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New data on the geochemistry of metabasic rocks from the eastern marginal part of the Madan-Davidkovo Structure, Central Rhodope

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Abstract. Metabasites from the eastern periphery of the Madan-Davidkovo Structure (MDS) are an interesting example of magmatic activity in the Rhodope crystalline complex. These rocks occur as several small bodies southeast of the village of Galabovo (Ahryane). They are hosted within the metamorphites of the Vishnevo Formation (Arda Group). The metabasite bodies show well preserved igneous texture and mineral composition. The high MgO, Ni and Cr abundances at intermediate SiO_2 and low Ti, Zr, and HREE are the most striking features of the rocks. Comparison of the MDS metabasites with petrographically and chemically analogous rocks from other regions shows their complicated geochemical character. According to their CaO/Al_2O_3, CaO/TiO_2 and Al_2O_3/TiO_2 ratios, Nb, Ti contents and REE patterns the studied rocks are close to boninites whereas the Ti/Zr, Ti/Y and Zr/Y ratios are typical of island arc tholeiites (IAT). The MDS metabasites show close similarity to IAT-like orthoamphibolites from the northern part of the Central Rhodope Mts. too. The geochemical features described define the rocks as transitional between boninites and IAT. Analogous composition is typical of some Precambrian high magnesian series with specific isotopic characteristics.

Key words: metagabbro, REE, trace elements, island arc tholeiite, boninite, Central Rhodope
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Д а и е в а, Л., С. П р и с т а в о в а 1998. Нови данни за геохимията на метабазити от източната периферия на Мадан-Давидковската структура, Централни Родопи. - *Геохим., минерал. и петрол.*, **35**, 47-54

Метабазитите от източната периферия на Мадан-Давидковската структура (МДС) се считат за една от интересните магматични прояви в Родопския кристалин. Тези скали се разкриват като няколко малки тела югоизточно от с. Гълъбово (Ахряне). Вместени са в метаморфитите от Вишневската свита (Арденска група). Метабазитовите тела притежават добре запазена магматична структура и минерален състав. Най-характерната особеност за тях са високите съдържания на MgO, Ni и Cr при средно съдържание на SiO_2 и ниски съдържания на Ti, Zr и тежки редки земи. Сравняването на метабазитите от МДС с подобни в петрографско и геохимично отношение скали от различни райони показва техния комплициран геохимичен характер. По отношенията CaO/Al_2O_3, CaO/TiO_2 и Al_2O_3/TiO_2, съдържанията на Nb, Ti и разпределенията на РЗЕ изследваните скали са подобни на бонинитите. Отношенията Ti/Zr, Ti/Y and Zr/Y в тях са типични за островнодъгови толеити (IAT). Метабазитите от МДС са близки също и до подобните на IAT ортоамфиболити от северната част на Централните Родопи. Тези геохимични особености определят изследваните скали като преходни между бонинитите и островно-дъговите толеити. Подобен състав е типичен за някои докамбрийски високо магнезиални серии със специфични изотопни характеристики.

Ключови думи: метагабро, REE, елементи следи, островно дъгови толеити, бонинити, Централни Родопи
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Introduction

The presence of basic magmatic relics in the polymetamorphic Rhodopian complex is well known in the geological literature (Kozhoukharov, 1966, and others). The metabasic rocks from the eastern periphery of the Madan Davidkovo Structure (MDS) are considered as an interesting example of the magmatic activity in the Rhodope crystalline complex. Several authors have studied these rocks from petrological and mineralogical point of view (Toprakchieva, 1963; Pristavova, 1996). Toprakchieva (1963) described them as Paleozoic magmatites intruded in the amphibolites. Kozhoukharova and Kozhoukharov (1978) included these metabasites in the Rhodopian magmatic complex. Zagorchev (1976) considered them as an important marker and element of the metamorphic evolution of the Rhodope crystalline complex. Special attention has been paid to the corona texture formation and processes of eclogitization of the rocks by Pristavova (1996). The metabasites from MDS contain magmatic minerals (olivine, plagioclase, ortho- and clinopyroxene, amphibole, biotite, and spinel), corona textures and geochemical parameters defining them as gabbro, gabbronorites and troctolites. These characteristics are similar to those of the druzites from the Baltic shield and some basites with typical corona textures from Norway and Canada shield. The published data on the metabasic rocks studied (Zakariadze et al., 1993; Pristavova, 1996) are insufficient to determine their specific geochemical character.

In this paper we give some new data for the composition of the MDS metagabbros. By comparing their geochemical features with those of analogous rocks from other regions we make an attempt to clarify their geochemical specialization and probable geodynamic setting.

Geological position and petrographic characteristics

The metabasites studied in this work occur as several small bodies in the eastern periphery of MDS southeast of the village of Galabovo (Fig. 1). They are hosted within the amphibolites belonging to the metamorphites of the Vishnevo Formation (Arda Group) as defined by Kozhoukharov (1984). The Vishnevo Formation is build up of gneisses affected by granitization and migmatization, intercalated by beds of amphibolites of different thickness, two-mica and muscovite schists as well as sillimanite schists. The metabasites are of lens-like, boudin shapes extended conformably to the foliation of the host metamorphites. They are characterized by fine-grained massive texture and dark green colour. Xenoliths from the amphibolites can be observed in the metagabbros. Two different types of cross-cutting pegmatites in the metagabbroids and host rocks are common.

The metabasite bodies are of well preserved igneous texture and mineral composition in their central parts. Magmatic minerals and textures gradually decrease and disappear towards their periphery. Gabbros, gabbronorites and troctolites - gabbro-amphibolites (intermediate phase) - amphibolites can be recognized from the central to the peripheral parts. The magmatic assemblage is represented by Mg-rich olivine, plagioclase, ortho- and clinopyroxene, biotite (high-Ti phlogopite) and spinel. All these minerals with garnet (pyrope type) form typical corona textures. Magmatic temperature of about 1160-1170°C/7 kbar has been determined for the metabasites (Pristavova, 1996). Garnet (probably indicating initial eclogitization), amphibole (hastingsite), plagioclase (andesine), titanite and chlorite replaced the primary mineral assemblage during a subsequent metamorphism at 550-570°C/6 kbar determined in the host amphibolites (Pristavova, 1996). The rocks analyzed in this work are from the well preserved magmatic relics.

Geochemistry

Major and trace elements of the rocks studied are listed in Table 1. The high MgO, Ni and Cr abundances at intermediate SiO_2 and low Ti, Zr, and HREE are the most striking features of these rocks. They have various magnesian contents (Pristavova, 1996) but the value of the MgO/MgO + FeO -ratio varies from 0.60 to 0.70 and shows that they are very close to the primitive mantle derived magmas

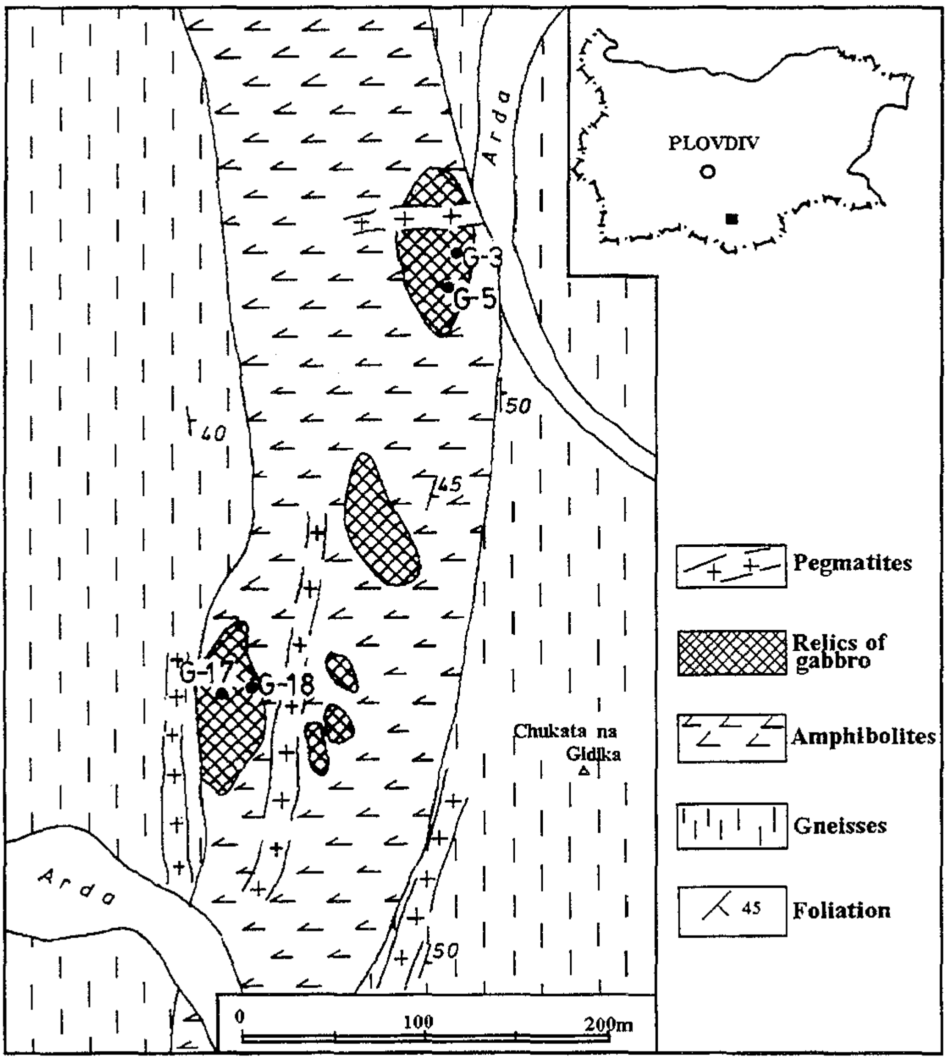

Fig. 1. Sketch map of the region with outcrops of magmatic basic relics
Фиг. 1. Геоложка схема на района с разкритията на реликти от базични магматити

(Bloomer, Hawkins, 1987). This primitive character is also supported by the contents of Cr and Ni in the most magnesian metabasic rocks (G-3 and G-18, Table 1), which approach those of some ultrabasites from the Rhodope Mts. (Zheljazkova-Panajotova et al., 1978).

On the AFM-diagram the samples studied and earlier data (G-2, G-3a, G-11, G-17) after Pristavova (1996) plot close to the differentiation trend of Proterozoic druzites from the Karelia region, Baltic sheild (Sharkov et al., 1994) which we use for comparison, and also they are near to the differentiation trend of modern boninites (Fig.2; Bloomer, Hawkins, 1987). The low concentration of TiO_2 and relatively high values of CaO/TiO_2 and Al_2O_3/TiO_2 ratios distinguish the rocks compared in this study from MORB. On the diagrams (Fig. 3 a, b) they plot inside or very close to the field of modern boninites and high-magnesian andesites (HMA). Two noritic parental magma compositions (B1, B2, Fig. 3 a, b) of the Bushveld complex (Hall, Hughes,1987) are situated in the same way. Because of the low K_2O contents in the metabasic rocks the ratio K_2O/Ti_2O approaches that of primordial mantle - M (Fig. 3 c; Hall, Hughes, 1987). Similarly but closer to MORB are situated the IAT-like orthoamphibolites from the northern part of the Central Rhodope (Kozhoukharova, Daieva, 1990; samples 515, 724, 727b, 360b) chosen by their Ti_2O contents. Only one metabasic rock (sample 606, Galabovo region) falls in the MORB field because of the very high TiO_2 content (0.77%), near that of magnesian MORB - 0.55% (Hall, Hughes, 1987). The Ti/Zr ratio in the samples from the MDS and IAT-like orthoamphibolites from the northern part of Central Rhodope Mts. shows different values typical for boninites (30-60) as well as for MORB (60-120; Fig. 4a, Hall, Hughes, 1987). On the same diagram

Table 1
Chemical composition of the metabasites
Таблица 1
Химичен състав на метабазитите

Sample	G-3	G-5	G-17	G-18	606	610	704	705	706
SiO_2	43.71	46.58	45.14	43.51	50.38	47.47	47.67	50.42	51.85
TiO_2	0.30	0.32	0.30	0.29	0.77	0.34	0.31	0.43	0.45
Al_2O_3	11.64	18.09	17.50	11.08	16.84	18.10	7.78	11.29	14.87
FeOt	10.40	7.18	9.00	10.85	6.44	8.21	11.36	9.30	9.88
MnO	0.29	0.11	0.15	0.18	0.13	0.12	0.15	0.14	0.14
MgO	24.18	14.56	13.36	24.35	9.06	12.65	23.76	16.23	8.63
CaO	7.47	10.72	10.06	7.21	12.35	10.03	4.36	7.11	7.70
Na_2O	0.94	1.60	1.48	1.69	2.07	1.75	0.85	2.11	3.78
K_2O	0.22	0.21	0.29	0.22	0.36	0.15	0.36	0.47	0.80
P_2O_5	0.04	0.03	0.04	0.03	0.12	0.10	0.09	0.13	0.12
Total	99.21	99.41	97.36	99.43	99.29	100.26	97.63	97.97	98.68
ppm									
Zr	26	15	28	16	48	33	46	65	59
Y	11	11	10	9	18	14	3	3	3
Sr	205	290	289	180	242	298	92	141	226
Rb	8	6	7	6	4	3	14	15	16
Cr	1382	212	293	1429	288	196	n.d.	n.d.	n.d.
Ni	671	336	542	654	55	236	n.d.	n.d.	n.d.
Ba	96	58	91	47	n.d.	n.d.	160	233	288
La	3.13	2.74	3.25	n.d.	3.16	3.37	5.50	8.78	7.97
Ce	6.19	6.05	6.89	n.d.	8.01	6.10	13.95	21.02	17.30
Pr	0.90	0.89	1.04	n.d.	1.10	0.72	n.d.	n.d.	n.d.
Nd	3.62	3.40	4.04	n.d.	5.40	3.00	3.84	8.31	8.18
Sm	0.87	0.89	0.95	n.d.	1.62	0.70	1.26	1.98	1.84
Eu	0.36	0.47	0.47	n.d.	0.63	0.48	0.38	0.55	0.76
Tb	0.16	0.15	0.16	n.d.	0.34	0.17	0.14	0.69	0.27
Gd	0.88	0.88	1.06	n.d.	2.00	0.93	-	-	-
Dy	0.99	0.93	0.90	n.d.	2.00	1.10	-	-	-
Ho	0.21	0.21	0.18	n.d.	0.48	0.29	n.d.	n.d.	n.d.
Er	0.52	0.56	0.49	n.d.	1.30	0.94	-	-	-
Yb	0.52	0.55	0.46	n.d.	1.15	0.94	-	-	-
Lu	0.01	0.09	0.09	n.d.	0.21	0.20	0.11	0.17	0.17
Hf	0.28	0.40	0.46	n.d.	-	0.30	n.d.	n.d.	n.d.
Nb	0.81	0.88	13.41	n.d.	n.d.	n.d.	8	10	13

G-3 and G-18 - olivine gabbro - troctolites; G-5 and G-17- gabbronorites from MDS; 606 - gabbro-amphibolites; 610 - olivine gabbro from MDS after Zakariadze et al. (1993); 704 - lhertzolite; 705 - olivine gabbronorite; 706 - hypersthene porphiryte after Sharkov et al. (1994). Major and trace elements of gabbroids from MDS - XRA carried out at the Dept. of Geology, University of Glasgow , REE and Nb - ICP-MS analyses at the SURRC, East Kilbride.
G -3 и G -18 - оливинови габра-троктолити от МДС; G -5 и G -17 - габро-норити от МДС, 606 - габро-амфиболит от МДС по Zakariadze et al. (1993); 610 - оливиново габро от МДС по Zakariadze et al. (1993); 705 - оливинов габронорит по Sharkov et al. (1994); 706 - хиперстенов порфирит по Sharkov et al. (1994). Макросъстав и елементи следи - XRA са извършени във Факултет по геология на Университета г.Глазгоу; РЗЕ и Nb - ICP-MS в SURRC, Ийст Килбрайд

metabasites from the Karelia region lie in the field of boninites. The relative abundances of Zr and Y in the Rhodope metagabbroids correspond closely to those in boninites and island-arc tholeiites (Fig. 4b). The metabasites from Karelia, Baltic shield fall outside this diagram because of their very low Y contents and high Zr/Y ratios.

The chondrite-normalized REE pattern of the metabasites (Fig. 5) is characterized by varying LREE enrichment (La/Sm ratio varies from 2.0 to 4.4) and flat or slightly U-shaped HREE pattern. The latter has been noted by several workers (Sun, Nesbit, 1978; Bloomer, Hawkins, 1987) and seems to be characteristic of boninites. In Fig. 5 it can be seen that the metabasites from Karelia region are more enriched in LREE than the rocks studied.

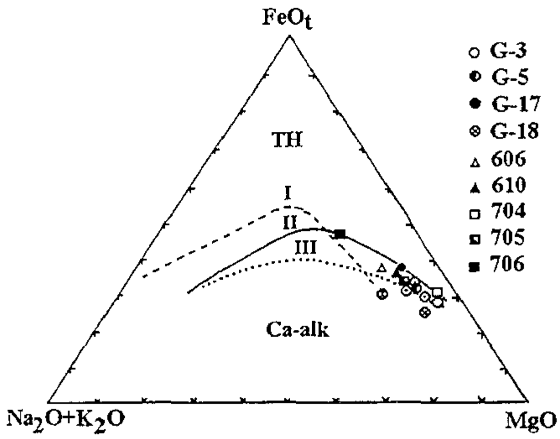

Fig. 2. AFM-diagram of metabasic rocks from the MDS and Karelia regions: I — line separating the tholeiite and calc-alkaline fields (Irvine, Baragar, 1971); II - differentiation trend of druzites (Sharkov et al., 1994); III - differentiation trend of boninites (Bloomer, Hawkins, 1987); crosses - samples 515, 724, 727b, 360b after Kozhoukharova and Daieva (1990); dotted circles - samples G-2, G-3a, G-11, G-17 after Pristavova (1996). Symbols are valid for all diagrams

Фиг. 2. AFM диаграма на метабазитите от МДС и Карелия: I - отделя толеитово от калциевоалкално поле (Irvine, Baragar, 1971); II - тренд на диференциация на друзити (Sharkov et al., 1994); III - тренд на диференциация на бонинити (Bloomer, Hawkins, 1987); кръстчета - образци 515, 724, 727b, 360b по Kozhoukharova, Daieva (1990); кръгчета с точка - образци G-2, G-3a, G-11, G-17 по Pristavova (1996). Символите са валидни за всички диаграми

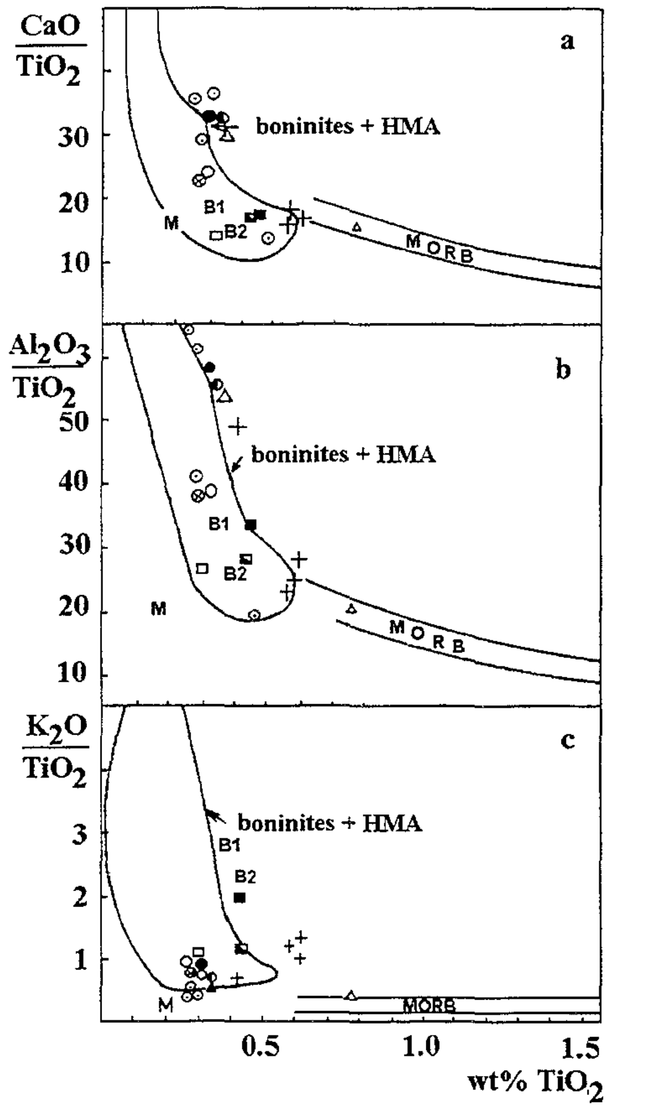

Fig. 3. CaO/TiO_2, Al_2O_3/TiO_2 and K_2O/TiO_2 in relation to TiO_2 content in the metabasites from MDS, Karelia region and IAT-like orthoamphibolites from the northern part of Central Rhodope. Fields, B1-, B2- and M compositions after Hall, Hughes (1987)

Фиг. 3. CaO/TiO_2, Al_2O_3/TiO_2 and K_2O/TiO_2 по отношение на TiO_2 съдържание в метабазитите от МДС, Карелия и IAT подобни ортоамфиболити от северната част на Централни Родопи. Полетата, B1-, B2- и M съставите са по Hall, Hughes (1987)

Compared to the fields of micropyroxenites from the Bushveld massif and boninites from the Izu-Bonin island arc (Sharkov et al., 1994) the rocks from the MDS and the IAT-like orthoamphibolites from the northern part of Central Rhodope lie in the field of boninites and partly of micropiroxenites while the rocks from Karelia region lie predominantly in the field of the Bushveld micropyroxenites.

The MORB-normalized (Taylor, McLennan, 1984) trace element patterns (Fig. 6) show clear LILE enrichment (Sr, Rb, Ba) and HFSE depletion (Zr, Ti, Y), characteristic of boninites. The patterns of MDS are in the field of boninites from the Pacific Ocean. The Baltic shield metabasites lie in the boninite field as well as in the island-arc tholeiite field (Sharkov et al., 1994).

The Zr/Sm - La/Sm diagram (Fig. 7) shows the fields of different types of Pacific Ocean boninites (Sharkov et al., 1994). Although the metabasites from MDS and Karelia regions are situated outside these fields they are closer to boninites than to tholeiites. The tholeiites lie in the left lower corner of this diagram (Sharkov at al., 1994). The IAT-like rocks from the northern part of Central Rhodope Mts are closer to the field of boninites and tholeiites from Mariana fore-arc zone (Fig. 7).

The above mentioned facts about the MDS metabasic rocks show that they are situated in various fields (MORB, IAT, boninites) on the used diagrams. The diversity of their character can be clearly seen in Table 2 where we compare the values of some indicative ratios for the metagabbros and those of druzite, bonninite, island-arc tholeiite, MORB and primitive mantle.

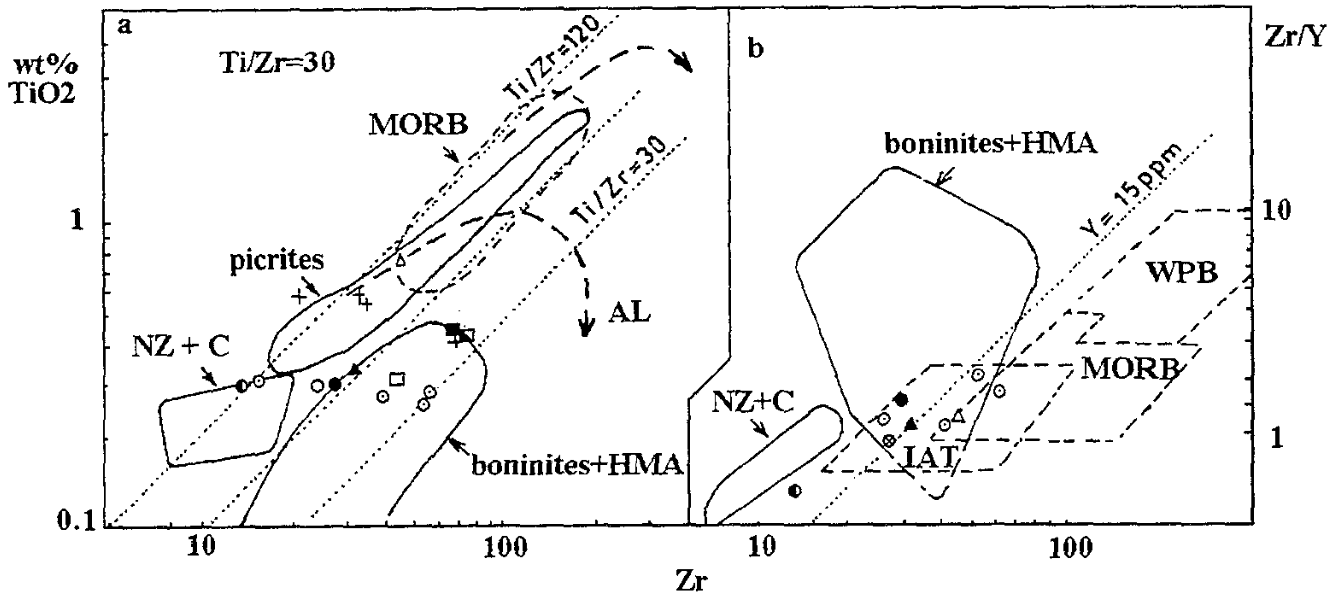

Fig. 4. *a* - TiO_2(wt%) - Zr(ppm); *b* - Zr/Y(ppm) - Zr(ppm) in the metabasites from MDS, Karelia region and IAT-like orthoamphibolites from the northern part of Central Rhodope. Fields and trends after Hall, Hughes (1987)
Фиг. 4 *a* - TiO_2(wt%) - Zr(ppm); *b* - Zr/Y(ppm) - Zr(ppm) в метабазитите от МДС, Карелия и IAT подобни ортоамфиболити от северната част на Централни Родопи. Полетата и трендовете са по Hall, Hughes (1987)

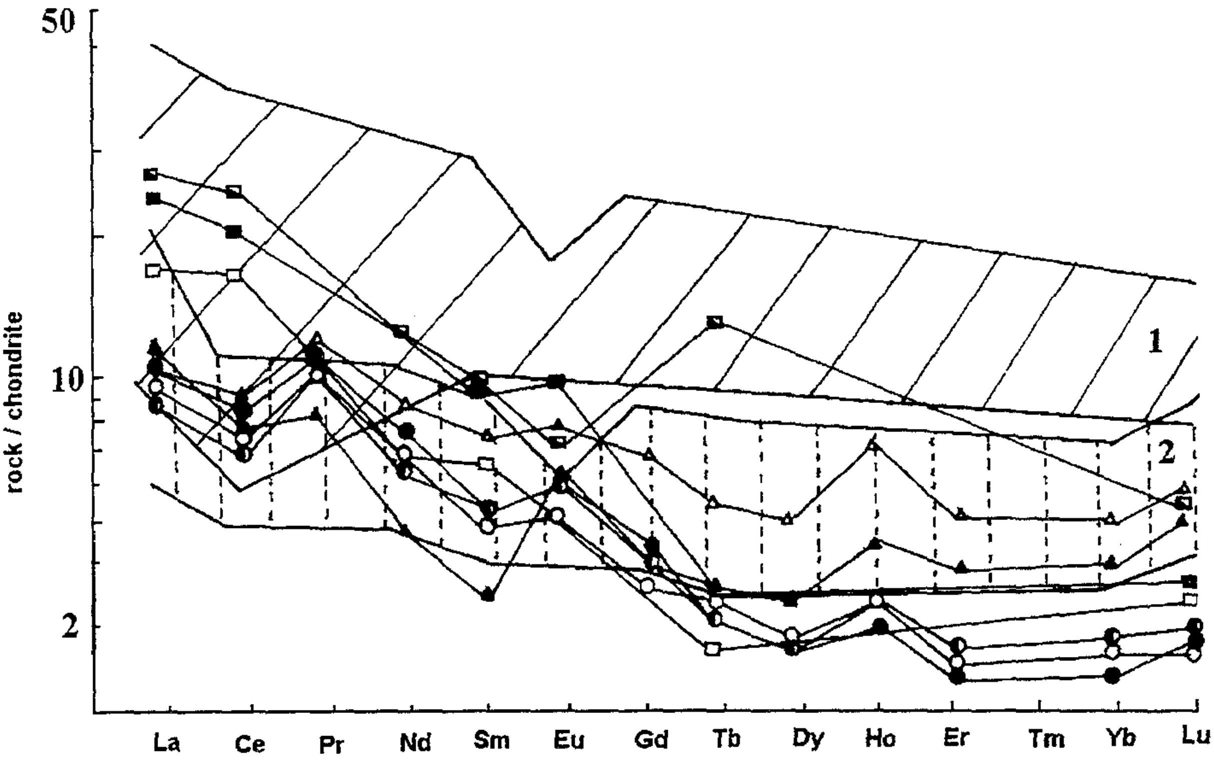

Fig. 5. Chondrite-normalized REE patterns in metabasites from MDS and Karelia region: 1 - field of micropyroxenites from the Bushveld massif; 2 - field of boninites from the Izu-Bonin island arc. Fields after Sharkov et al. (1994)
Фиг. 5. Хондрит-нормирано разпределение на РЗЕ в метабазитите от МДС и Карелия: 1 - поле на микропироксенитите от масива Бушвелд; 2 - поле на бонинитите от Изу-Бонинската островна дъга. Полета по Sharkov et al. (1994)

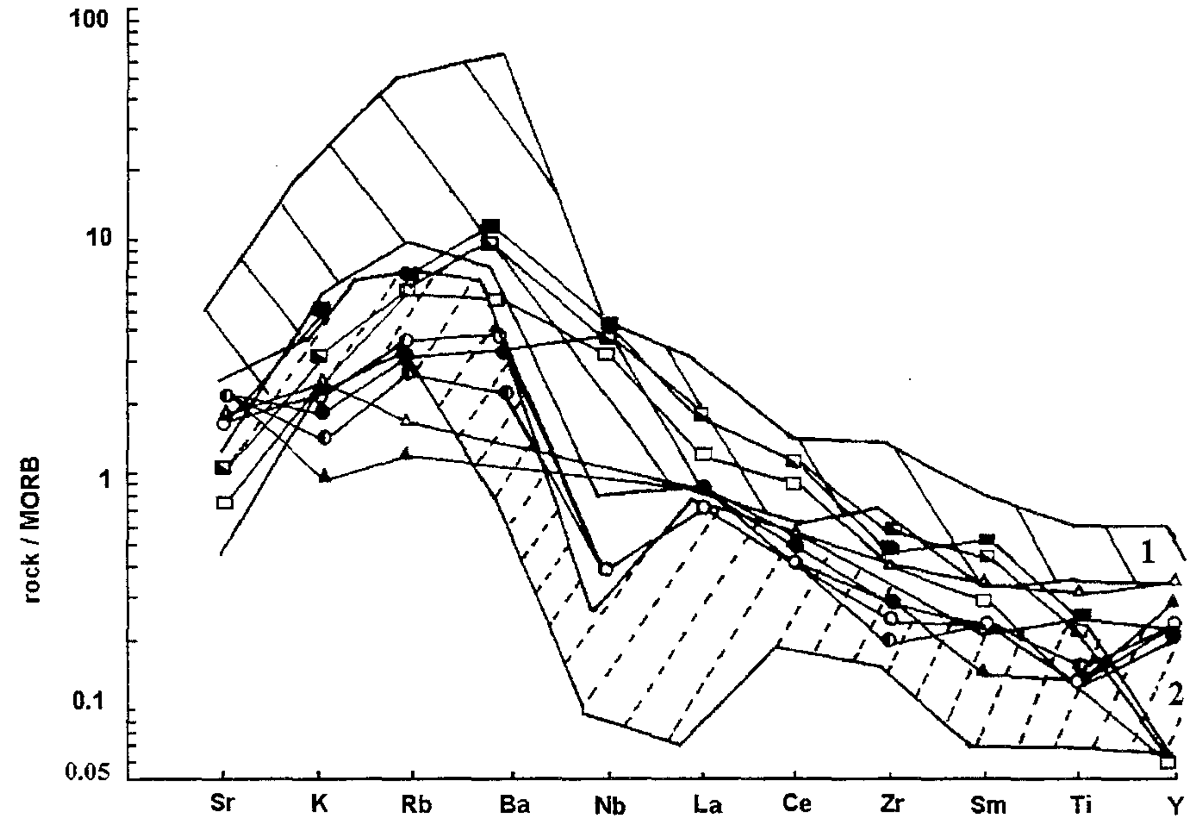

Fig. 6. MORB-normalized trace element patterns in metabasites from MDS and Karelia region: 1 - field of Mariana volcanic-arc tholeiites; 2 - field of Pacific Ocean boninites. MORB data after Taylor, McLennan (1985); fields after Sharkov et al. (1994)

Фиг. 6. MORB-нормирано разпределение на редките и разсеяни елементи в метабазитите от МДС и Карелия: 1 - поле на толеитите от Марианската вулканска дъга; 2 - поле на бонинитите от Тихия океан. Данни за MORB по Taylor, McLennan (1985); полета по Sharkov et al. (1994)

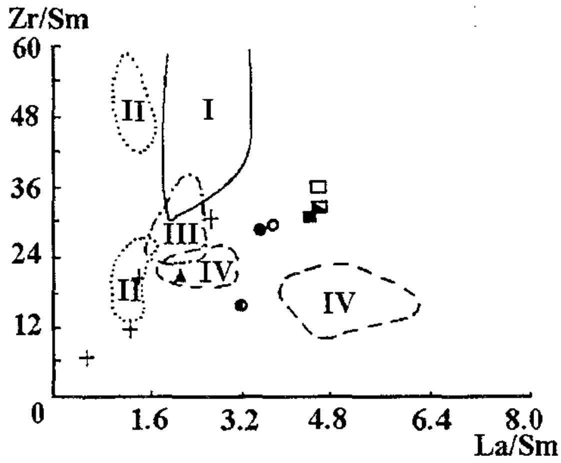

Fig. 7. La/Sm - Zr/Sm - diagram for metabasites from MDS and Karelia region: I -field of Mariana Trench boninites and Izu-Bonin fore-arc zone; II - field of boninites and tholeiites from the Mariana fore-arc zone; III - field of Guam boninites; IV - field of boninites from the Mariana active volcanic arc. Fields after Sharkov et al. (1994)

Фиг. 7. La/Sm - Zr/Sm - диаграма за метабазитите от МДС, Карелия и IAT от северната част на Централни Родопи: I - поле на бонинити от Марианския жлеб и Изу-Бонинската преддъгова зона; II - Поле на бонинитите и толеитите от Марианската преддъгова зона; III - поле на бонинитите от Гуам; IV - поле на бонинитите от Марианската активна вулканска дъга. Полета по Sharkov et al. (1994)

Conclusion

The content of major, some trace elements and REE of the rocks from MDS, their CaO/Al_2O_3, CaO/TiO_2 and Al_2O_3/TiO_2 ratios (Table 2), the negative Nb- and Ti-anomalies in the spidergrams (Fig. 5) are typical of modern boninitic lavas. Boninites are one of the few arc-volcanic rocks that have petrographic and chemical characteristics of primitive mantle-derived magmas. By their Ti/Zr, Ti/Y and Zr/Y ratios (Table 2) the metabasic rocks from MDS are closer to IAT. They are also similar to IAT-like orthoamphibolites from the northern part of Central Rhodope Mts. The geochemical characteristics of the MDS metabasites define them as transitional between modern boninite rocks and island-arc tholeiites and show their marked affinity to primitive island-arc rocks.

Hall and Hughes (1987) and Sharkov et al. (1994) have pointed out that analogous transitional compositions are typical of the Early Proterozoic high-magnesian series from a number of Precambrian terrains. The most dis-

Table 2
Indicative ratios for the studied rocks
Таблица 2
Индикаторни отношения за изследваните скали

Ratios	gabbro G3	gabbro G5	gabbro G17	606	610	704	boninite 50-28-r	IAT D27-3	MORB	primitive mantle
	this study			Zakariadze et al., 1993		Sharêov et al., 1994	Bloomer, Hawkins, 1987		Taylor, McLennan, 1985	
CaO/Al_2O_3	0.64	0.59	0.57	0.73	0.55	0.56	0.58	0.58	1.04	0.82
CaO/TiO_2	24	33	33	16	29	14	28	9	5.9	16
Al_2O_3/TiO_2	38	56	57	22	53	25	48	16	5.6	20
Ti/Zr	70	130	65	96	62	40	34	88	112	110
Ti/Y	166	177	182	256	145	619	263	184	281	291
Zr/Y	2.4	1.4	2.8	2.7	2.4	15.3	7.8	2.1	2.5	2.5
Zr/Nb	32.1	17.1	2.1	-	-	5.8	7.8	16	36.4	15
Y/Nb	14	12	0.8	-	-	0.4	1	7.5	14.5	6
Sr/Y	19	26	29	13	21	31	7.8	4.7	4.1	5
La/Ce	0.50	0.40	0.47	0.39	0.55	0.39	-	-	0.32	0.39

tinctive features of the Precambrian high-magnesian series are their isotopic characteristics, displaying ancient sialic crustal contamination. Further isotopic analyses of the MDS metabasic rocks can determine their relation to the Precambrian magmatic activity.

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