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EARLY PALEOZOIC METABASALTS AND METASEDIMENTARY ROCKS FROM THE MALÉ KARPATY MTS (WESTERN CARPATHIANS): EVIDENCE FOR RIFT BASIN AND ANCIENT OCEANIC CRUST

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Abstract: Most of the Malé Karpaty Mts, which form a geographical connecting link between the Eastern Alps and Western Carpathians, consists of an Early Paleozoic low-grade metamorphic complex intruded by Lower Carboniferous granitoid plutons. Metamorphic recrystallization connected with granite emplacement led to the formation of a crystalline complex metamorphosed under greenschist to amphibolite facies conditions. Major and trace element contents of metabasalts and clastic metasedimentary rocks have been studied in this crystalline complex. Distribution of relatively immobile trace elements (REE, HFSE) was unaffected by metamorphism and reflects original magmatic or sedimentary compositions. Two geochemical types of metabasalts have been indentified in relation to their geological position: (1) metabasalts occurring in association with metagabbros, metadolerites and small amounts of black shales and metacherts are of N-MORB type and (2) small metabasalt bodies in clastic metasedimentary rocks with sporadic carbonates are close to E-MORB/OIT or CT in composition. The clastic sedimentary rocks are represented by alternating metapsammitic rocks with variable admixture of pelitic component and organic matter together with a smaller amount of metapelitic rocks and black shales. Relatively uniform major and trace element distribution in the clastic metasedimentary rocks indicates uniformity of the composition and source area of protolith. The protolith of the metasedimentary rocks were close to greywackes from the ensialic back-arc basin depositional setting, with a source comprising mostly a mixture of acid and intermediate magmatic rocks in the upper continental crust. A new lithostratigraphical division of the Early Paleozoic complex of the Malé Karpaty Mts is proposed. We define here two groups: (1) the Pernek Group — a metamorphosed incomplete (dismembered) ophiolite sequence representing a relic of the upper part of the oceanic crust Pre-Lower Carboniferous in age and (2) the Pezinok Group composed of clastic metasedimentary rocks with a small amount of metacarbonates and metabasalts with E-MORB/OIT or CT signature Silurian–Devonian in age which represents a part of the rift basin fill probably inboard of an ensialic island arc. Both groups came into contact during strong shortening and nappe formation processes in the Pre-Early Carboniferous (Late Devonian?) time.

Key words: Western Carpathians, Early Paleozoic, rift basin, oceanic crust, metabasalts, metasedimentary rocks, geochemistry.

Introduction

The Malé Karpaty Mts form a link between the Western Carpathians and the Alps. The geological structure of the Malé Karpaty Mts bears several specific features concerning both its main elements — pre-Alpine and also Alpine rock complexes. The pre-Alpine complex, generally designated as a crystalline complex: in contrast to the majority of West-Carpathian crystalline complexes, is distinct in: (1) the presence of relatively lower-grade metamorphic rocks, (2) a clearly intrusive relation of the granitoids to the overlying rocks and (3) widespread contact metamorphism. Although numerous studies have been made during recent decades, there are many crucial problems of this complex, which remain still unsolved such its tectonic position, lithostratigraphy, geodynamic setting and sedimentary environment and source of sediments. The aim of this work is an attempt to solve the above mentioned problems using the geochemical data obtained by study of two most widespread rock types of the Malé Karpaty Mts crystalline complex (MKMCC) — metabasalts and metasedimentary rocks.

Geology

The MKMCC forms the westernmost part of the Tatric Unit of the Central Western Carpathians. It comprises metasedimentary rocks and metamorphosed basic rocks intruded by the Bratislava and Modra granitoid massifs (Fig. 1). In relation to both massifs, the metasedimentary rocks and metabasites are located by several ways as follows: (1) a relatively thin strip of these rocks fringing the NW margin of the Bratislava Massif, (2) a similar strip fringing the SE side of the Modra Massif, (3) a relatively compact area between both massifs (Pezinok-Pernek area), (4) inliers in the Modra Massif and (5) small enclaves in the Bratislava Massif between the Bratislava suburbs of Lamač and Rača or near the village of Jur (Fig. 1). This localization results from a combination of: (1) primary relations between Variscan granitoid massifs and their mantle, (2) Alpine tectonism and nappe forming and (3) present-day erosion level. In practically all the above-mentioned positions the sedimentary and basic magmatic rocks were variably intruded by small granitoid bodies and experienced metamorphic recrys-

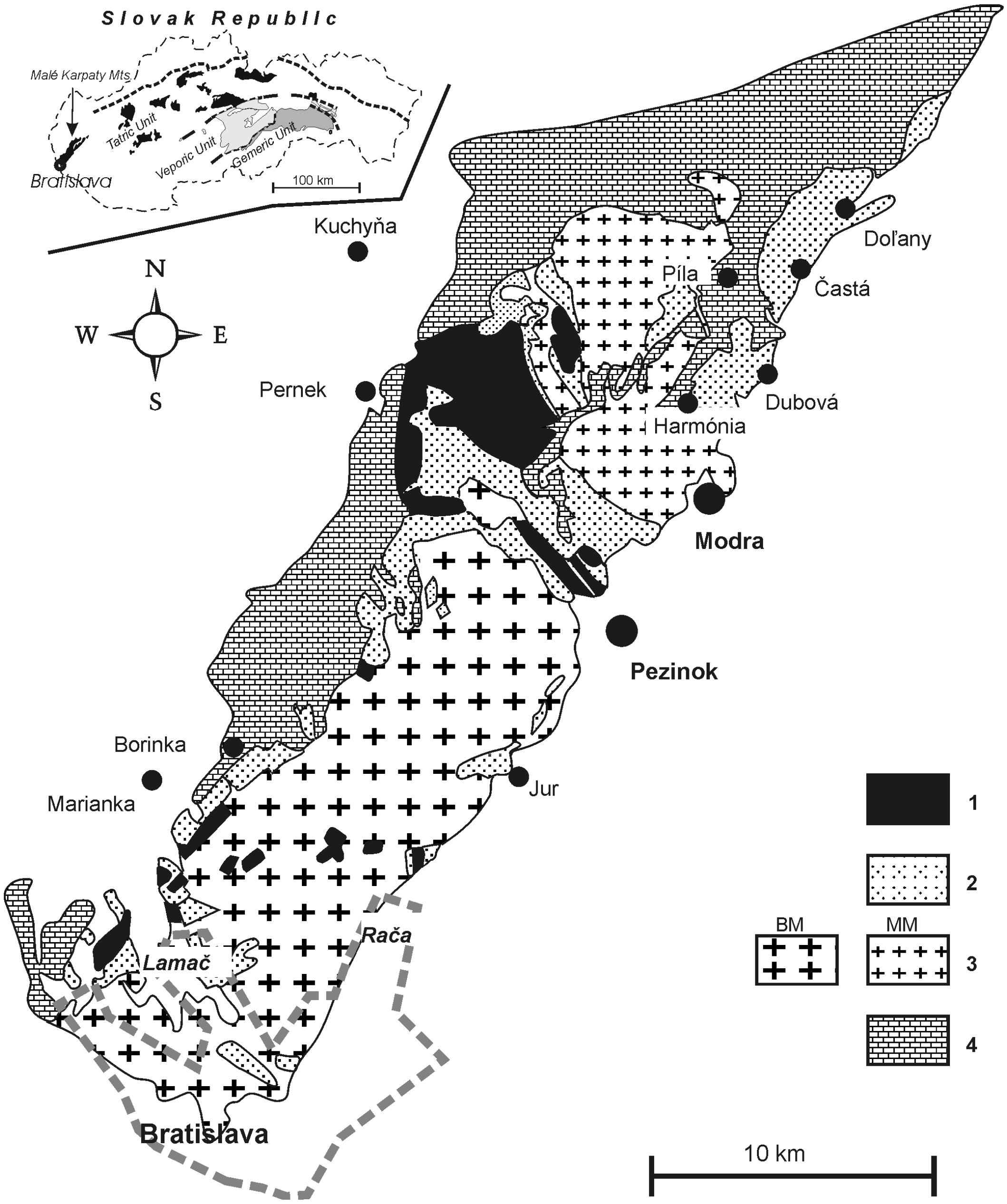

Fig. 1. Schematic geological map of the Malé Karpaty Mts illustrating the extent of Early Paleozoic metabasite and metasedimentary complexes. *Explanations:* 1 — Metabasite complex (Pernek Fm), 2 — Metasedimentary complex (Pezinok Fm), (1–2 — Early Paleozoic), 3 — Granitoids (BM — Bratislava Massif, MM — Modra Massif, both Lower Carboniferous), 4 — Mesozoic formations of the Malé Karpaty Mts. Blank areas represent the Tertiary cover.

tallization related to the emplacement of granitoid massifs. The prevailing rock types include various types of psammitic and to a lesser extent also pelitic metasedimentary rocks, locally with organic matter as well as metabasites — massive magmatogenic amphibolites, actinolite schists and coarse-grained amphibolites. There are obvious spatial differences in the original character of sedimentation. Although psammitic sedimentation was dominant, around Harmónia–Dubová villages (N of the Modra town) frequently alternated various types of pelitic sediments predominat and sporadic small bodies of organogenic limestones have also been found here (Cambel 1962). Moreover rhythmic flysch sedimentation has been identified at some places (Putiš 1986, 1987).

The studied metamorphosed basic rocks occur in two separate settings. Most of them form a compact whole enclosing several belts of black shales and stratiform sulphide bodies (so called "productive zones"). Only a small part of metabasic rocks occurs as small bodies (up to several tens of meters) in the formation containing metamorphosed pelitic sediments, black shales and rare carbonates in the Harmónia-Dubová area. In areas where psammitic sediments are dominant no metabasic rocks have been found.

Palynological research in the Harmónia area determined the age of the MKMCC as Late Silurian to Devonian (Andrusov 1959; Cambel & Čorná 1974; Planderová & Pahr 1983; Cambel & Planderová 1985). This age is also supported by the results of the whole-rock Rb-Sr dating of gneisses which revealed the whole-rock isochron age 380±20 My (minimal age of the isotopic homogenization interpreted as the age of the first metamorphic alteration; Cambel et al. 1990).

The MKMCC experienced a multi-staged metamorphic alteration. Cambel (1962) described them as a combination of the regional pre-granite metamorphic episode, deep contact (periplutonic) and contact metamorphism. Korikovsky et al. (1984) suppose that during the intrusion of the Bratislava Massif, metamorphic zones were created around it, from the thermally lowest biotite, through garnet and staurolite-chlorite, to the highest temperature staurolite-sillimanite zone. Contact metamorphism occurred mainly at the contact between the Modra granitoids and the overlying rocks. Overlapping of contact metamorphism and zones of regional metamorphism led to various types of contact hornfelses (Korikovsky et al. 1985).

Several schemes of lithostratigraphic division of the MKMCC have been developed. The complex was originally defined as a single lithostratigraphic unit: the Pezinok-Pernek Crystalline Complex with the Harmónia Series as its local member (Cambel 1962). Putiš (1986, 1987) defined this complex as “the Malé Karpaty Group” which he divided into two formations: a lower A formation — a rhythmic flysch with thin layers of basic volcanics and volcanoclastics in its upper part, and an upper B formation originally composed of dark quartzites and schists with a limestone layer, over which lie voluminous extrusive basalts with accompanying tuffs and dykes of gabbrodiorites. Later this scheme was modified by the definition of the four local members taking into account regional differences in lithology and tectonic position (Plašienka & Putiš 1987). A different scheme was proposed by Hovorka (in Grecula & Hovorka 1987) who discerned three formations in the MKMCC as follows: (1) Pernek Fm, formed mostly by metabasites, (2) Pezinok Fm, containing mainly clastic sediments and (3) Harmónia Fm, identical with the Harmónia Series defined by Cambel (1962).

The present-day position of the whole MKMCC including the intrusive granitoids is thought to be tectonic forming a part of the Alpine nappe structure (Plašienka & Putiš 1987; Plašienka et al. 1991; Putiš 1991, 1992).

Petrography

Metamorphosed basic magmatic rocks (mostly basalts) and clastic sedimentary rocks form the main rock types in the Early Paleozoic MKMCC. Subordinate black shales and occasional limestones are also present.

Detailed petrography of all the above-mentioned rocks (Cambel 1962 and references therein) showed variability in petrographic rock types, particularly in metabasites, which was correctly ascribed by the author to the differences in (1) protolith and (2) metamorphic evolution.

No primary magmatic minerals have been found in the metabasites and original magmatic textures are only sporadically preserved. On the basis of these textural relics, grain-size and pseudomorphs after magmatic plagioclase grains and phenocrysts, various types of gabbros, dolerites, basalts and basaltic volcaniclastics have been identified.

Basaltic rocks were transformed by metamorphism into rocks with petrographic characteristics ranging from greenstones (greenschists) to amphibolites. Badly preserved relics of doleritic, ophitic, intersertal, porphyric, amygdaloidal and hyaloclastite textures were locally found. Oriented acicular amphibole is a most widespread constituent in the mineral composition of all these rocks. In textures and mineral association they resemble rocks described in Alpine literature as prasinites (e.g. Eskola 1939). Differences in metamorphic evolution resulted in variable chemical composition (and colour) of amphibole and also small changes of the mineral association and textures. On the basis of these petrographic features the metabasalts of the MKMCC can be tentatively divided into the following petrographic types: (1) greenstones (greenschists), (2) lower temperature amphibolites, (3) higher temperature amphibolites and (4) hornfelsed amphibolites.

Greenstones (greenschists) are light green massive or foliated rocks composed mainly of actinolite, albitic plagioclase, prehnite or clinozoisite formed in its place or less frequently epidote. They also contain accessory carbonate, titanite and pyrite. All other petrographic types originated as a result of further progressive greenstone transformation.

Lower temperature amphibolites contain blue-green amphibole (mostly magnesiohornblende or tschermakite) and albitic plagioclase. Actinolite is locally preserved in the form of relic cores in some amphibole porphyroblasts. Small relics of prehnite or clinozoisite and epidote are also sporadically preserved. Disseminated small grains of magnetite or pyrite rimmed by magnetite are common. Textural patterns are almost identical to greenstones.

Higher temperature amphibolites are composed of brown-green amphibole (magnesiohornblende or pargasite) and albitic plagioclase. In some larger amphibole grains blue-green amphibole cores are preserved. Original small epigenetic carbonate veins have been transformed to metamorphic diopside. Textures originally inherited from the greenstone stage have been modified by metamorphic recrystallization, which led to a grain coarsening and also to more perfect evolution of amphibole crystals.

Hornfelsed amphibolites are grey-brown in colour as a result of the presence of light brown amphibole and a small amount of Mg-biotite. They occur only occasionally in pelitic metasedimentary rocks of the Harmónia-Dubová area and display well preserved textures of original greenstone with typical prismatic amphibole. A partial recrystallization, colour changes in amphibole and locally also formation of a small amount of Mg-biotite are the only results of the thermal effect of the Modra granitoid massif.

Metasedimentary rocks of the MKMCC were petrographically described by Cambel (1962) and Cambel et al. (1990). Various types of phyllite and gneiss are especially common. According to Korikovsky et al. (1984) the almandine isograd represents the boundary between phyllites and gneisses. Black shales, contact hornfelses, skarns and marbles are also typical for the MKMCC.

Greenschist facies metapelites, classified as phyllites, are light grey to dark grey in colour, and banded. An augen texture is characteristic of associated metapsammites. The eyes are mostly composed of plagioclase and quartz, clastic in origin. Alternating metapelitic and metapsammitic layers millimetres to centimetres in thickness are relatively common. The most frequent minerals in the phyllites are chlorite, sericite, quartz, plagioclase and biotite. Zircon, apatite, tourmaline and ore minerals represent the most widespread accessory minerals. Also organic matter usually in the form of tiny pigment is frequently preserved in these rocks.

Mid-amphibolite facies metapelitic and metapsammitic gneisses of the MKMCC display oriented and often also banded textures. They contain biotite, muscovite, garnet, staurolite, sillimanite, plagioclase and quartz with accessory zircon, apatite, tourmaline, pyrite and pyrrhotite.

Areally-widespread metamorphism of the sediments was overprinted at the contacts of granitoid plutons (mainly Modra pluton) by local contact metamorphism, which led to the formation of contact hornfelses (Cambel 1962; Korikovsky et al. 1985; Cambel et al. 1989) composed of biotite, muscovite, cordierite, andalusite, plagioclase and quartz. The contact hornfelses frequently have well preserved relicts of the original textures and structures of the metapelites and metapsammites. Impure carbonatic sediments were transformed to skarns containing clinopyroxene, garnet, zoisite, wollastonite and vesuvianite (Cambel 1962; Cambel et al. 1989).

Analytical methods

The distribution of major and trace elements has been studied in selected samples of metabasaltic and metasedimentary rocks chosen for their variety of petrographic type, metamorphic alteration, lithostratigraphic relations and geographic localization. For the reconstruction of the protoliths, their geochemical type and geodynamic setting or petrographic type, provenance and source material, we used trace elements. We concentrated on petrologically significant elements thought to be "immobile" in metamorphic and hydrothermal fluid as the high-field strength elements (HFSE — Zr, Nb, Hf, Th), the rare earth elements (REE), and also Y, Sc, Ti and Cr (e.g. Taylor & McLennan 1985; Bhatia & Crook 1986; Grauch 1989; Schlaegel-Blaut 1990; Verma 1992; McLennan et al. 1993; Rollinson 1993; Bach & Irber 1998).

All major elements, as well as Nb, Zr, Y, Ni, Rb and Sr were determined by XRF method, by the company Gematrix, Prague-Černošice (Czech Republic) in metabasalt samples and by the UNIGEO Company, Brno (Czech Republic) in samples of metasedimentary rocks. CO_2 in metabasalt samples were determined coulometrically, sulphur by the LECO method, H_2O^- and loss on ignition (LOI) gravimetrically also by the Gematrix. The analyses of other elements in all samples were performed by the INAA using the slightly modified method by Kotas & Bouda (1983) in laboratories of the company MEGA, Stráž pod Ralskem (Czech Republic).

Geochemistry

Major and trace element analyses of metabasalts of the Early Paleozoic MKMCC are summarized in Table 1. The distribution of the major elements in the studied rocks is relatively uniform and compatible with original character of these rocks. Low contents of titanium, alkalies and phosphorus are characteristic. Low loss on ignition (LOI) is a result of an absolute dominance of amphiboles over other rock hydrosilicates in the rocks. The reliability of petrographic criteria for identification metabasalts in the whole group of metamorphosed basic rocks was verified by testing in the diagram Al_2O_3 vs. TiO_2 (Pearce 1984 in Miller & Thoni 1997; Fig. 2). The subalkalic (tholeiitic) character of these metabasalts is indicated by diagrams SiO_2 vs. Zr/TiO_2 and Zr/TiO_2 vs. Nb/Y (Winchester & Floyd 1977).

Two geochemically different groups of metabasalts can be distinguished, based on the distribution of REE and other trace elements. The first group is represented by metabasalts forming a complex unit with metagabbros, metadolerites and black shales with stratiform pyrite deposits, the second one by small metabasaltic bodies in clastic metasedimentery rocks. The flat chondrite normalized REE patterns (La_N/Yb_N= 0.87–1.39) for metabasalts of the former group (Fig. 3) are similar to oceanic basalts of N-MORB (normal mid-ocean ridge basalt) type including of typical LREE (light rare earth element) depletion (La_N/Sm_N= 0.66–0.89). Observed differences among the individual samples (total REE concentration, small Eu-anomaly) seem to be unrelated to the character of metamorphic alteration, but they are caused by fractionation effects. Actinolitic rocks with an admixture of organic matter, thought to be metamorphosed volcaniclastic

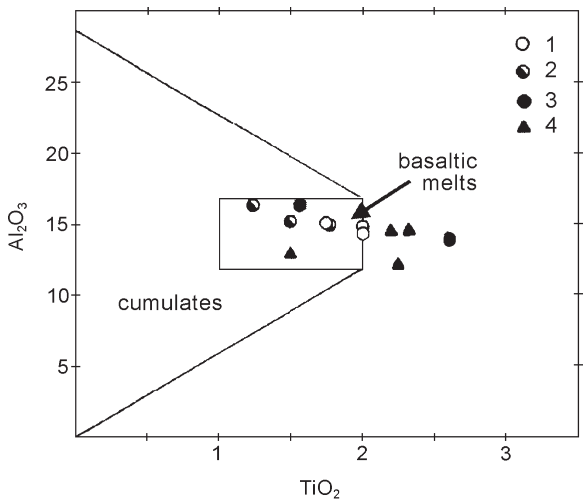

Fig. 2. Early Paleozoic metabasalts from the Malé Karpaty Mts in the diagram Al_2O_3 vs. TiO_2 (Pearce 1984 in Miller & Thöni 1997). No sample is projected into cumulate field which indicate the reliability of their petrographic identification as volcanic rocks. *Explanations:* **1** — Greenstones, **2** — Lower temperature amphibolites, **3** — Higher temperature amphibolites, (1–3 — metabasite complex/ Pernek Fm), **4** — Hornfelsed amphibolites from the metasedimentary complex (Pezinok Fm).

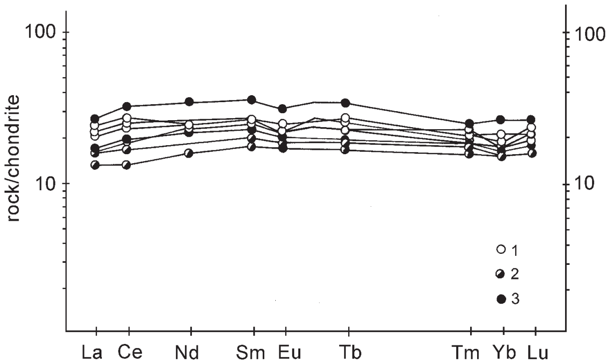

Fig. 3. Chondrite normalized REE patterns of the metabasalts from the metabasite complex of the Malé Karpaty Mts (Pernek Fm). Normalization by Evensen et al. (1978). Explanation of symbols — see Fig. 2.

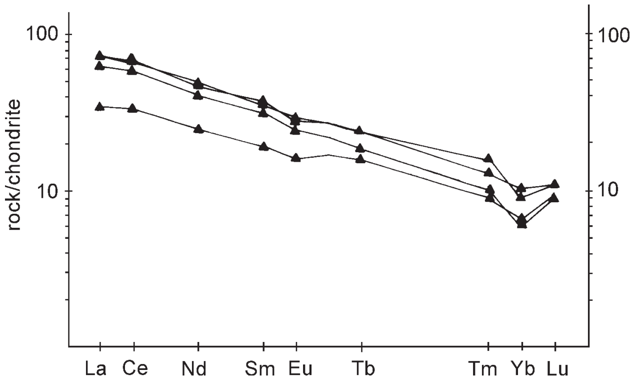

Fig. 4. Chondrite normalized REE patterns of the metabasalts from the complex of metasediments (Pezinok Fm) of the Malé Karpaty Mts. Normalization by Evensen et al. (1978).

rocks, display a comparable pattern. REE patterns of the latter group of metabasalts are relatively steeply sloping as a result of LREE enrichment (La_N= 35.2–74.8) and LREE/HREE fractionation (La_N/Yb_N= 4.83–9.58; Fig. 4).

More specific identification of both geochemical types of metabasalts was made by study of the distribution of further trace elements. In the Cr-Y and TiO_2-Zr diagrams (Pearce et al. 1981; Fig. 5) both groups of metabasalts are projected in

Table 1: Representative chemical analyses of metabasalts of the Malé Karpaty Mts. *Explanations:* Samples VMK-15 to VMK-30 are from the Pernek Group, the others from the Pezinok Group, sample RMK-66 is metamorphosed basic volcaniclastic rock. **A** — greenstones, **B** — lower temperature amphibolites, **C** — higher temperature amphibolites of a relatively upper level, **D** — hornfelsed amphibolite; Fe_2O_3 = total Fe as Fe_2O_3, major oxides in wt. %, trace elements in ppm. LOI = loss on ignition. * — elements determined with a relative standard deviation of 20 to 30 %, ** — over 30 %.

	VMK-15	VMK-48	VMK-45	VMK-41	VMK-52	VMK-33	VMK-1	VMK-30	VMK-19	VMK-26	VMK-21	VMK-22	RMK-66
	B	A	A	B	A	B	C	C	D	D	D	D	B
SiO_2	45.52	46.48	48.95	50.31	47.21	48.05	46.48	47.38	50.50	47.13	47.07	46.70	50.72
TiO_2	1.23	1.74	1.99	1.98	1.75	1.49	2.61	1.56	2.32	2.20	2.25	1.49	2.14
Al_2O_3	16.31	15.08	14.69	14.29	15.04	15.09	14.01	16.34	14.52	14.52	12.12	12.81	14.22
Fe_2O_3	10.21	11.78	11.47	10.98	12.53	10.88	14.17	10.73	12.50	13.32	14.45	13.77	12.61
MnO	0.17	0.18	0.22	0.18	0.21	0.17	0.22	0.17	0.19	0.19	0.21	0.26	0.13
MgO	9.19	6.66	7.11	6.14	6.98	8.21	5.73	6.88	6.60	6.20	14.16	12.25	7.88
CaO	13.09	12.02	9.25	8.97	10.46	11.68	11.44	11.94	8.03	11.24	6.68	7.71	5.56
Na_2O	1.47	2.11	2.52	3.06	2.22	2.66	2.91	2.76	3.63	2.57	1.47	1.23	3.01
K_2O	0.29	0.90	1.08	0.44	0.88	0.33	0.11	0.12	0.35	0.64	0.08	0.46	0.46
P_2O_5	0.09	0.16	0.18	0.19	0.14	0.09	0.22	0.13	0.24	0.31	0.30	0.13	0.35
H_2O	0.43	0.22	0.10	0.19	0.27	0.19	0.30	0.18	0.22	0.18	0.13	0.17	0.53
LOI	2.14	2.62	2.28	2.18	2.15	1.09	1.77	0.88	0.85	1.41	0.91	1.78	3.15
Total	100.14	99.95	99.84	98.91	99.84	99.93	99.97	99.07	99.95	99.91	99.83	98.86	100.76
CO_2	0.12	0.44	0.04	0.05	0.14	0.06	1.38	0.10	0.02	0.17	0.03	0.03	
SO_3	0.02	0.04	0.02	1.08	0.57	0.02	0.04	0.86	<0.01	0.42	0.02	1.16	
Cr	425	231	146	98.5	176	330	70.5	300	292	435	620	925	415
Ni	157	58	50	40	46	61	40	51	61	100	290	293	115
Co	47.5	44.5	49.5	46.5	55.5	50.5	46.0	48.0	41.0	49.5	69.0	94.0	50.0
Sc	36.5	44.5	46.5	45.0	48.0	45.0	48.0	42.5	27.9	25.4	23.4	25.1	26.2
Rb	22	45	49	32	50	24	19	25	24	34	15	36	20
Sr	177	282	206	166	179	212	230	533	212	397	70	527	189
Ba	179*		173*					455	217	380			130
Zr	67	105	124	129	102	88	152	115	88	153	134	92	193
Y	20	25	31	29	27	23	37	22	23	19	14	12	24
Nb										14	16	7	18
Ta	0.078*	0.299	0.236*	0.35	0.126**	0.158*	0.42	0.154*	0.89	1.10	1.25	0.59	0.95
Hf	1.95	2.90	3.3	3.3	2.70	2.40	4.2	2.90	3.6	4.2	3.5	2.15	3.9
Th	<0.077	<0.096	0.34*	<0.082	<0.10	<0.084	0.42	<0.087	1.40	2.95	1.95	0.97	2.70
La	3.2	5.1	5.4	6.1	4.1	3.9	6.6	4.2	13.0	18.2	15.6	8.6	16.8
Ce	8.7	15.0	17.0	18.0	12.6	10.9	21.2	13.3	31.5	43.0	38.5	22.1	39.0
Nd	7.5*	11.6*	17.5	11.8	10.8*	11.4	16.7	10.3	20.7*	24.3*	19.9*	12.1	31.0
Sm	2.75	3.8	4.3	4.3	3.5	3.1	5.6	3.6	5.0	5.8	5.1	3.1	5.4
Eu	1.05	1.30	1.50	1.30	1.25	1.10	1.85	1.30	1.60	1.85	1.50	0.98	1.95
Tb	0.64	0.88	0.99	1.05	0.88	0.68	1.30	0.73	0.92	0.95	0.75	0.64	0.77
Tm	0.40	0.42*	0.54	0.55	0.60	0.44	0.63	0.47	0.38*	0.44	0.286*	0.255	0.282
Yb	2.50	3.0	3.5	3.2	3.00	2.60	4.4	2.75	1.75	1.65	1.10	1.20	1.85*
Lu	0.40	0.52	0.54*	0.60	0.54	0.39	0.66	0.50	0.36	0.31	0.256	0.265	0.38

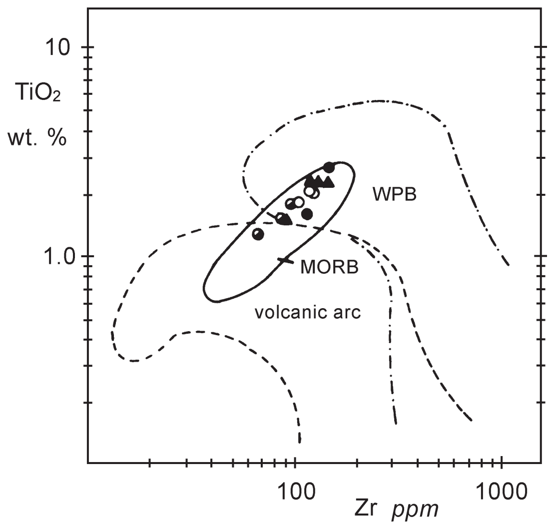

Fig. 5. Diagram TiO_2 vs. Zr (Pearce et al. 1981) for the Early Paleozoic metabasalts from the crystalline complexes of the Malé Karpaty Mts. *Explanations:* symbols — see Fig. 2, **MORB** — mid-ocean ridge basalt, **WPB** — within plate basalt.

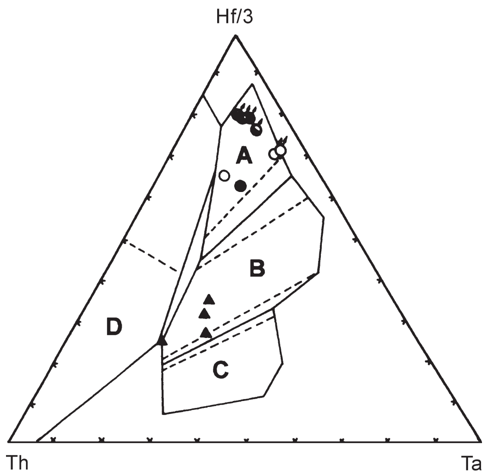

Fig. 6. Hf/3-Th-Ta diagram (Wood 1980) for the Early Paleozoic metabasalts from the Malé Karpaty Mts. Presence of two different geochemical types is evident. *Explanations:* symbols — see Fig. 2; fields in the diagram: **A** — N-MORB (normal mid-ocean ridge basalt), **B** — E-MORB (enriched mid-ocean ridge basalt), **C** — within plate alkaline basalt, **D** — basalts of the destructive margins of lithosphere plates.

the MORB field although where it overlaps with WPB (within plate basalt) field. Hf/3-Th-Ta diagram (Wood 1980; Fig. 6) identified the metabasalts from the complex of metabasites as the N-MORB type, while the metabasalts from the metasediments correspond to the E-MORB/OIT type. The same results followed from the diagram Th/Yb vs. Ta/Yb (Pearce et al. 1981). The transitional tholeiitic/alkali character of metabasalts from metasediments is also supported by discrimination in diagram 2Nb-Zr/4-Y (Meschede 1986) and also in diagram 3Tb-Th-2Ta (Cabanis & Thieblemont 1988) which shows their conformity with continental tholeiites (CT). Taking into account relative immobility of all chemical elements in the above-mentioned diagrams, a redistribution of these elements in the thermal aureole of granitoid massif and possible effect on the discrimination can be excluded.

The metabasalts from the complex of metabasites display some differences in comparison with typical N-MORB. A low Th and higher Zr/Y ratio are present in the more fractionated types, as seen in the Y-Zr diagram (Le Roex et al. 1983; Fig. 7).

Major and trace element analyses of the metasedimentary rocks of the MKMCC are presented in Table 2. Metasedimentary rocks from various local members (in the sense of Putiš 1987) and metamorphic zones were included.

A SiO_2/Al_2O_3 vs. Na_2O/K_2O diagram (Pettijohn 1973; Fig. 8) indicates a possible greywacke protolith. A clear dominance of Na_2O over K_2O in most analysed samples and high content of Na_2O are a characteristic feature of such immature sediments. As follows from Na_2O/K_2O ratio (diagram by Crook 1974) original greywackes might belong to the types with an average content of quartz, which are typical for back-arc ba-

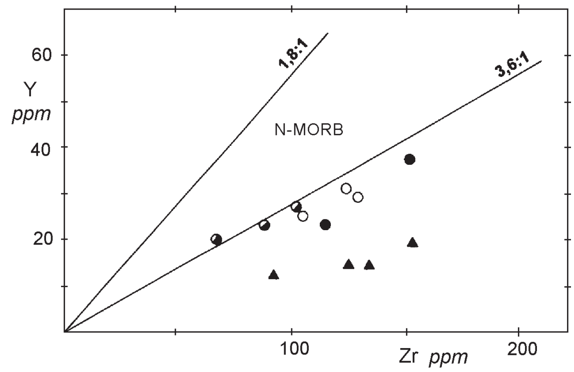

Fig. 7. Early Paleozoic metabasalts of the Malé Karpaty Mts in the diagram Y vs. Zr (Le Roex et al. 1983) discriminated N-MORB from other basalt types. The trend following the boundary of the field is a result of relative depletion in Y. Explanation of symbols — see Fig. 2.

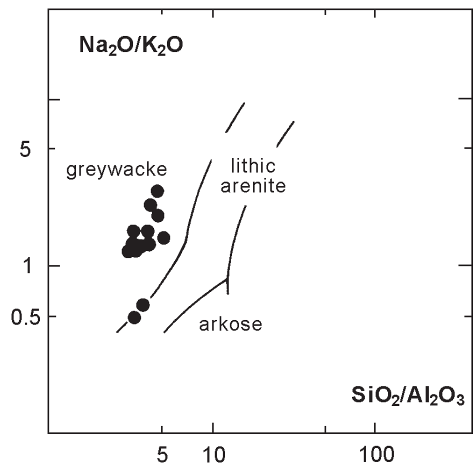

Fig. 8. Diagram Na_2O/K_2O vs. SiO_2/Al_2O_3 (Pettijohn et al. 1973) for the Early Paleozoic metasedimentary rocks of the Malé Karpaty Mts which indicate greywackes as a probable protolith of these rocks.

sins. The distribution of TiO_2 and Ni in these greywackes display magmatic trend and fall on magmatogenic greywacke field (Floyd et al. 1989; Fig. 9). This indicates derivation from a magmatic source probably of acidic composition, and this is confirmed by the distribution of La/Th vs. Hf (Floyd & Laveridge 1987; Fig. 10). On the other hand these rocks in Th/Sc-La/Sc diagram (Totten et al. 2000; Fig. 11) or in Th/Sc-Zr/Sc diagram (McLennan et al. 1993) plot as rather mixed acid-intermedial arc source. Elevated Cr/Th ratios, in comparison to acid magmatic rocks, also indicate the presence of other material in the sediment source.

The chondrite normalized REE patterns of metasedimentary rocks from the MKMCC are practically identical (Fig. 12). There is no relevant influence of the type and intensity of metamorphism on REE patterns. Some moderate differences in total REE contents (REE^{tot}) and intensity of Eu-anomaly are probably caused by original variation in sediment granularity and quartz contents. The effect of the quartz content on REE^{tot} is manifested by close correlation between REE^{tot} and SiO_2 in these metasedimentary rocks. The metapsammite patterns are practically parallel and also display negative Eu-anomalies, typical for greywacke (Eu/Eu*= 0.75–0.8). Elevated REE^{tot} and lower negative Eu-anomaly (Eu/Eu*= 0.6–0.7) in the metapelites (located mostly in the Harmónia-Dubová area) are a geochemical result of the sedimentologically more mature character of their protolith containing more of a clayey component (highest values for Al_2O_3/SiO_2 and K_2O/Na_2O).

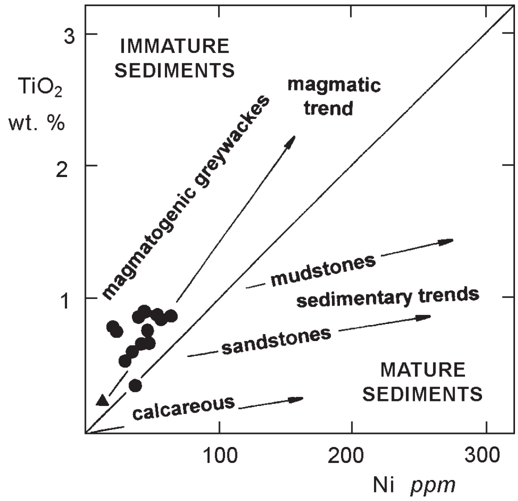

Fig. 9. TiO_2-Ni diagram for the Malé Karpaty Mts. metasedimentary rocks testifying their derivation from a magmatic precursor of predominantly acidic composition. Trends and fields were taken from Floyd et al. (1989).

According to the discriminant diagram of Bhatia & Crook (1986), the low and stable ratio of La/Sc and the broad vari-

Table 2: Representative chemical analyses of metasedimentary rocks of the Malé Karpaty Mts. *Explanations:* Fe_2O_3 = total Fe as Fe_2O_3, major oxides in wt. %, trace elements in ppm. LOI = loss on ignition. * — elements determined with a relative standard deviation of 20 to 30 %.

	RMK-1	RMK-3	RMK-10	RMK-28	RMK-33	RMK-39	RMK-41	RMK-45	RMK-47	RMK-53	RMK-61	RMK-64	RMK-65
SiO_2	55.88	63.80	59.80	61.38	62.25	70.04	65.55	66.85	64.31	66.68	64.13	60.92	64.79
TiO_2	0.85	0.79	0.85	0.09	0.75	0.35	0.54	0.78	0.60	0.67	0.68	0.89	0.86
Al_2O_3	18.09	17.44	17.42	17.66	17.43	14.07	15.59	14.68	15.76	14.68	16.03	17.75	16.53
Fe_2O_3	8.12	6.00	7.97	7.46	7.51	4.62	5.52	5.64	5.35	4.94	5.61	7.19	6.51
MnO	0.11	0.09	0.09	0.11	0.12	0.05	0.07	0.10	0.08	0.07	0.10	0.13	0.10
MgO	3.47	2.05	3.88	2.73	2.88	1.89	2.24	2.32	2.88	2.40	2.83	2.26	2.11
CaO	3.58	1.78	2.81	1.29	1.71	1.26	1.98	2.18	2.78	1.08	1.84	0.57	0.90
Na_2O	3.13	3.46	3.02	2.73	2.89	2.91	4.02	3.64	3.63	3.68	3.04	1.90	2.08
K_2O	2.44	2.49	1.89	2.12	2.28	2.09	1.72	1.32	2.55	1.86	1.89	3.93	3.29
P_2O_5	0.18	0.17	0.20	0.18	0.17	0.07	0.19	0.18	0.19	0.16	0.19	0.20	0.30
H_2O^-	0.47	0.49	0.52	0.44	0.26	0.41	0.46	0.54	0.43	0.60	0.56	0.90	0.48
LOI	1.69	1.65	1.65	3.56	1.69	2.31	2.45	2.10	1.57	2.97	2.85	3.42	2.06
Total	100.68	100.21	100.10	100.56	99.94	100.07	100.33	100.33	100.13	99.79	99.75	100.06	100.01
SO_3	0.23	0.01	0.36	0.01	0.01	0.58	0.21	0.01	0.01	0.01	0.01	0.01	0.01
Cr	116	62.5	106	98	95.5	67	74	71	72	68.5	133	106	91.5
Ni	56	20	64	44	48	39	30	22	35	22	48	52	40
V	141	112	153	165	145	130	131	103	105	102	127	162	142
Co	27.3	16.7	28.1	20.6	24.9	26.1	17.7	15.8	18.8	5.5	20.9	25.7	20.9
Sc	20.1	16.5	18.7	19.7	20.7	14.4	15.5	13.8	14.7	14.7	16.4	20.6	17.2
Rb	81	82	80	74	84	62	60	48	79	51	65	109	121
Sr	294	206	257	173	230	155	250	226	201	215	211	121	124
Ba	960	830	690	650	670	610	770	500	680	930	610	1060	1430
Zr	166	233	145	213	180	135	211	287	173	279	182	249	125
Y	27	36	26	32	32	22	26	29	19	18	22	23	35
Nb	14	18	15	16	13	12	17	13	11	11	9	16	15
Ta	0.75	0.81	0.74	0.77	0.75	0.53	0.65	0.63	0.54	0.65	0.59	0.90	0.87
Hf	4.2	5.7	4.0	4.9	4.7	3.5	5.0	6.8	3.9	5.4	3.7	5.0	5.0
Th	7.4	9.1	7.1	8.4	8.1	5.6	6.7	10.5	4.7	8.5	5.3	10.2	10.6
La	25.6	27.4	29.0	27.9	26.6	16.0	24.0	26.8	21.9	31.5	21.0	33.5	52.0
Ce	59.0	65.8	64.0	62.5	61.0	39.5	56.0	63.0	49.5	68.0	50.0	77.0	113.0
Nd	28.5	33.0	29.2	33.0	30.5	18.2	26.7	30.5	23.2*	32.0*	26.4	31.5	58.5*
Sm	5.1	6.0	5.4	5.7	5.7	3.7	4.8	5.3	4.2	5.2	4.2	6.1	9.2
Eu	1.3	1.4	1.35	1.35	1.30	0.94	1.2	1.25	1.15	1.35	1.15	1.35	1.9
Tb	0.77	0.89	0.81	0.81	0.83	0.52	0.68	0.71	0.54	0.73	0.58	0.76	1.30
Tm	0.39*	0.36	0.36	0.39*	0.29*	0.29	0.22*	0.30	0.30*	0.28	0.24*	0.31*	0.51
Yb	2.55	2.90	2.45	2.55	2.90	1.85	2.45	2.40	1.85*	2.20*	1.70*	2.65	3.1
Lu	0.47	0.55	0.44	0.48	0.53	0.39	0.44	0.45	0.38	0.44	0.34	0.44	0.49

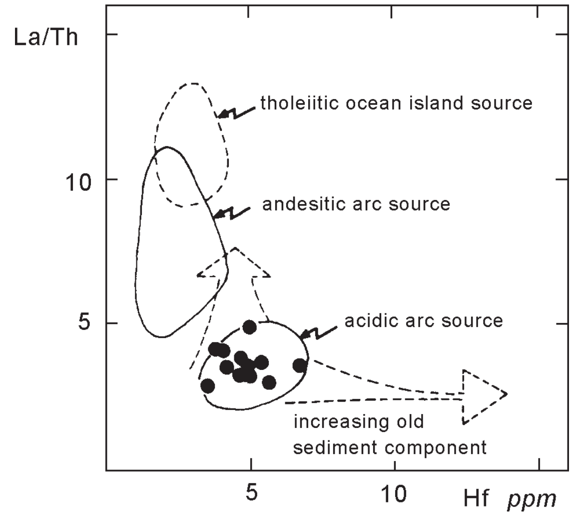

Fig. 10. Discrimination diagram Hf vs. La/Th for the Malé Karpaty Mts metasedimentary rocks indicating derivation from an acidic arc source (fields after Floyd & Leveridge 1987).

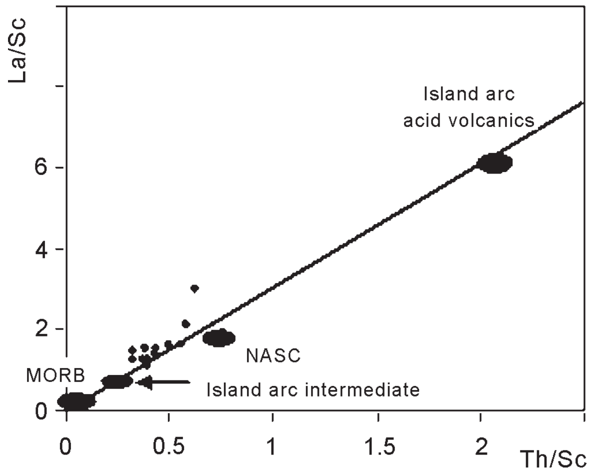

Fig. 11. Diagram Th/Sc vs. La/Sc (Totten et al. 2000) for the Early Paleozoic metasedimentary rocks from the Malé Karpaty Mts.

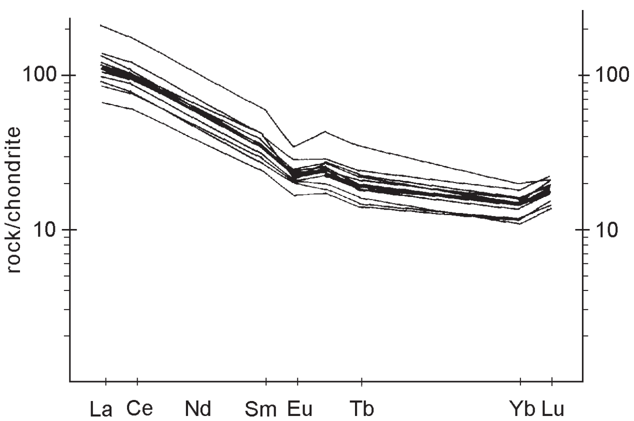

Fig. 12. Chondrite normalized REE patterns of the Early Paleozoic metasedimentary rocks from the Malé Karpaty Mts. Despite their various metamorphic recrystallization (see Appendix: Petrographic description of samples) identical or very similar patters testify to immobility of REE during metamorphism.

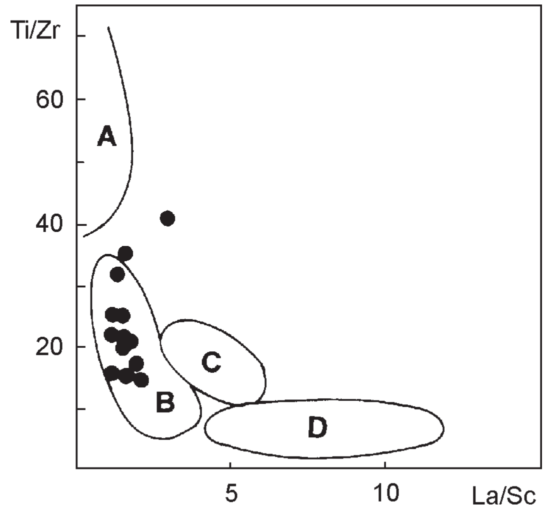

Fig. 13. Chemical discrimination of the geodynamic setting in the diagram La/Sc vs. Ti/Zr for the Malé Karpaty Mts metasedimentary rocks. Fields after Bhatia & Crook (1986): **A** — oceanic island arc; **B** — continental island arc; **C** — active continental margin; **D** — passive margin.

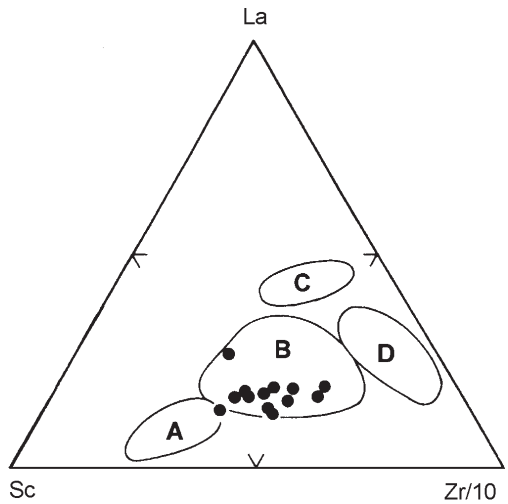

Fig. 14. Chemical discrimination of the geodynamic setting in the La-Sc-Zr/10 diagram for the Malé Karpaty Mts metasedimentary rocks. Fields after Bhatia & Crook (1986). *Explanations:* see Fig. 13.

ability in the ratio of Ti/Zr in the Early Paleozoic metasediments of the Malé Karpaty Mts are compatible with the greywackes of continental island arc provenance (Fig. 13). The identical result follows from diagram La-Th-Zr/10 (Fig. 14) by the same authors which testifies to the geochemically relatively homogeneous protoliths of these metasediments, and the same source area.

Discussion

Previously published papers (Miklóš 1989; Cambel et al. 1990) using major element distribution demonstrated that the protolith of the metasedimentary rocks of the MKMCC were greywackes or subgreywackes with local admixture of pelitic, carbonatic, bituminous and volcaniclastic components. On the basis of REE and other trace element studies Cambel & Khun (1983, 1985) found geochemical differences between black shales from the complex of basic rocks and the metasedimentary complex. Cambel & Spišiak (1979) and Cambel & Kamenický (1982) established the original tholeiitic character of metamorphosed basic rocks and their similarity to oceanic basalts.

Our geochemical study of the metabasalts and metasedimentary rocks shows that primary concentrations and ratios of the most petrogenetically important elements in these rocks were not changed during multi-stage metamorphism, which reached amphibolite facies. This fact allows us to use distribution of these elements for geodynamic and sedimentological reconstructions.

Major and particularly trace element distribution including REEs in metasedimentary rocks indicates that their clastic protolith was petrographically close to the greywackes with plagioclase as a main component, with average content of quartz and a locally small admixture of organic matter. The identical source area and homogeneous composition of the protoliths of the metapelites and metapsammites is documented by the small variation in most of the discrimination graphs. The observed fractionation of some elements is caused mainly by the variation of granularity and quartz content in the protolith. No significant chemical differences exist between phyllitic rocks and gneisses. The REE patterns of the metasediments of the Malé Karpaty Mts crystalline complexes as well as the results of discrimination based on other elements with limited fractionation during weathering, transport and sedimentation, indicate an acid or acid/intermedial magmatic source and ensialic island arc provenance of sedimentation. The age of the source is unknown, but the low initial $^{87}Sr/^{86}Sr$ ratio (0.7101±4) in the detritic material indicates rather a short geological life of the source in the crust as well as low probability of its multistage magmatic reworking (Cambel et al. 1990).

The results of the geochemical study of metabasalts reveal the existence of two different geochemical types in the MKMCC. One type is represented by metabasalts from the complex of basic rocks in which they are associated with metadolerites, metagabbros and also with black shales and small amounts of metacherts accompanied by sulphide deposits. The association, and badly preserved relic textures indicate rather non-explosive lava outflow in a deep-sea environment. Primitive chondrite normalized REE patterns and specific HFSE contents are consistent with N-MORB type. A moderately elevated Zr/Y ratio caused by small depletion in Y is relatively common in some N-MORB formed in back-arc basins (c.f. Sinton & Fryer 1987) and might reflect complex evolution in a mantle source. The complex of basic rocks as a whole can be interpreted as an incomplete (dismembered) ophiolite sequence — a relict of upper part of ancient oceanic crust.

Another metabasalt type occurs as small (tens of meters across) bodies in the metasedimentary complex. Relic amygdaloidal textures preserved in effusive volcanics and original hyaloclastites and volcaniclastic bands associated with the metacarbonate lenses indicate a shallow-water sedimentary environment. REE patterns and the distribution of other relatively immobile incompatible elements in these metabasalts reveal their geochemical similarity to E-MORB/OIT or more exactly to the CT. Metabasalts of the E-MORB/OIT type occur not only in places of coincidence hot spots and oceanic ridges or over hot spots (Saunders 1984), but also in back-arc basins of convergent zones, where they appear in the initial stages of their formation (Volpe et al. 1988; Ikeda & Yuasa 1989; Hochstaedter et al. 1990; Wever & Storey 1992; Ford et al. 1996; Márquez et al. 1999). The CT signature shown by some part of them seems to be a result of the continental crust contamination.

The results of the geochemical study of the metabasalts and metasedimentary rocks are not fully compatible with existing schemes of the lithostratigraphic division of the MKMCC. Strictly different geodynamic setting of magma generation for basalts occurring in metabasic and metasedimentary complexes, together with differences in lithology, sedimentary environment and provenance of sediments suggest that two main lithostratigraphic units are present in the Early Paleozoic MKMCC, which we refer to as the Pezinok and the Pernek Groups.

The Pezinok Group mostly comprises metagreywackes with variable admixture of pelitic and organic matter and less amounts of metaquarzites, metapelitic rocks and black shales. The last two mentioned rock types are locally developed together with some metacarbonates, metabasalts and their volcaniclastics (Harmónia-Dubová area) and are thought to be a consequence of lateral or vertical variability in the Pezinok Group and are considered as members of the group. The age of the whole group is supposed to be contemporary with the Harmónia Member — Late Silurian to Devonian. Metabasalt chemistry (continental tholeiites) together with the source and provenance of metasediments (magmatic source, ensialic island arc provenance) indicate that Pezinok Group originated as a rift basin fill inboard of an ensialic island arc. The Pernek Group, composed of metabasalts, metadolerites, metagabbros with small amount of black shales, metacherts and pyrite stratabound mineralization at the top of the section represents a metamorphosed incomplete (dismembered) ophiolite. The absence of gabbroic cumulates and ultramafic rocks suggests they originated by obduction of the upper part of an ancient oceanic crust, most probably belonging to a back-arc basin in its mature stage of opening. The age of the Pernek Group is unknown but it predates the Early Carboniferous. The Pernek Group corresponds in previous lithostratigraphic schemes to the upper part of Formation B of Putiš (1986, 1987) and is close to the Pernek Formation of Grecula & Hovorka (1987).

Although the Pezinok and Pernek Groups were formed in very different tectonic settings, both they are intruded by the Bratislava and Modra granitoid massifs (Rb-Sr isochron age 348±4 My, Cambel et al. 1990). This shows that both formations were already close together by that time and hence a strong spatial shortening and nappe formation were realized before the Early Carboniferous. Fan-like tectonic structure observed in these formations in the area between the two granitoid massifs may be a result of deformation during their emplacement.

The lack of reliable geochronological dating is a serious handicap when correlating the Early Paleozoic groups of the

Malé Karpaty Mts with other similar Variscan complexes of surrounding regions. Possible relations of the Pezinok and Pernek Groups exist with the so called fossiliferous Paleozoic units of the Eastern Alps, because the Western Carpathian Tatric Unit is usually correlated with Austroalpine unit of the Eastern Alps (e.g. Häusler et al. 1993). Silurian-Devonian complexes with rift-related volcanism similar to that in Pezinok Group are known from the Northern Greywacke Zone (NGZ), Paleozoic of Graz or the Gurktal Nappe (Loeschke & Heinisch 1993). Geochemically identical metabasalts to the CT-type of the Pezinok Group were found in lower part of Saalach Valley (eastern part of NGZ; Schlaegel-Blaut 1990). The Pernek Group, with its clear oceanic affinity has no close equivalent in the above-mentioned units, although volcanics with a back-arc basin basalt (BABB) signature occur in the eastern part of NGZ (Admont-Selztal area; Schlaegel-Blaut 1990). In the Western Carpathians metabasalts of both CT and BABB types occur in the Ordovician-Silurian Gelnica Group of the Gemeric Unit but their exact age is unknown (Ivan 1994). In the Western European Variscides most Devonian volcanics display a rift-related affinity (e.g. Wedepohl et al. 1983; Werner et al. 1987; Pin & Paquette 1997) but also some relics of Devonian oceanic crust with true N-MORB were found (Pin 1990). Interpretation of the geodynamic setting in all the above-mentioned areas is generally the same as in the Malé Karpaty Mts — back-arc rifting.

Conclusions

Geochemical study of the metabasalts and metasediments from the Early Paleozoic crystalline complex of the Malé Karpaty Mts led to the following conclusions:

— Abundances of relatively immobile elements (REE, HFSE) in both metabasalts and metasediments reflects their original distribution in the magmatic or sedimentary protolith. No significant chemical change caused by metamorphic processes has been found.

— Two geochemical types of metabasalts have been identified: (1) N-MORB type in the complex of metabasites and (2) E-MORB/OIT or CT type in the metasedimentary complex.

— The protolith of the metasedimentary rocks were greywackes of the ensialic island arc provenance derived from an acidic/intermedial magmatic source.

— The Early Paleozoic MKMCC can be divided into two lithostratigraphic units: (1) the Pezinok Group and (2) the Pernek Group.

— The Silurian-Devonian Pezinok Group represents a rift basin fill probably formed inboard of an ensialic magmatic arc.

— The Pernek Group is an incomplete (dismembered) ophiolite complex — a relic of the upper part of Pre-Lower Carboniferous oceanic crust.

— The Pezinok and the Pernek Groups experienced major shortening and nappe formation before the Early Carboniferous intrusion of granitoid massifs.

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Appendix

Localization of the analysed samples included in Table 1 and Table 2:

VMK-15, metabasalt, Pernek village, level point Dubník, upper part.
VMK-33, metabasalt, Bratislava, Dúbravka suburb, the western slope of Dúbravská Hlavica hill, outcrop in the slope above the fork of a stream.
VMK-52, metabasalt, Borinka village, Svätý vrch hill, ca. 300 m to the W of the summit.
VMK-41, metabasalt, Borinka village, Svätý vrch hill, hillside placer in the upper part.
VMK-45, metabasalt, Borinka village, Svätý vrch hill, ca. 150 m W of the summit.
VMK-48, metabasalt, Borinka village, Svätý vrch hill, ca. 250 m SW of the summit.
VMK-1, metabasalt, Kuchyňa village, Modranský potok valley, ca. 500 m N from boundary of Kuchyňa village, placer outcrop.
VMK-30, metabasalt, Modranská Baba hill, upper part, placer outcrop.
VMK-26, metabasalt, Dubová village, ridge of Dolinkovský vrch hill, NE slope, placer outcrop.
VMK-22, metabasalt, Harmónia village, valley SW of Dolinkovský vrch hill, NE slope ca. 1 km from the edge of the forest.
VMK-21, metabasalt, Harmónia village, valley on the SW slope of Dolinkovský vrch hill, placer outcrop above a road cutting, ca. 200 m from the edge of the forest.
VMK-19, metabasalt, Dubová village, ridge of Dolinkovský vrch hill, edge of the NE slope, outcrop.
RMK-66, basic metavolcaniclastic rock, Harmónia village, valley SW of the summit of Dolinkovský vrch hill, dump from an old mine gallery.
RMK-1, garnet-biotite gneiss, Kuchyňa village, N slope of the Vývrať valley, 500 m above sea level, outcrop by a road.
RMK-3, biotite gneiss, Kuchyňa village, N slope of the Vývrať valley, 500 m above sea level, outcrop in a road cutting.
RMK-10, garnet-biotite gneiss, Kuchyňa, Modranský potok valley, road cutting in a fork.
RMK-28, garnet-biotite gneiss, Pernek-Baba road, 200 m S of Mäsiarský Ostrovec, below a bend.
RMK-33, garnet-staurolite-biotite gneiss, 300 m NW of Baba settlement, road cutting in a bend.
RMK-39, contact chert-metapelite, Častovská dolina valley, 300 m SE of the two quarries, 335 m above sea level.
RMK-41, biotite metapsammite, Častovská dolina valley, 300 m SE of two quarries, 335 m above sea level, outcrop on the right side of the crossroads.
RMK-45, biotite-sericite metapsammite, Dubová village, E of the gamekeeper house Fúgelka.
RMK-47, biotite-sericite metapsammite, Dubová village, E of the gamekeeper house Fúgelka.
RMK-53, muscovite-sericite metapsammite, NW of Pezinok, Šalátová, 390 m above sea level.
RMK-61, sericite metapsammite, Píla village, Kobylská dolina valley, Papiernička settlement, 300 m to the N, contact with granite.
RMK-64, contact hornfels - metapelite, Harmónia village, Dolinkovský vrch hill, ca. 300 M SW of the summit, placer outcrop.
RMK-65, contact hornfels - metapelite, Harmónia village, Dolinkovský vrch hill, valley on SW slope, mouth of the third small side valley from the NE, scree.