Mg) is somewhat higher (0.56) than that of the coexisting chlorite. The amount of biotite in the rocks does not exceed 3-5 vol.%.

Calcite (Cal) occurs in the cores of amygdules or as irregular aggregates in the matrix. Spinel (Spn) forms small isolated subhedral grains in chlorite. Ti and Fe oxides are ilmenite (Ilm) and

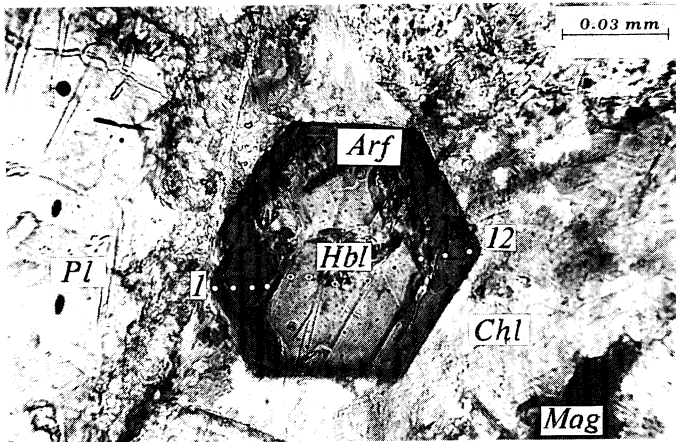


Fig. 4. Micrograph of hornblende grain rimmed by arfvedsonite (dark), plane light. The length of the profile (1-12) is = 0.075 mm. For chemical analysis data see Table 2.

magnetite (Mag), respectively. Magnetite composition is close to the solid solution of magnetite-ulvospinel, with a Ti content of 0.19 atoms per formula unit.

On the basis of the metabasite mineral assemblages (Hbl + Olg + Ilm + Mag + Cal + Chl \pm Bt \pm Spn) and temperature conditions (500-550°C) estimated using the amphibole-biotite and amphibole-plagioclase geothermometers (Perchuk & Rjabchikov, 1976), the contact metamorphism can be considered as transitional between muscovite and amphibole hornfels facies (Reverdatto, 1973; Dobretsov *et al.*, 1972; Pattison & Tracy, 1991).

A low, total pressure of 1.0-1.5 kbar was obtained for cordierite-biotite hornfels in the middle part of contact aureole (Likhanov *et al.*, 1994) using the cordierite-biotite geobarometer (Perchuk *et al.*, 1983).

Mineral reactions, the origin of arfvedsonite and mass balance determination

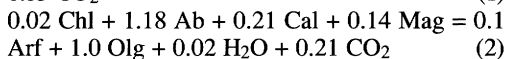
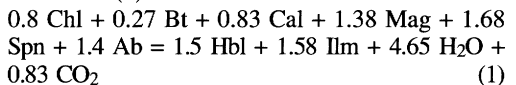
Many examples of interaction between metabasites and metapelites during thermal metamorphism are reported in the literature: the Tongulack Complex in the Altay Mountains (Lepezin, 1972; Lepezin *et al.*, 1984), the Sangilen block, the Tuva region (Lepezin & Seroglsov, 1990) and the Rioke belt, Japan (Ono, 1977). The metabasites and metapelites were modified by diffusional exchange of components, with metabasites enriched in SiO₂ and K₂O, and simultaneously depleted in TiO₂, FeO, MgO and CaO. The character of compositional zoning in plagioclase was also modified with reversed zoning in metapelites and normal zoning in metabasites. Average compositions of plagioclase became similar at the boundary between non-equilibrium rocks.

The authors initially assumed that the amphiboles in the metabasites of the Kharlovo gabbro massif contact aureole were formed as a reaction between diabase and metapelite (Likhanov & Reverdatto, 1991). However, the peculiarities of chemical component distribution in the diabase body and surrounding metapelites (Fig. 2) and their mineral compositions conflict with this explanation. In fact, in the contact aureole of the Karlovo massif, there is no tendency to equalize component concentrations (Fig. 2). The reason for this is the short duration of heating and

temperatures that were not sufficiently high (steep T-t trajectories).

If the normal zoning of plagioclase (from labradorite to albite) in the metabasites in the contact aureole is the result of magmatic differentiation or greenstone alteration (spilitization) of basalt (Zavaritsky, 1946; Turner & Verhoogen, 1960), then the reversed zoning (from albite to oligoclase) could be caused by the subsequent thermal metamorphism. The Na and Si could be removed *via* incongruent dissolution of plagioclase and would lead to increased anorthite content in the grain margins. Thus, both the growth of arfvedsonite and origin of reversed plagioclase zoning may be associated with a single process that occurred during the contact metamorphism.

Taking account of the peculiarities of plagioclase zoning and the fact that hornblende is not replaced by arfvedsonite, we calculated the reactions of amphibole formation based upon the actual chemical compositions of the coexisting phases. These calculations were performed for the system SiO₂-Al₂O₃-TiO₂-FeO-MgO-MnO-CaO-Na₂O-K₂O-H₂O-CO₂ for hornblende formation (1) and for SiO₂-Al₂O₃-TiO₂-FeO-MgO-CaO-Na₂O-K₂O-H₂O-CO₂ for the arfvedsonite formation (2):



Equation (1) conforms with the experimental study of phase relations carried out by Liou *et al.* (1974) for the basalt system. Calcite solubility and Ca concentration with decreasing fluid and increasing temperature were studied experimentally by Sharp & Kennedy (1965) and Fein & Walther (1987, 1989); this process could underlie the deceleration and arrest of hornblende growth. Isobaric experiments by the same authors have shown that calcite solubility in terms of calcium molality at P = 1-2 kbar decreased from 10^{-3.2} at T = 300°C to 10^{-5.2} at T = 550°C, with X_{CO₂} between 0.02 and 0.15 in a supercritical CO₂-H₂O fluid.

Equation (2) agrees with experimental data on Na and Si solubility in a fluid phase by incongruent dissolution of plagioclase at T = 400-800°C and P = 1-3 kbar (Kotelnikov & Schekina, 1986; Dujon & Lagache, 1984; Shvedenkova & Shvedenkova, 1990). Presumably higher anorthite content in the near-surface zone of grains is due to reaction of Ca in the fluid with residual alum-

inum in the plagioclase. The dissolution mechanism seems to be similar to that studied by Johannes (1989) in experiments on the melting of plagioclase-quartz assemblages at 2 kbar water pressure and at $T = 850^{\circ}\text{C}$.

The reliability of reaction (2) is supported by comparison of the calculated volume ratios of mineral with the observed volume ratios of phase contents. The volume ratios of phases participating in reaction (2) were first compared with the volume of newly formed arfvedsonite and then with the volume ratios of phases calculated on the basis of quantitative determination of mineral contents in thin sections. Arfvedsonite and oligoclase were found close together only near calcite-chlorite amygdules, where incongruent dissolution of plagioclase took place. During the reaction, Al_2O_3 was almost completely retained in plagioclase, SiO_2 and Na_2O were transferred from plagioclase to arfvedsonite while CaO was transferred from calcite to plagioclase. The volume ratios of phases participating in reaction (2) correspond to the observed volume distribution of minerals in the rock (Table 3). Analysis of petrogenetic component balance confirmed the character of mineral transformations during arfvedsonite growth (Table 4). The rocks were not altered in this case by metasomatic supply. Balance analysis showed that mass transfer for

the main petrogenetic components in the course of the arfvedsonite-forming reaction was limited to very small volumes (microsites) of about $0.06\text{--}0.1\text{ mm}^3$. These volumes were evaluated from examples of specific reactions with specific sizes and compositions of reacting phases. This conclusion may be extended to other microdomains of the rock. Chemical element redistributions during hornblende and arfvedsonite formation are diagrammatically shown in Fig. 5.

Conclusion

Hornblende- and arfvedsonite-forming reactions in metabasites of the contact aureole of the Karlovo gabbro massif indicate that redistribution of the main petrogenetic components was confined to microsites of about $0.06\text{--}0.1\text{ mm}^3$. In fact, due to short term and low-temperature thermal metamorphism, diffusion flows and concentration gradients were so short-ranged that they did not lead to alteration of the whole rock composition.

A rare combination of moderate PT parameters and the short duration of thermal influence on the nonuniform basaltic rock led to the formation of arfvedsonite, which is unusual in isochemical metamorphism. The formation of arfvedsonite rims around the hornblende grains could be due

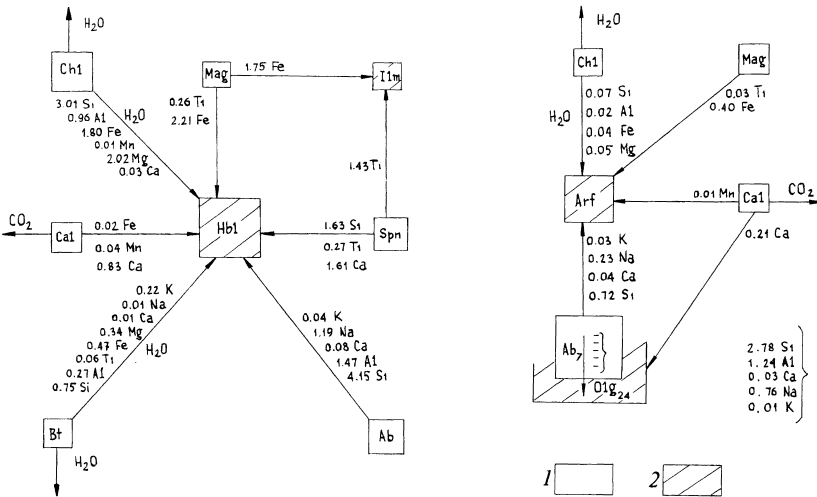


Fig. 5. Chemical element redistribution during hornblende and arfvedsonite formation. 1 - reacting phases, 2 - reaction products.

to the epitaxial nucleation of this mineral. This later growth took place in the stability field of arfvedsonite under the conditions of local saturation of Na, Si and Fe in H₂O-CO₂ solution, as a result of diffusion-controlled reactions coupled with Na and Si production during incongruent dissolution of albitic plagioclase. With higher temperature or longer duration, the reaction would probably have involved larger volume and a greater number of minerals. Under these conditions, further arfvedsonite formation would have been impossible without an additional supply of Na, Si and Fe and a relative deficiency of Ca and Al in the system; arfvedsonite would be unstable and would be replaced by a more stable mineral association.

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References

- Bayliss, P. (1975): Nomenclature of the trioctahedral chlorites. *Can. Mineral.*, **13**, 178-180.
- Beard, J.S. (1990): Partial melting of metabasites in the contact aureoles of gabbroic plutons in the Smartville Complex, Sierra Nevada, California. in "The nature and origin of Cordillerian Magmatism" (Anderson J. L. : ed.) *Geol. Soc. Amer. Memoir.*, **174**, 303-313.
- Carmichael, I. S. E. (1967): The iron-titanium oxides of sialic volcanic rocks and their associated ferromagnesian silicates. *Contrib. Mineral. Petrol.*, **14**, 36-64.
- Chukhrov, F.V. (1981): Minerals. Reference book. Nauka, Moscow, 613 p. (in Russian).
- Dobretsov, N.L., Reverdatto, V.V., Khlestov, V.V., Sobolev, N.V., Sobolev, V.S. (1972): The facies of metamorphism. Australian National University, Department of Geology Publ. 214, Canberra, 417 p.
- Dujon, S.C. & Lagache, M. (1984): Echanges entre plagioclases et solutions aqueuses de chlorures sodi-calciques à différentes pressions et températures (400 à 800°C, 1 à 3 kilobars). *Bull. Minéral.*, **107**, 553-569.
- Fein, J.B. & Walther, J.V. (1987): Calcite solubility in supercritical CO₂-H₂O fluids. *Geochim. Cosmochim. Acta*, **51**, 1665-1673.
- (1989): Calcite solubility and speciation in supercritical NaCl-HCl aqueous fluids. *Contrib. Mineral. Petrol.*, **103**, 317-324.
- Ferry, J.M., Mutti, L.J., Zuccala, G.J. (1987): Contact metamorphism/hydrothermal alteration of tertiary basalts from the Isle of Skje, northwest Scotland. *Contrib. Mineral. Petrol.*, **95**, 166-181.
- Grant, J.A. & Frost, B.R. (1990): Contact metamorphism and partial melting of pelitic rocks in the aureole of the laramie Anorthosite Complex, Morton Pass, Wyoming. *Amer. Jour. Sci.*, **290**, 425-572.
- Griffin, W.L. & Heier, K.S. (1973): Petrological implications of some corona structures. *Lithos*, **6**, 315-335.
- Johannes, W. (1989): Melting of plagioclase-quartz assemblages at 2 kbar water pressure. *Contrib. Mineral. Petrol.*, **103**, 270-276.
- Karpov, I.K., Kiselijov, A.I., Letnikov, F.A. (1976): Modelling of natural mineral formation on computer. Nedra, Moscow, 254 p. (in Russian).
- Karzhavin, V.K. (1991): Amphiboles. Thermodynamic properties. *Geokhimiya*, **12**, 1724-1732. (in Russian).
- Kretz, R. (1983): Symbols for rock-forming minerals. *Am. Mineral.*, **68**, 277-279.
- Kotelnikov, A.R. & Schekina, T.I. (1986): Experimental investigation of kinetic interaction of plagioclases with water-salt fluid at 500°C and P = 1 kbar. *Geokhimiya*, **9**, 1233-1244. (in Russian).
- Kuniyoshi, S. & Liou, J.G. (1976): Contact metamorphism of the Karmutsen volcanic rocks, north-eastern Vancouver Island, British Columbia. *J. Petrol.*, **17**, 73-99.
- Leake, B.E. (1978): Nomenclature of amphiboles. *Can. Mineral.*, **16**, 501-520.
- Lepezin, G.G., Mirievskaya, O.S. Anoshin, G.N. (1984): Geochemistry of the Tongulalack metamorphic complex. *Geologija i Geofisika*, **7**, 84-99. (in Russian).
- Lepezin, G.G. & Seroglasov, V.V. (1990): The scales of mass transfer on the contact, of metapelites and metabasites. *Dokl. Acad. Nauk SSSR*, **314**, 5, 1217-1221. (in Russian).
- Likhanov, I.I. (1989): Low-grade biotite isograd within contact aureole of the Kharlovo gabbro massif. *Geologija i Geofisika*, **7**, 46-54 (in Russian).
- (1990): Epidote consuming reaction at low-temperature contact metamorphism of metapelites. *Zapiski Vses. miner. Obsch.*, **119**, 40-48. (in Russian).
- Likhanov, I.I. & Reverdatto, V.V. (1991): Arfvedsonite as a product of reacting interaction between diabasites and metapelites. *Dokl. Acad. Nauk SSSR*, **317**, 6, 1461-1465. (in Russian).
- Likhanov, I.I., Reverdatto, V.V., Memmi, I. (1994):

- Short-range mobilization of elements in the biotite zone of contact aureole of the Kharlovo gabbro intrusive. *Eur. J. Mineral.*, **6**, 133-144.
- Liou, J.G., Kuniyoshi, S., Ito, K. (1974): Experimental studies of the phase relations between greenschist and amphibolite in a basaltic system. *Amer. Jour. Sci.*, **274**, 613-632.
- Loomis, A.A. (1966): Contact metamorphic reactions and processes in the Mt. Tallac roof remnant, Sierra Nevada, California. *J. Petrol.*, **7**, 221-245.
- Manning, C.E. & Bird, D.K. (1991): Porosity evolution and fluid flow in the basalts of the Skaergaard magma-hydrothermal system, east Greenland. *Amer. Jour. Sci.*, **291**, 201-257.
- Miller, C. (1974): Reaction rims between olivine and plagioclase in metaperidotites, Otztal Alps, Bavaria. *Contrib. Mineral. Petrol.*, **43**, 333-342.
- Oberti, R., Ungaretti, L., Cannillo, E., Hawthorne, F. C. (1992): The behaviour of Ti in amphiboles. I. Four- and six-coordinate Ti in richterite. *Eur. J. Mineral.*, **4**, 425-439.
- Ono, A. (1977): Chemical reaction at the boundary between gneiss and amphibolite in the Ryoke metamorphic terrain at Tarato, Japan. *Jour. Geol. Soc. Japan*, **1**, 33-40.
- Pattison, D.R.M. & Tracy, R.J. (1991): Phase equilibria and thermobarometry of metapelites in: "Contact metamorphism" (ed. Kerrick D.). *Reviews in Mineralogy*, **26**, 105-187.
- Perchuk, L.L. & Rjabchikov, I.D. (1976): The phase compliancy in mineral systems. Nedra, Moscow, 288 p. (in Russian).
- Perchuk, L.L., Lavrent'eva, I.V., Aranovich, L.J., Podlesski, K.K. (1983): Biotite-garnet-cordierite equilibria and metamorphic evolution. Nauka, Moscow, 197 pp. (in Russian).
- Reverdatto, V.V. (1967): A contact metamorphism of the Kharlovo gabbro massif. *Geologiya i Geofisika*, **7**, 25-32 (in Russian).
- (1970): On the isochemical nature of contact metamorphism. *Geologiya i Geofisika*, **5**, 53-63 (in Russian).
- (1973): The facies of contact metamorphism. Australian National University, Department of Geology, Publ.233, Canberra, 263 p.
- Reverdatto, V.V., Anoshin, G.N., Cymblist, V.G., Kholodova, L.D., Vasilenko, V.B. (1976): Gold-bearing metapelites isochemically metamorphosed near the intrusive contact. *Chem. Erde. Bd.*, **35**, 289-298.
- Reverdatto, V.V., Anoshin, G.N., Vasilenko, V.B. (1978): Behaviour of U, Th, Au, Fe and P at contact metamorphism of metapelites. *Dokl. Acad. Nauk SSSR*, **260**, 424-429 (in Russian).
- Reverdatto, V.V., Sharapov, V.N., Lavrent'ev, YU.G., Pokachalova, O.S. (1974): Investigation in isochemical contact metamorphism. *Contrib. Mineral. Petrol.*, **48**, 287-299.
- Robinson, P., Jaffe, H.W., Ross, M., Klein, C. (1971): Orientation of exsolution lamellae in clinopyroxenes and clin amphiboles: consideration of optimal phase boundaries. *Am. Mineral.*, **56**, 909-939.
- Robinson, P., Spear, F. S., Schumacher, J. C., Laird, J., Klein, C., Evans, B. W., Doolan, B.L. (1982): Phase relations of metamorphic amphiboles: Natural occurrence and theory. in: "Amphiboles: Petrology and experimental phase relations" (eds. Veblen, D. R. & Ribbe, P. H.). *Reviews in Mineralogy*, **9B**, 3-9.
- Russ-Nabelek, C. (1989): Isochemical contact metamorphism of mafic schist, Laramie Anorthosite Complex, Wyoming: Amphibole compositions and reactions. *Am. Mineral.*, **74**, 530-549.
- Sakovych, G.M. (1969): Kharlovo titanomagnetite deposit. in: "Ore deposit of the Altay-Sayan mountain range". Acad. Nak. Press, Moscow, 68-70 (in Russian).
- Sharp, W.E. & Kennedy, G.C. (1965): The system CaO-CO₂-H₂O in two-phase region calcite-aqueous solution. *J. Geol.*, **73**, 2, 391-403.
- Shive, P.N., Yei, Y., Frost, B.R. Swapp, S. (1991): Effect of prograde metamorphism on magnetic properties of basalt. *Trans. Amer. Geophys. Union*, **72**, 100.
- Schumacher, J. C. (1991): Empirical ferric iron corrections of electron microprobe mineral analyses. Necessity, assumptions, and effects on some geothermometers and geobarometers. *Min. Mag.*, **55**, 3-18.
- Shvedenkova, S.V. & Shvedenkov, G.Yu. (1990): Experimental investigation of calcium and sodium distribution between plagioclase and solution at 350°C and 100 MPa. *Geologiya i Geofisika*, **2**, 75-80. (in Russian).
- Turner, F.J. & Verhoogen, J. (1960): Igneous and metamorphic petrology. McGraw-Hill Book Company, Inc. New-York, Toronto, London, 519 p.
- Zavaristki, V.A. (1946): Spilite-keratophyre formation of Bljavi deposit on the Ural mountain range. *Trudy Geol. Inst.*, **71**, 24, 44-62 (in Russian).

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