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Major, trace element and REE geochemistry of metamorphosed sedimentary rocks from the Malé Karpaty Mts. (Western Carpathians, Slovak Republic): Implications for sedimentary and metamorphic processes

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Abstract. In Lower Paleozoic crystalline basement of the Malé Karpaty Mts., two geochemical groups of metamorphosed sedimentary rocks were observed: (1) the Active Continental Margin Environment Sedimentary Rocks (ACMESR) and (2) the Deep Ocean Basin Ridge Environment Sedimentary Rocks (DOBRESR). The chemical composition of ACMESR (variable composition, values of the ratio Th/U > 1, values Th/Sc 0.3-0.8, values $La_N/Yb_N > 5$ and values Eu/Eu* 0.6-0.9) indicates components derived from the Young Differentiated Arc (YDA) provenance type. The same geochemical parameters of various types of metamorphosed sedimentary rocks (metapelites, metapsammites, black schists, gneisses, contact metamorphosed rocks) of this group indicate: the same protolith (greywackes, lithic arenites ± organic matter), the same parental rocks (tonalite-granodiorite alternatively dacite-rhyodacite), the same source area (active continental margin) and the same sedimentary environment (continental slope). The chemical composition of DOBRESR indicates the components being derived from the Young Undifferentiated Arc (YUA) provenance type (variable composition, ratio Th/U < 1, ratio Th/Sc < 0.25, ratio $La_N/Yb_N < 6$ and values Eu/Eu* ~1). The protolith of metamorphosed sedimentary rocks of this group consisted of pelagic shales + organic matter, protolith of metacherts formed by deep marine siliceous sedimentary rocks + organic matter, protolith of actinolite schists and chlorite-actinolite schists represented by halmyrolytic altered hyaloclastites, and basalts of N-MORB type + organic matter. The sedimentary environment of the protolith of these metamorphosed sedimentary rocks was the ocean floor. Sedimentation was accompanied by rift volcanism producing basalts of N-MORB type and hydrothermal activity forming the stratiform hydrothermal sulphidic bodies in sediments.

Key words: metamorphosed sedimentary rocks, geochemistry, protolith, paleoweathering, sedimentary environment, geotectonic setting

Introduction

Metamorphosed sedimentary rocks of the Malé Karpaty Mts. are, for the purposes of geochemical paleoreconstruction, most suitable from all metamorphosed rocks of the pre-Alpine crystalline basement of the Western Carpathians. Detailed geological mapping (Mahel' and Cambel, 1972) shows changes in chemical composition of metamorphosed sedimentary rocks in relation to their geological position. Known sedimentological properties allow observing and verifying the variability of chemical composition of metamorphosed sedimentary rocks in relations to distribution of chemical elements in the process of sedimentogenesis. The mobility/immobility of chemical elements in metamorphosed sedimentary rocks can be investigated from the viewpoint of the influence of regional and contact metamorphism. In this work the chemical composition of metamorphosed sedimentary rocks was subjected to geochemical analysis aiming to verify the behaviour trends of oxides of the main elements, trace elements and lanthanoids (REE): (a) as a result of pre-metamorphic sedimentary processes, (b) from the viewpoint of various intensity and type of metamorphism, (c) regarding the geological position and lithostratigraphic division.

Geological setting

The Malé Karpaty Mts. (MK) represent a part of the Tatra-Fatra Belt of the Central Western Carpathians (Plašienka et al., 1997). The crystalline basement of MK build-up the metabasites (amphibolites, actinolite schists), metamorphosed sedimentary rocks (phyllites, gneisses, black schists, hornfelses, and calc-silicates) as well as the Bratislava and Modra granitoid massifs (Koutek and Zoubek, 1936; Cambel 1954, 1962). In comparison with further Tatric cores the crystalline basement of MK can be characterized by several peculiarities: (1) The presence of higher (gneisses) and lower (phyllites) grade metamorphic rocks, (2) in metamorphosed sedimentary rocks relict sedimentary structures are preserved, (3) relatively large spread of the black schists, (4) clear intrusive relation of granitoids with their mantle/core, and (5) extended manifestations of the contact and periplutonic metamorphism (Cambel, 1962; Korikovsky et al., 1984). The Silurian-Carboniferous age of the complex of magmatic and sedimentary rocks of the MK crystalline basement was determined by paleontological investigation (Andrusov, 1959; Cambel and Čorná, 1974; Planderová and Pahr, 1983; Cambel and Planderová, 1985). In the Lower Carboniferous period the complex was intruded by Bratislava and Modra granitoid massifs.

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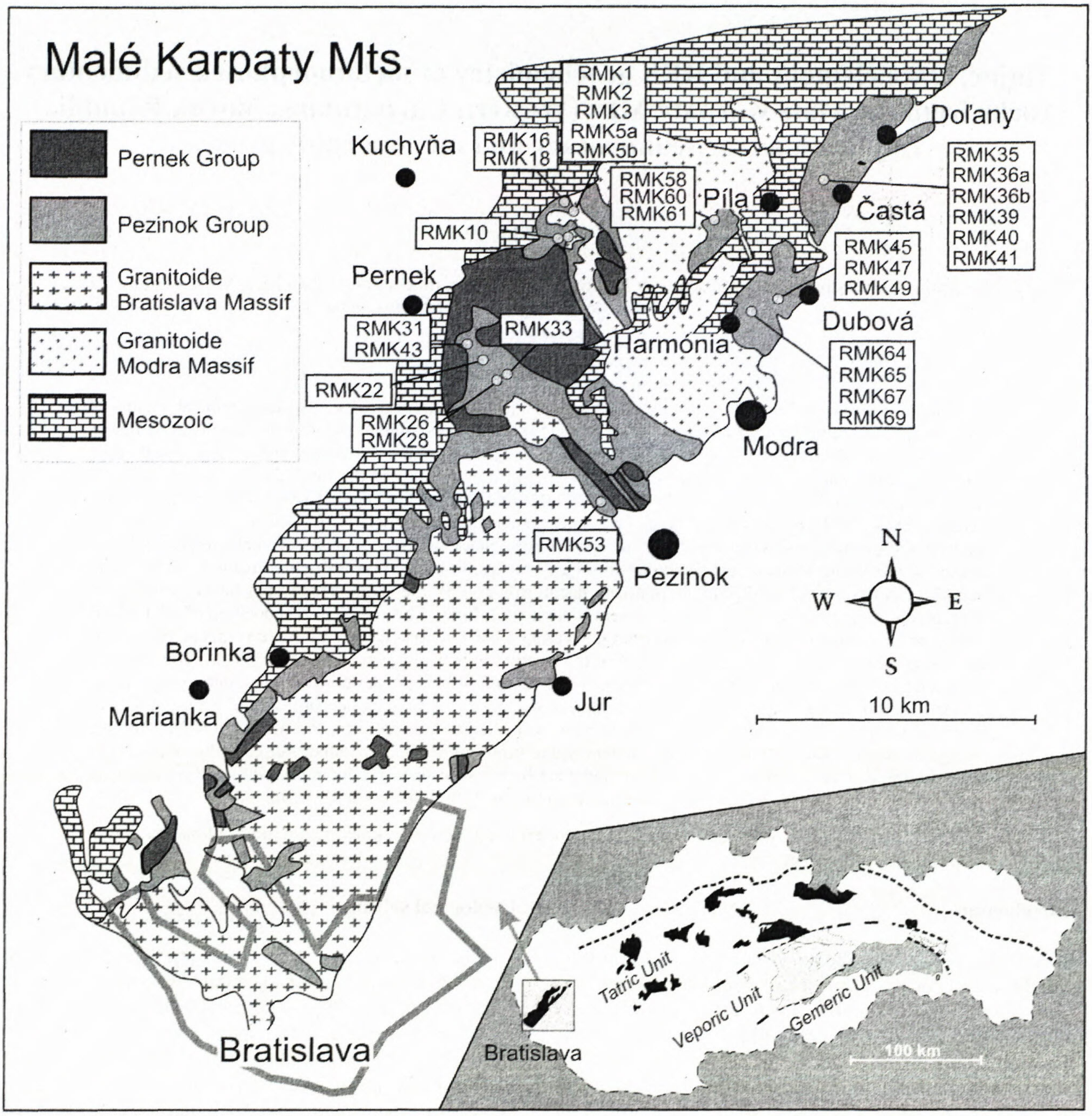


Fig. 1. Schematic geological map of the Malé Karpaty Mts. with location of the studied samples (Table 1 - this work, Table 2 taken from Ivan et al., 2001).

Two principally different opinions exist about the pre-metamorphic development of the crystalline basement of the MK.

(1) The first opinion interprets the crystalline basement as one pre-metamorphic volcanosedimentary lithostratigraphic unit. The variability in metamorphosed sedimentary rock compositions is explained as a result of pre-metamorphic gradual changes of sedimentary conditions in time and space (Cambel, 1954; Hovorka, 1985 in Grecula and Hovorka, 1987; Putiš, 1992).

Cambel (1954) distinguished two regional units: ***Pezinok-Pernek crystalline basement*** and ***Harmónia Series***. Pelitic-psammitic metamorphosed sedimentary rocks, locally containing organic matter, metabasalts, metavolcaniclastics and metagabbros, were in the Pezinok-Pernek crystalline basement (Cambel, 1954). Sulphidic mineralization concentrated mainly in black schists of so-called productive zones (= uppermost part of the Pezinok-Pernek crystalline basement) was proposed by Cambel (1959) as syngenetic with the basalt volcanism in Pezinok-Pernek crystalline basement. The Harmónia Series differs with more frequent alternating of psammitic and pelitic compounds and also contains limestones of organogenic origin with sporadic mafic volcaniclastics (Cambel, 1954).

Hovorka (1985, in Grecula and Hovorka, 1987) defined three formations: (1) ***Pernek Fm.***, formed prevailingly with metabasites, (2) ***Pezinok Fm.***, containing mainly clastic sediments including black schists with intercalations of mafic volcanites and volcaniclastics, the "productive zones" were affiliated also with this formation, and (3) ***Harmónia Fm.*** (identically with Harmónia Series according to Cambel, 1954).

Plašienka and Putiš (1987) divided all metamorphosed igneous rocks and metamorphosed sedimentary rocks of the MK crystalline basement into two Paleoalpine tectonic units: the ***Bratislava nappe*** and ***Orešany nappe***. The complex of metamorphosed igneous rocks and metamorphosed sedimentary rocks of the MK crystalline basement was divided more precisely by Putiš (1992).

2) The second opinion proposes two pre-metamorphic lithostratigraphic groups, originating principally in differing sedimentary and geotectonic environment: ***Pernek Group*** and ***Pezinok Group*** (Fig. 1, Ivan et al., 2001; Méres and Ivan, 2003; Ivan and Méres, 2003).

The complex of metabasites and metamorphosed sedimentary rocks of MK crystalline basement, together with granitoid massifs, was originally regarded as autochthonous (Cambel, 1962). This opinion was later exchanged by the concept of nappe setting (Plašienka and Putiš, 1987; Plašienka et al., 1991; Putiš, 1992; Ivan and Méres, 2003).

Petrography

Metamorphosed sedimentary rocks from the Malé Karpaty Mts. were, in this work, divided into several groups by petrographic characteristics and geological position (in the sense of Cambel, 1954). ***The first group*** is formed by the metamorphosed sedimentary rocks tied to Bratislava granitoid massif and metamorphosed sedimentary rocks in **Pezinok-Pernek crystalline basement** as well as **Harmónia Series**: *phyllites (MPEL & MPSA = metapelites and metapsammites), gneisses* (**G**), *contact metamorphosed rocks (**CMR** = hornfelses, spotted phyllites and spotted gneisses), and black schists (**BS1**).* ***The second group*** is formed by metamorphosed sedimentary rocks outcropping in so-called ***productive zones*** (according to Cambel, 1959): *black schists (**BS2**).*

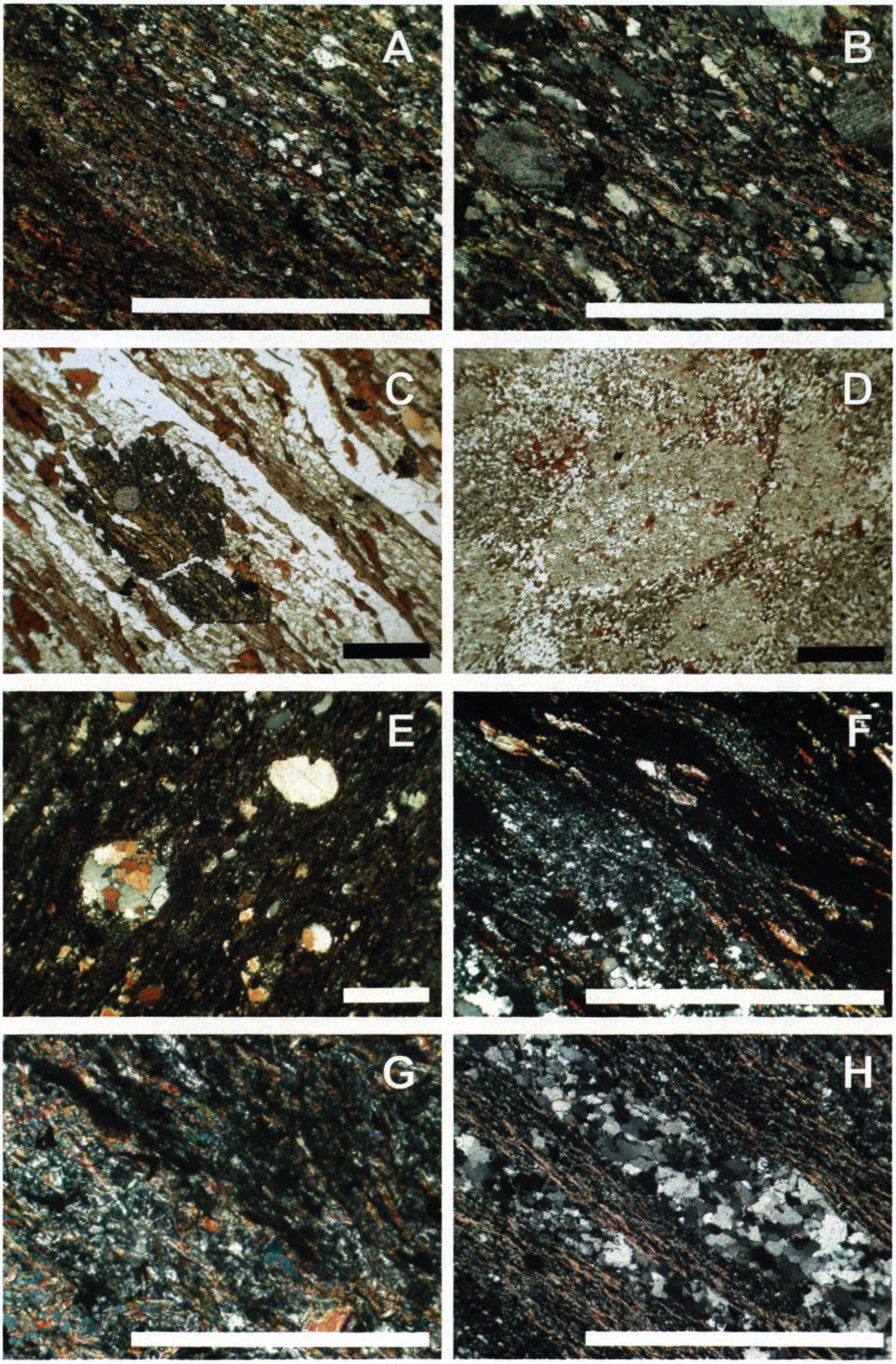
Phyllites (MPEL&MPSA). Greenschist facies pelitic-psammitic sediments were originally included among phyllites. The boundary between phyllites and gneisses is formed by almandine isograde. The phyllites manifest characteristic frequent alternating of mm to cm thick intercalations of metapelites (MPEL) and metapsammites (MPSA). The metamorphic grain-size of phyllites often evidently copies the former sedimentogenous grain-size (Fig. 2A, B, D, E, F). MPEL according to grain-size scale (Wentworth, 1922) range from silt (siltstone, clay, mud) to very fine-grained sand (grain-size less than 0.0625 mm). MPEL are fine-schistose and often have the darker colour as MPSA caused by the higher content of chlorite, biotite and frequently organic pigment (Fig. 2A). In MPEL the millimetre lamina with prevalence of quartz-plagioclase frequently alternate with lamina having prevalence of sericite ± organic pigment. Because the granularity of MPSA usually varies between 0.2-0.5 mm, they correspond to medium- to coarse-grained sandstones. The lighter colour of MPSA is caused by the prevalence of quartz and plagioclase in their composition. MPSA have often the augen (eye-shaped) structure - individual augens are formed by plagioclase and quartz, having character of former clasts and usually they are present in fine-grained matrix (Fig. 2B). Sporadically the polymineral clasts are also present consisting of plagioclase (with indications of former zonal setting) and quartz. Metapelitic and metapsammitic structures are the most common in phyllites. The characteristic minerals of phyllites are represented by chlorite, sericite, quartz, plagioclase and biotite. Zircon, apatite, tourmaline and ore minerals are the dominant accessories.

Gneisses (G). Former pelitic-psammitic sediments metamorphosed to amphibolite facies were originally included among gneisses. Banded structures in gneisses are scarcer than in phyllites. The finer-grained matrix (granularity below 0.0625 mm), formed by quartz, plagioclase and muscovite, alternates with coarser-grained matrix (0.2-0.5 mm) of the same composition. Lepidogranoblastic, granoblastic, porphyroblastic and fibroblastic structures are the most common in gneisses. The characteristic minerals of gneisses are represented by biotite, muscovite, garnet, staurolite, sillimanite, plagioclase and quartz (Fig. 2C) with accessory minerals of zircon, apatite, tourmaline and ore-minerals.

***The contact metamorphosed rocks (CMR** = hornfelses, spotty phyllites and spotty gneisses)* often have well preserved relics of former sedimentary structures and metamorphic minerals of regionally metamorphosed metapelites (more often) and metapsammites. They differ from regionally metamorphosed rocks mainly by more massive texture and typical spotted structure (Fig. 2D). The main minerals of hornfelses include biotite, muscovite, cordierite, andalusite, plagioclase and quartz. Biotite, muscovite, plagioclase and quartz usually form the fine-grained matrix of hornfelses. Porphyroblasts of cordierite and andalusite (dimensions up to 1 cm) poikilitically enclose minerals of fine-grained matrix.

Black schists (BS1) are petrographically similar to the finest-grained phyllitic fraction (MPEL) outcropping in the Pezinok-Pernek crystalline basement and in the Harmónia Series. BS1 differ from MPEL only by the darker colour caused by the content of organic pigment (up to 5 % C_{org} according to Cambel and Khun, 1983) and by the relatively higher content of sulphides (Fig. 2E).

Black schists (BS2). Black schists of the so-called productive zones Cambel (1959) are included in this group. The BS2 are represented by the very fine-grained (less than 0.06 mm) rocks usually demonstrating detail lamination. They can be divided into three subgroups: (1) very fine-grained black schists (BS2a) characteristic with very thin lamination without more distinct presence of basic material ± sulphides. In the scale of thin section the 0.0X mm thick lamina with dominant quartz and lamina with prevalence of sericite containing disseminated organic pigment are alternating (Fig. 2H), (2) very fine-grained metacherts (BS2b) dominated by quartz and also containing organic pigment ± amphibole ± sericite ± sulphides, and (3) very fine-grained black schists with the presence of altered mafic rocks (BS2c),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having a very fine-grained matrix composed mainly of sericite, quartz, organic pigment, amphibole, epidote, sulphides ± carbonate.

Geochemistry

Chemical analyses for the geochemical study of the Malé Karpaty metamorphosed sedimentary rocks in our study were used from several sources (Cambel and Khun 1983, Cambel et al. 1990, Ivan et al. 2001 and our original chemical analyses - see Table 1).

Major element geochemistry. The initial geochemical approach to study the nature of the source area and the tectonic setting of the depositional basin was attempted using discrimination plots based on major elements composition of the Malé Karpaty Mts. (MK) metamorphosed sedimentary rocks. SiO_2 (64 wt.%) and Al_2O_3 (15 wt.%) contents divide the phyllites of the MK into two groups – metapelites and metapsammites (Fig. 3). From the distribution of samples in the plot, it is obvious that the protolith suffered neither intensive weathering nor sorting. One of the main factors of variability in composition of

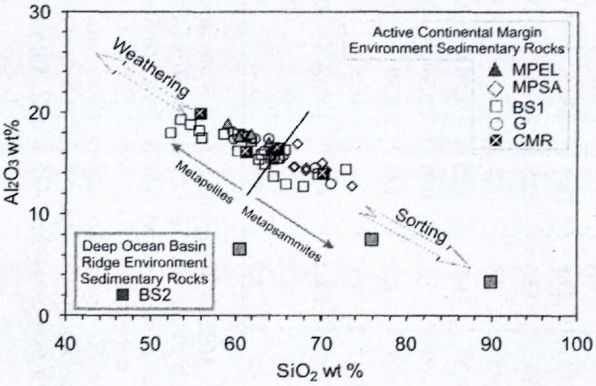

Fig. 3. Plots of Al_2O_3 vs. SiO_2 for the Early Paleozoic metamorphosed sedimentary rocks from the Malé Karpaty Mts. ACMESR = the Active Continental Margin Environment Sedimentary Rocks: MPEL = metapelites, MPSA = metapsammites, G = gneisses, CMR = contact metamorphosed rocks, BS1 = black schists from the Pezinok-Pernek crystalline complex and from the Harmonia Series (after Cambel l.c.). DOBRESR = the Deep Ocean Basin Ridge Environment Sedimentary Rocks: BS2 = black schists from "productive zones". (Analyses in Table 1.)

of observed oxides is the granularity of studied samples. The majority of fine-grained samples (MPEL and BS1) have higher contents of Al_2O_3 and the coarser-grained samples (MPSA) have the higher contents of SiO_2. The higher contents of Al_2O_3 are a result of the relatively higher content of clayey minerals in finer-grained protolith of MPEL and BS1. The samples BS1 occur in the whole range of values of these oxides and together with the samples MPEL & MPSA, G and CMR they form **the first geochemical group**. The presence of organic matter also in MPEL as well as in MPSA indicates the quick transport and burial of the protolith of metamorphosed sedimentary rocks from one source area. We suppose that samples with the position in the immediate surrounding of the boundary dividing MPEL and MPSA have a composition close to composition of the parental rocks. **The second geochemical group** is formed by black schists outcropping in so-called productive zones (BS2) having distinctly different contents of SiO_2 and Al_2O_3. It indicates another protolith and another the source area than in the case of the first group.

The metamorphosed sedimentary rocks of the first geochemical group form in geochemical classification plot for sediments (Herron, 1988) the relatively homogenous field with position corresponding to greywackes and shales (Fig. 4). MPSA have the higher values log SiO_2/Al_2O_3 as MPEL and black schists (BS1) at comparable values log Fe_2O_3/K_2O. The gneisses (G) have in this geochemical classification plot essentially the same position as phyllites and CMR. The metamorphosed sedimentary rocks of second geochemical group (BS2) had evidently different protolith.

In geochemical classification plot for sediments (Garrels and McKenzie, 1971) the metamorphosed sedimentary rocks of the first geochemical group demonstrate the position in the compositional fields of lithic arenites and greywackes (Fig. 5). The parameter (Na+Ca)//Na+Ca+ K) well divides the MPSA and MPEL and is relatively higher in MPSA. The gneisses have in this plot the same position as phyllites. The black schists (BS1) and contact metamorphosed rocks (CMR) demonstrated comparable parameters with MPEL. The metamorphosed sedimentary rocks of the second geochemical group (BS2) manifest

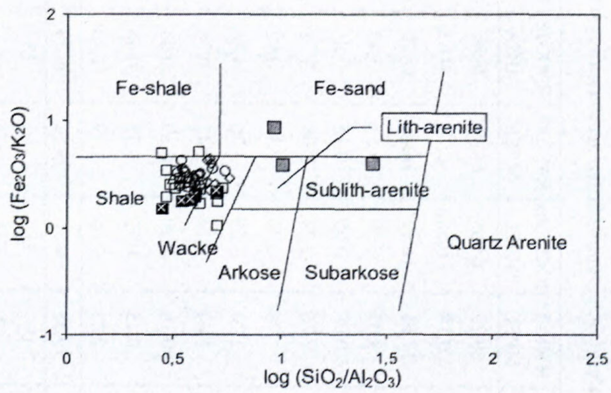

Fig. 4. The major element chemical classification plot of the terrigenous clastic rock types (after Herron, 1988) for metamorphosed sedimentary rocks from the Malé Karpaty Mts. Explanations in Fig. 3

Fig. 2. The Early Paleozoic metamorphosed sedimentary rocks of the Malé Karpaty Mts. - the Pezinok Group: 2A = metapelite (sample RMK-36a), 2B = metapsammite (sample RMK-36b), 2C = gneiss (sample RMK 33), 2D = spotted metapelite (sample RMK 64), 2E = black schist (BS1) from Pezinok Group (sample RMK-17). The Pernek Group: 2F = metachert (BS2b) sample RMK-13, 2G = actinolite schist (BS2c) sample RMK 03-23, 2H = black schist (BS2a) sample RMK 04-23. Scale in all figures is 1 mm.

Table 1. Representative chemical analyses of metamorphosed sedimentary rocks of the Malé Karpaty Mts.

	RMK-13 chert	RMK-5b MPEL	RMK-16 MPEL	RMK-22 MPEL	RMK-36a MPEL	RMK-49 MPEL	RMK-18 MPSA	RMK-5a MPSA	RMK-36b MPSA	RMK-40 MPSA	RMK-52 MPSA	RMK-2 G	RMK-26 G	RMK-31 G	RMK-43 G	RMK-58 G	RMK-60 G	RMK-67 CMR	RMK-69 CMR
SiO_2	89,78	59,00	61,79	60,29	63,85	64,47	70,06	67,21	73,63	70,45	68,16	69,15	64,64	61,83	60,79	65,13	63,26	55,70	61,07
TiO_2	0,22	0,89	0,88	0,78	0,68	0,78	0,63	0,82	0,45	0,62	0,68	0,64	0,84	0,75	0,70	0,85	0,77	0,95	0,72
Al_2O_3	3,35	18,98	17,86	17,61	16,97	16,43	15,00	16,95	12,70	14,31	14,51	14,48	16,29	17,41	17,87	15,42	16,16	19,98	16,24
Fe_2O_3tot	0,47	6,21	6,73	8,07	6,39	5,57	3,43	5,00	3,99	4,27	4,33	5,15	6,30	7,09	7,20	5,79	6,00	6,39	6,95
MnO	0,02	0,07	0,04	0,08	0,05	0,15	0,03	0,06	0,04	0,05	0,06	0,07	0,08	0,11	0,12	0,13	0,09	0,07	0,11
MgO	0,49	2,85	2,34	3,26	2,24	2,00	1,74	1,83	1,47	1,62	2,32	2,13	2,42	2,86	2,83	2,23	2,28	3,08	2,51
CaO	0,62	2,11	0,79	1,76	0,39	1,36	0,92	1,61	0,43	1,25	0,78	2,88	1,29	1,37	1,77	2,17	2,77	0,95	1,54
Na_2O	0,29	5,43	3,27	2,20	3,35	3,76	4,86	3,90	3,33	3,57	3,65	2,78	2,72	2,67	2,99	4,10	3,58	5,34	2,70
K_2O	0,12	2,15	2,58	2,69	2,24	2,47	0,78	1,72	1,38	1,68	1,93	1,43	2,81	2,11	2,93	1,80	2,28	4,19	3,71
P_2O_5	0,03	0,17	0,14	0,16	0,20	0,19	0,08	0,15	0,14	0,13	0,13	0,14	0,18	0,20	0,19	0,18	0,18	0,19	0,27
H_2O	0,73	0,70	0,95	0,45	0,72	0,55	0,46	0,40	0,42	0,62	0,71	0,42	0,53	0,30	0,71	0,69	0,54	0,39	0,96
LOI	4,80	1,41	2,93	2,23	2,68	1,79	1,30	0,93	1,87	1,69	2,09	1,12	1,59	2,66	1,96	1,77	1,55	1,44	2,62
Total	100,92	99,97	100,30	99,58	99,76	99,52	99,29	100,58	99,85	100,26	99,35	100,39	99,69	99,36	100,06	100,26	99,46	98,67	99,40
Sc	7	17	20	19	18	16	13	13	12	14	15	13	17	19	20	15	17	20	16
Hf	2,0	5,5	4,7	3,2	5,3	5,0	5,8	6,2	5,3	5,5	5,2	6,3	5,1	4,9	4,9	5,9	5,1	5,1	4,7
Ta	0,35	0,81	0,64	0,70	0,78	0,74	0,55	0,62	0,60	0,60	0,62	0,53	0,69	0,79	0,82	0,68	0,83	0,94	0,97
Th	2,5	9,7	7,6	7,7	8,3	9,0	8,3	7,0	7,4	7,4	9,0	7,4	7,5	8,9	8,0	10,1	8,7	11,2	10,0
La	3,7	28	21,5	28,2	28	28,2	28,7	23,2	27,8	28,7	30,5	25,6	29,2	27	26,5	25,6	27,9	39	33,5
Ce	7,3	67	49,5	62	64	68	64	56	63,5	62,5	67,5	57	67,5	62	62,5	63	67,5	97,5	79
Sm	1,1	6,4	4,2	5	5,6	6,2	4,3	4,8	4,9	5,2	4,9	4,1	5,5	5,8	5,4	5,7	6	6,3	5,8
Eu	0,29	1,70	1,05	1,30	1,20	1,35	1,15	1,20	1,15	1,25	1,20	1,05	1,35	1,30	1,35	1,30	1,35	1,30	1,30
Tb	0,22	0,93	0,60	0,65	0,76	0,89	0,56	0,69	0,63	0,71	0,56	0,55	0,77	0,85	0,82	0,77	0,85	0,93	0,71
Yb	1,30	2,50	2,10	1,95	2,55	2,80	1,70	2,05	2,15	2,15	1,80	1,80	2,45	2,50	3,00	2,90	2,90	3,30	2,50
Lu	0,28	0,56	0,48	0,39	0,49	0,54	0,32	0,43	0,37	0,46	0,38	0,32	0,49	0,55	0,53	0,48	0,50	0,54	0,52
REE_{tot}	14,19	107,09	79,43	99,49	102,6	107,98	100,73	88,37	100,5	100,97	106,84	90,42	107,26	100	100,1	99,75	107	148,87	123,33
Eu/Eu*	0,75	0,82	0,78	0,83	0,68	0,68	0,85	0,78	0,75	0,76	0,81	0,81	0,77	0,69	0,77	0,72	0,70	0,64	0,73
La_N/Yb_N	1,9	7,6	6,9	9,8	7,4	8,0	11,4	7,6	8,7	9,0	11,4	9,6	8,0	7,3	6,0	6,0	6,5	8,0	9,0

Explanations: major oxides in wt.%, trace elements in ppm, LOI = loss on ignition, MPEL = metapelite, MPSA = metapsammite, G = gneiss, CMR = contact metamorphosed rocks.
All major elements were determined by XRF method, H_2O and LOI gravimetrically by the UNIGEO Company, Brno, Czech Republic. The analyses of the other elements were performed by the INAA using the slightly modified method by Kotas and Bouda (1983) in laboratories of the company MEGA, Stráž pod Ralskem, Czech Republic.
***Location of the samples in Table 1**: RMK-2 - gneiss, Kuchyňa village, northern slope of the Vývrať valley, 500 m a.s.l., outcrop in a road cutting. RMK-5a - metapsammite, Kuchyňa village, northern slope of the Vývrať valley, 500 m a.s.l., outcrop in a road cutting. RMK-5b - metapelite, adjacent layer near the position of sample RMK-5a. RMK-13 - metachert, Kuchyňa village, Modranský potok valley, 0.5 km south from Kuchynský revír, RMK-16 - metapelite, Kuchyňa village, Vývrať valley, east from Ostrý hill, east from the altitude 418, 410 m a.s.l. RMK-18 - metapsammite (the same location as sample RMK-16), RMK-22 - metapelite, 150 m west from Šingrában, 475 m a.s.l. RMK-26 - gneiss, road Pernek-Baba, 300 m south-east from Mäsiarsky ostrovec,*

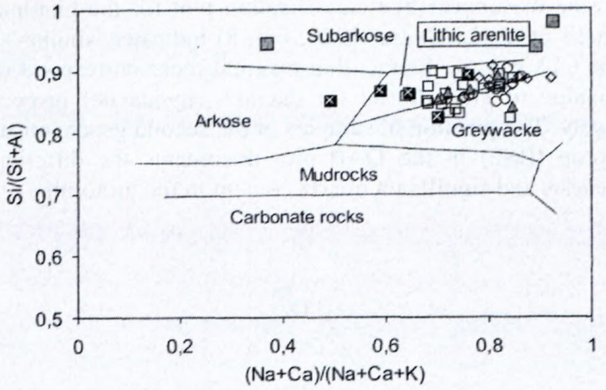

Fig. 5. The major element chemical classification plot of the sedimentary rocks (after Garrels & McKenzie, 1971, range value in molecular proportions). Explanations in Fig. 3.

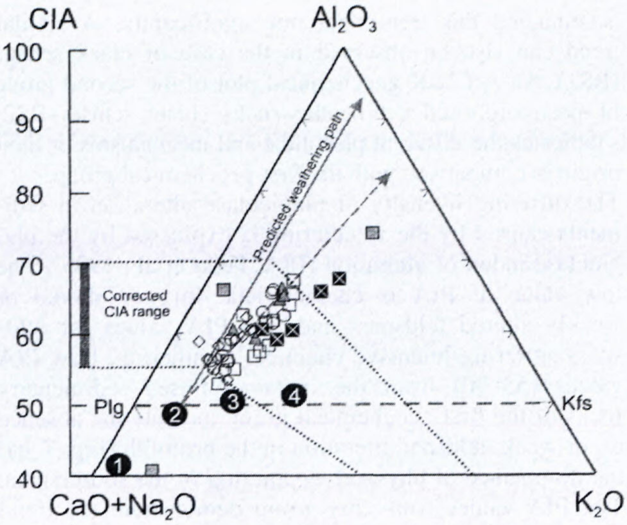

Fig. 6. A–CN–K ternary plot for the metamorphosed sedimentary rocks from the Malé Karpaty Mts. Pre-metasomatized CIA values can range from ~50 for fresh primary igneous rocks to a maximum of 100 for the most weathered rocks (Fedo et al., 1995). Average data of gabbro (1), tonalite (2), granodiorite (3) and granite (4) taken from Le Maitre (1976). Dash line = trend of the weathering of the protolith. Explanations in Fig. 3.

the large dispersion of values (Na+Ca)//Na+Ca+K) and higher values of Si/(Si+Al), which indicates the higher quartz content in the protolith.

Paleoweathering conditions. The range of chemical changes caused by the weathering in source area or during transport of sediments into the sedimentary basin is expressed by the paleoweathering index (CIA=100* $[Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)]$ all in molecular proportions and CaO* represents the CaO in silicate fraction only; Nesbitt and Young, 1982; Fedo et al., 1995). The low CIA values (50–60) indicate the absence or poor chemical weathering in the source area. For medium phase of weathering the values CIA 70–75 are characteristic, the higher CIA values demonstrate the intensive chemical weathering (Nesbitt and Young, 1982; Fedo et al., 1995). The low CIA values of metamorphosed sedimentary rocks of the first geochemical group indicate the absence (or near absence) of chemical weathering in the source area (Fig. 6). The higher CIA values in MPEL relative to MPSA can be explained by the relatively higher clay ratio in finer-grained protolith resulting from depositional sorting. From the intersection point of the trend formed by samples of this group with the line between Plg and K-feldspar it can be supposed that composition of rocks in the source area was similar to tonalite/dacite. The corrected values of CIA (pre-metasomatic) have ranged from 55-70 and from calculated values they more distinctly differ only by insignificant number of samples (mainly in the case of CMR). The MPSA lies close to supposed weathering trend and their computed and corrected CIA values are nearly identical. It indicates the minimum influence of MPSA by K-metasomatism. This fact confirms the assumption that chemical composition of MPSA closely corresponds with the composition of parental rocks. Gneisses (G) have a range of CIA values, as well as a range of corrected CIA values, similar to phyllites. This indicates the influence of metamorphism and metasomatism on distribution of discussed chemical elements is insignificant. The position of MPEL in the A-CN-K ternary plot farthest from the supposed weathering trend towards K_2O can be caused by relatively higher content of clays in the fine-grained protolith, or it can be a result of K-metasomatism. CMR have the CIA range values similar to MPEL. CMR have corresponding granularity like MPEL, so we suppose, that higher K_2O contents in MPEL and in CMR are caused mainly by relatively higher presence of clays in fine-grained protolith. It is possible that K-metasomatism has

over the road curve. RMK-31 - gneiss, Pernek village, east slope of the Klokočina, outcrop. RMK-36a metapelite, Častovská valley, 300 m south-east from Dolina house, 410 m a.s.l. RMK-36b - metapsammite, adjacent layer near position of the sample RMK-36a. RMK-40 - metapsammite, Častovská valley, 300 m south-east from two quarries, 335 m a.s.l. RMK-43 - gneiss, near Pernek village, east slope of the Klokočina. RMK-49 - metapelite, Dubová, east of the Fúgelka. RMK-52 - metapsammite, south-west from Pezinok village, Šalátová, 390 m a.s.l. RMK-58 - gneiss, Píla village, Kobylská valley, Papiernička, 300 m to north. RMK-60 - gneiss, Píla village, Kobylská valley, Papiernička, 300 m to north, contact with granite. RMK-67 - spotted metapelite, Harmónia village, Dolinkovský hill, valley on the south-west slope. RMK-69 spotted metapelite (same location as the sample RMK-67).

Sources of the other chemical analyses. *The group "MPSA" samples RMK: 41, 45, 47, 53, 61 are from the work by Ivan et al. (2001), Table 2. The group "G" samples RMK: 1, 3, 10, 28, 33 are from the work by Ivan et al. (2001), Table 2. The group "CMR" included the samples RMK: 39, 64, 65 from the work by Ivan et al. (2001), Table 2. The group "BS1" had enlisted the samples from the work by Cambel et al. (1990; 31/63-JV, KV-43/368, KV-43/20, KV-43/10, 176-B, 179A, 181A, 182B, 187A) and samples from the work by Cambel and Khun (1983; 13A, 19A, 26A, 11-C, KV-43/423, 175A, 177B, 178A, 183B, 184A, 21/63-JV, 185A). The group "BS2" included the samples from the work by Cambel and Khun (1983): the subgroup BS1a = samples 41A, 47B, 53B, 54A, 60A, 61A, 62A, 70B, 145A, 164A, 165B, 166A, 170A, 171A, 173A, 174A, samples BS1b = samples 57A, 172A.*

accentuated this trend, but not significantly. A similar trend can also be observed in the case of black schists (BS1). An A-CN-K geochemical plot of the second group of metamorphosed sedimentary rocks - black schists (BS2) - indicates the different protoliths and mechanisms of their origin in comparison with the first geochemical group.

The differing intensity of plagioclase alteration in sediments caused by the weathering is expressed by the plagioclase index of alteration (PIA, Fedo et al., 1995). The low value of PIA is characteristic for non-altered or weakly altered feldspars and high PIA values for feldspars suffering intensive chemical weathering. Low PIA values (55–70) from the metamorphosed sedimentary rocks of the first geochemical group indicate the absence of, or weak, feldspar alteration in the protolith (Fig. 7 and the dominance of physical weathering in the source area. The PIA values from this group demonstrate the trend from labradorite to albite. This trend is distinct mainly in samples MPSA, having the lowest values of CIA as well as PIA values. This trend can theoretically reflect also the magmatic fractionation of feldspars in former plutonic/volcanic (?) parental rocks. The position of MPEL is, in comparison with MPSA, closer to the Al_2O_3-K_2O peak. It is a result of relatively more intensive alteration of plagioclases and confirms the assumption about the relatively higher clay content in MPEL protolith. The PIA values of the metamorphosed sedimentary rocks of the second geochemical group indicate different genesis of the protolith.

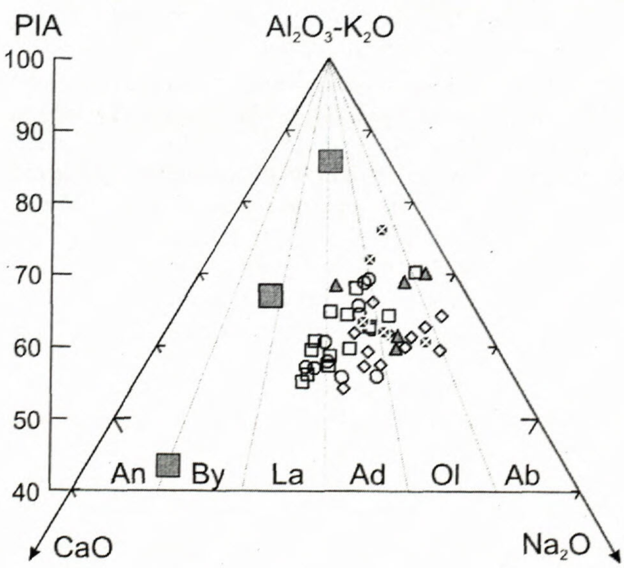

Fig. 7. (A–K)–C–N ternary plot for the studied rocks. Compositions: Ab = albite, Ol = oligoclase, Ad = andesine, La = labradorite, By = bytownite, An = anorthite (Fedo et al., 1995). Explanations in Fig. 3.

The indices about the siliciclastic protolith, which could correspond in composition with the parent rocks mainly in the case of the first geochemical group of metamorphosed sedimentary rocks of the MK, led us to testing of chemical composition in classification schemes for plutonic and volcanic rocks. The position of metamorphosed sedimentary rocks of the first geochemical group in the mesonormative classification plot for the plutonic rocks QAP (LeMaitre, 1989, Fig. 8) indicates, similar to the CIA values, the fact that parental rocks correspond to tonalite to granodiorite (or dacite - rhyodacite) respectively. The position of samples of the second geochemical group (BS2) in the QAP plot documents the different genesis and significant quartz content in the protolith.

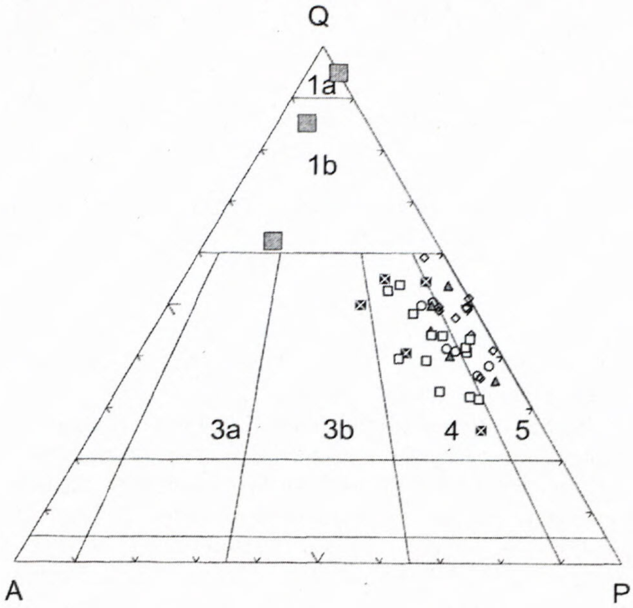

Fig. 8. The metamorphosed sedimentary rocks from the Malé Karpaty Mts. in the QAP mesonormative classification plot for plutonic rocks (LeMaitre, 1989): 1a - quartzolite, 1b - quartz-rich granitoids, 3a - syeno-granite, 3b - monzo-granite, 4 - granodiorite, 5 - tonalite. Explanations in Fig. 3.

Trace element geochemistry. The High Field Strength Elements (HFSE) and certain trace elements have proved to be very useful for provenance and tectonic setting discrimination (Bhatia and Crook, 1986; Cullers, 1995). Particularly, Th, Zr, Sc, Ti, La, Ce, Nd, Hf, Nb, and Y are the most suited for provenance and tectonic setting determinations because of their relatively low mobility during sedimentary processes and their low residence time in sea water (Taylor and McLennan, 1985).

Variable contents of Th and U in metamorphosed sedimentary rocks of the Malé Karpaty Mts. indicate variable oxidation-reduction conditions during their sedimentation (Cambel et al., 1981; Cambel and Khun, 1983, 1985). Relatively high values of the ratio Th/U (>1) at higher contents of Th (>5 ppm) and lower contents of U (>5 ppm) in metamorphosed sedimentary rocks of the first geochemical group indicate oxidizing conditions during sedimentation. The similar Th/U ratio and Th range of the values also indicates a common source area and the same parental rocks. It is also confirmed by the similar range of Th/U ratios in metamorphosed sedimentary rocks of this group and in metabasalts of E-MORB type from the Malé Karpaty Mts. (Ivan et al., 2001).

Low contents of Th (<5 ppm) and high contents of U (5-60 ppm) in metamorphosed sedimentary rocks of the second geochemical group indicate reducing conditions present during sedimentation. The similar range of Th/U ratios in metamorphosed sedimentary rocks of the second geochemical group and metabasalts of N-MORB type indicates the synchronous basic volcanism during sedimentation of the protolith of metamorphosed sedimentary rocks of this group.

The La/Sc ratio in very fine-grained siliciclastic sediments correspond well with the average La/Sc ratio in the source area of sedimentary rocks (Cullers 1995). The metamorphosed sedimentary rocks of the first geochemical group have a positive correlation of La/Sc and Th/Sc, higher values La/Sc (> 1) and Th/Sc (> 0.25) compared to metamorphosed sedimentary rocks of the second geochemical group and have a relatively tight span of range of the values of Th and La/Sc ratio (1-3, Fig. 9). Such values are close to the average value of sediments from the continental island arc (La/Sc = 1.8; Bhatia and Crook, 1986). The range of values of La/Sc and Th/Sc ratios in metamorphosed sedimentary rocks of the first geochemical groups indicates the prevalence of intermediate island arc sources (La/Sc around 1; Th/Sc <0.5) and have trend to acid island arc sources (expressed with arrow, La/Sc ~ 6; Th/Sc ~ 2). The metamorphosed sedimentary rocks of second geochemical group have prevailingly lower values of the ratio La/Sc (<1). Such values are similar to sediments from oceanic island arcs (Bhatia and Crook, 1986). In the case when the La/Sc ratio in metamorphosed sedimentary rocks of the second group is higher, this group is discriminated from the first by lower Th/Sc ratio. The range of the ratios La/Sc vs. Th/Sc in metamorphosed sedimentary rocks of the second group indicates the substantial influence of a mafic source in the chemical composition of protolith. It is documented by the range of the La/Sc ratio and Th/Sc ratio in subgroups BS2a and BS2c which are very similar to these values in metabasalt of N-MORB type (Ivan et al., 2001). The ratios Th/Sc, being lower in all studied samples of metamorphosed sedimentary rocks of MK as in the upper continental crust (UCC= Th/Sc >1, Taylor and McLennan, 1985), indicate that protolith was produced from an immature source area.

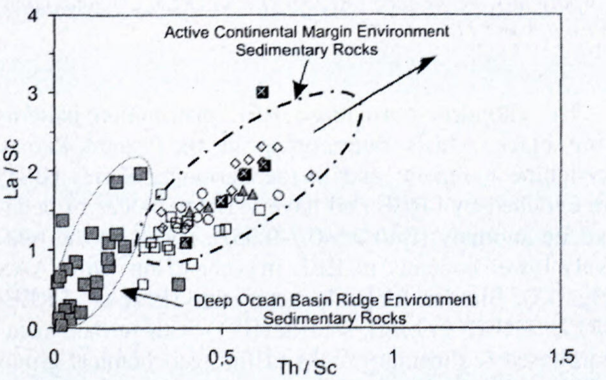

Fig. 9. The metamorphosed sedimentary rocks from the Malé Karpaty Mts. in the plot La/Sc vs. Th/Sc. Explanations in Fig. 3.

First and second geochemical group of MK metamorphosed sedimentary rocks is very well discriminated by values of ratios La/Yb vs. La/Ce (Fig. 10). The higher value La/Yb (8-30) in metamorphosed sedimentary rocks of the first group indicates the higher measure of crustal fractionation of the parental rocks in the source area. At the same time, the lower value of La/Yb (<8) in metamorphosed sedimentary rocks of the second group indicates a less differentiated protolith. The range of the La/Ce values in metamorphosed sedimentary rocks of the second group indicates the measure of Ce depletion in the protolith as a result of interaction by sea water, hydrothermal fluids and basalts of N-MORB type, and their hyaloclastites on the ocean bottom.

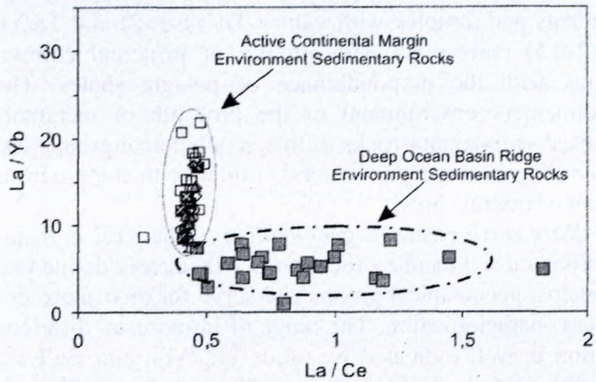

Fig. 10. The metamorphosed sedimentary rocks from the Malé Karpaty Mts. in the plot La/Yb vs. La/Ce. Explanations in Fig. 3.

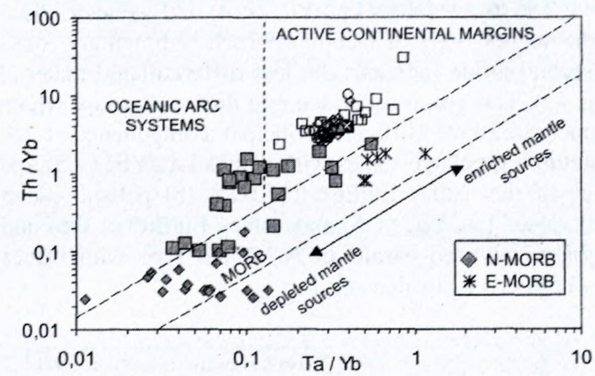

Fig. 11. The metamorphosed sedimentary rocks from the Malé Karpaty Mts. in the plot Th/Yb vs. Ta/Yb. Fields after Cluzel et al. (2001). N-MORB = metabasalts of N-MORB type from Pernek Group, E-MORB = metabasalts of E-MORB type from Pezinok Group (chemical composition of the metabasalts from Ivan et al., 2001). Further explanations in Fig. 3.

The higher values Th/Yb (> 3.5) and Ta/Yb (> 0.2) in plot in Fig. 11 indicate the more felsic parental rocks of the first group of metamorphosed sedimentary rocks including the black schists (BS1). Similar range of Th/Yb values and range of Ta/Yb values are characteristic for rocks, originating in environment of active continental margins. The similarity of this range of values in metamorphosed sedimentary rocks of this group with the range of values in metabasalts of E-MORB type from Pezinok Group (Ivan et al., 2001) shows a common environment of sedimentation. The metamorphosed sedimentary rocks of second geochemical group have lower values of the ratio Th/Yb (< 2) and majority also the lower values of the ratio Ta/Yb (< 0.2). Part of samples of this group has distinct affinity to values of Th/Yb and Th/Yb typical for metabasalts of N-MORB type. The metamorphosed sedimentary rocks of the second group form in this plot three subgroups, indicating besides the organic matter next three next basic components of the protolith: a) pelagic shales, b) pelagic cherts and c) altered mafic rocks. Samples with values Th/Yb (< 0.3) and Ta/Yb (< 0.1) correspond with altered mafic rocks and pelagic cherts, samples with values Th/Yb (0.3-2) and Ta/Yb (0.3-0.5) correspond with mixing of all three components and samples with values Th/Yb (>2) and Ta/Yb (0.2-0.5) correspond with mixing of principal components with the preponderance of pelagic shales. The sedimentary environment of the protolith of metamorphosed sedimentary rocks of this geochemical group was, according to these parameters, similar with the environment of oceanic arcs.

Rare earth elements geochemistry. The REE in metamorphosed sedimentary rocks from MK clearly define two principal geochemical groups and serve for their more detailed characterization. The range of intracrustal differentiation is well indicated by ratios La_N/Yb_N and Eu/Eu*. The higher values of La_N/Yb_N (> 5) and values Eu/Eu* in the range of the values 0.6-0.9 indicate, that protolith of metamorphosed sedimentary rocks of the first geochemical group represented the more differentiated crustal material. The lower values La_N/Yb_N (< 6) and values Eu/Eu* in the range 0.5-1.1 of metamorphosed sedimentary rocks of second group indicates the less differentiated material (Fig. 12). This group is divided into three subgroups which characterize three different principal components of the protolith: (a) pelagic shales with values La_N/Yb_N (~ 5) and range of the values Eu/Eu* (0.7-0.8), (b) pelagic cherts with values La_N/Yb_N (< 5) and values Eu/Eu* (~ 0,6) and (c) halmyrolytized basalts of N-MORB type with values La_N/Yb_N (< 4) and values Eu/Eu* (~ 1).

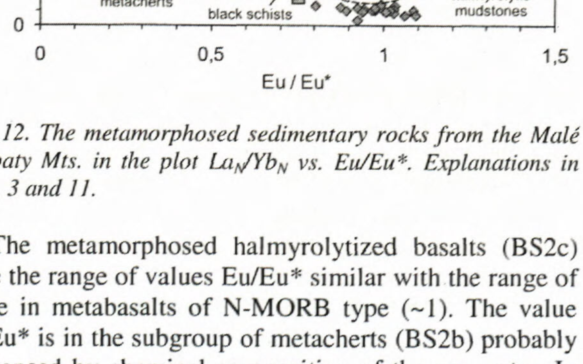

Fig. 12. The metamorphosed sedimentary rocks from the Malé Karpaty Mts. in the plot La_N/Yb_N vs. Eu/Eu. Explanations in Figs. 3 and 11.*

The metamorphosed halmyrolytized basalts (BS2c) have the range of values Eu/Eu* similar with the range of value in metabasalts of N-MORB type (~1). The value Eu/Eu* is in the subgroup of metacherts (BS2b) probably influenced by chemical composition of the sea water. In the subgroup (BS2a) the range of the value Eu/Eu* is influenced mainly by the prevalence of pelagic shales in the protolith (Fig. 12). The presence of chemogenous alternatively organogenous SiO_2 in the protolith of subgroup BS2b also confirms relatively small dispersion of range of values La_N/Yb_N and range of values Eu/Eu*. The generally low values La_N/Yb_N in all samples BS2 can be interpreted as a result of the same environment of protolith sedimentation of metamorphosed sedimentary rocks of this group - the ocean floor.

Also higher values LREE/HREE (ratio > 20) and higher values REE_{tot} (> 80 ppm) in metamorphosed sedimentary rocks of the first group (Fig. 13) indicate a source area with more differentiated parental rocks. It is also confirmed by the affinity of their chemical composition to the composition of metabasalts of E-MORB type. Metamorphosed sedimentary rocks of the second group have low values of both these parameters, which are similar with these values in basalts of N-MORB type. The low values LREE/HREE and REE_{tot} confirm the important ratio of less differentiated material in composition of the protolith of metamorphosed sedimentary rocks of the second group. In the frame of subgroups (a, b, c) the lowest values of LREE/HREE and REE_{tot} are in majority of samples with the prevalence of basic material (BS2c).

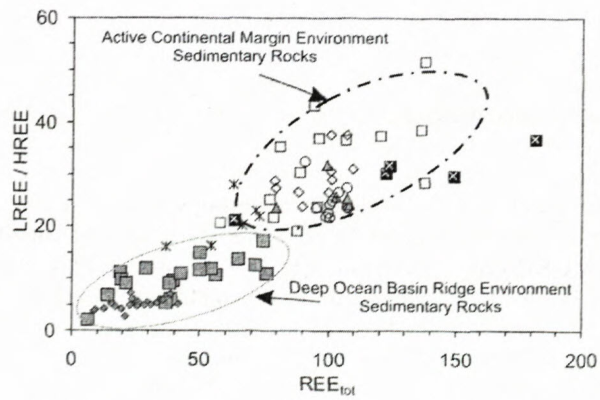

Fig. 13. The metamorphosed sedimentary rocks from the Malé Karpaty Mts. in the plot LREE/HREE vs. REE_{tot}. Explanations in Figs. 3 and 11.

The chondrite-normalized REE distribution patterns from black schists outcropping in the Pezinok-Pernek crystalline basement and in the Harmónia Series (BS1) are enriched by LREE and have variable values of negative Eu-anomaly (Eu/Eu*=0.7-0.95) as well as the relatively lower contents of REE in comparison with PAAS (Fig. 15). Similar REE characteristics (Eu/Eu*, LREE/HREE, ΣREE) in black schists (BS1) with further metamorphosed sedimentary rocks of first geochemical group (MPEL, MPSA, G and CMR, Fig. 14) indicate the differentiated intermediate to acid rocks in common source area.

The chondrite-normalized REE distribution patterns from black schists of the second geochemical group (BS2) distinctly differ from the REE patterns from the black schists of the first group (Fig. 15). The chondrite-normalized REE patterns from BS2a have the distinct negative Ce-anomaly, negative or none Eu-anomaly (Eu/Eu*=0.55-1.05) and have relatively lower content of LREE and higher content of HREE in comparison with BS1.

The PAAS-normalized REE patterns from the samples BS2 (a, b, c) have typical negative Ce-anomaly, positive Eu-anomaly and are depleted by LREE and moderately enriched by HREE. These REE characteristics are known from abyssal marine sediments (Toyoda et al., 1990; Sholkovitz and Schneider, 1991; Holser, 1997; Kato et al., 2002).

The chondrite-normalized REE patterns from metacherts (BS2b, Fig. 15) show characteristic negative Ce-anomaly, negative or none Eu-anomaly and are only

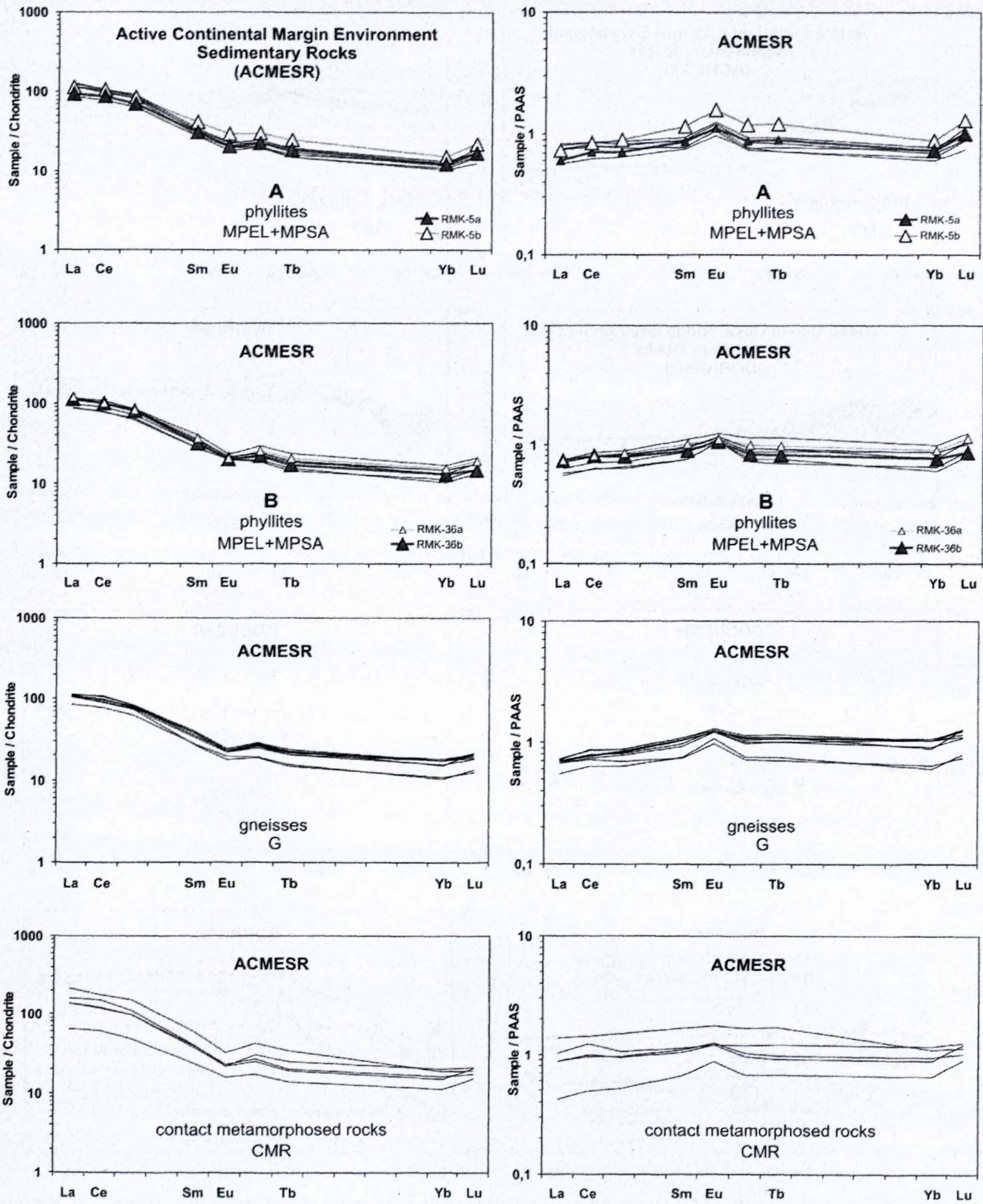

Fig. 14. The normalized REE patterns of the metamorphosed sedimentary rocks from Pezinok Group (after Ivan et al., 2001, in following Figs. too). On the left - the chondrite-normalized REE patterns (Evensen et al., 1988). On the right - the PAAS normalized REE patterns (Taylor & McLennan, 1985).

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moderately enriched by LREE. The PAAS-normalized REE patterns from metacherts have a negative Ce-anomaly and show the depletion of LREE in metacherts. In the sample with lower ΣREE the depletion is more distinct and the positive Eu-anomaly (RMK13, 172A) is distinct as in the case of higher ΣREE (RMK 57A). The lowermost ΣREE was found in the case of sample with highest SiO_2 content (RMK13 ~ 90 wt.% SiO_2). Such REE characteristics resemble these characteristics in sea water (Elderfield, 1988; White, 1998) and indicate the presence of chemogenous quartz, which can represent the residual components in halmyrolytically altered volcanic glass (halmyrolytic mudstone). In modern seafloor environments, hydrothermal, hydrogenous, halmyrolytic, and

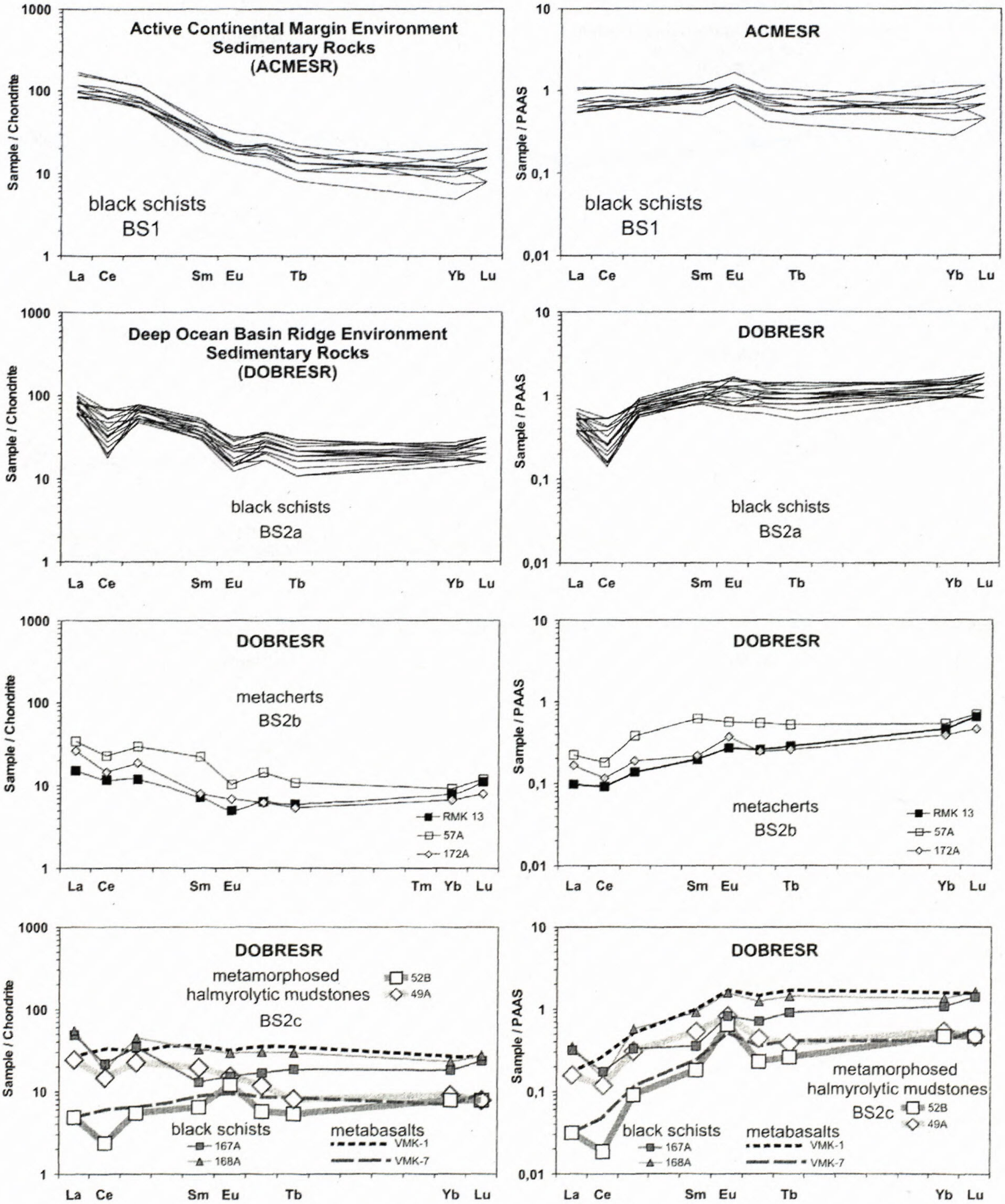

Fig. 15. The normalized REE patterns of the metamorphosed sedimentary rocks from the Malé Karpaty Mts. On the left - the chondrite-normalized REE patterns (Evensen et al., 1988). On the right - the average post-Archean Australian Shale normalized REE patterns (PAAS, Taylor & McLennan, 1985). Pezinok Group: BS1 = black schists, Pernek Group: BS2a = black schists, BS2b = metachert, BS2c = metamorphosed halmyrolytically altered basalts (49A, 52B), typical black schists from Pernek Group (167A and 168A), metabasalts N-MORB types (VMK 1 and VMK 7).

diagenetic processes contribute to the formation of sea-floor sediments (Sivell, 2002). Similar REE characteristics are also known from radiolarites (Murray, 1994), which would also be present in the quartz compound of the metacherts protolith.

In plots designated BS2c (Fig. 15) the normalized REE patterns from typical samples of pelagic shales (BS2a) are compared with halmyrolytic mudstone (BS2c) from the second geochemical group of metamorphosed sedimentary rocks of MK with patterns of normalized REE from metabasites of N-MORB type from the Pernek Group (Ivan et al., 2001). Sample 52B (= actinolite schist with sulphides and C_{org} = 1.26 %) represents the former altered basalt hyaloclastite. Sample 49A (= amphibolite with sulphides, C_{org} and carbonates) represents the former altered basalt. Samples 167A and 168A (= black schists from the productive zones) represent the typical pelagic clay (analyses from the work by Cambel and Khun, 1983; Cambel et al., 1985). Sample VMK 1 represents metabasalt of N-MORB type with the highest ΣREE and sample VMK 7 represents metagabbro of N-MORB type with the lowest ΣREE (analyses from the work by Ivan et al., 2001).

Chondrite-normalized REE patterns and PAAS-normalized REE patterns from selected samples BS2c have the position in the range of normalized REE patterns from the metabasites of N-MORB type (between VMK 1 and VMK 7) and will copy the principal characteristics of metabasites (Fig. 15). Chondrite-normalized REE patterns of sample 49A are moderately enriched by LREE, which is caused by the higher content of clay admixture in protolith. The normalized REE patterns of samples BS2c have a typical negative Ce anomaly at both normalizations. The negative Ce anomaly is typical for basalts disintegrated by sea water and hydrothermal solutions in the rift systems (Sivell, 2002). The PAAS-normalized REE patterns from samples BS2c have a positive Eu anomaly; they are depleted by LREE and enriched by HREE. Samples representing the subgroup BS2c are from a geochemical viewpoint similar to halmyrolytically altered hyaloclastites and halmyrolytically altered basalts of N-MORB type (Sivell, 2002). The total variability of REE contents in metamorphosed sedimentary rocks in the second geochemical group is evidently caused by various quantitative content of principal components in protolith of this group of metamorphosed sedimentary rocks: (a) pelagic shales, (b) pelagic chemogenous/organogenous cherts, (c) halmyrolytic muds derived from N-MORB type basites and (d) organic matter.

Chondrite-normalized REE patterns and PAAS-normalized REE patterns from phyllites (MPEL&MPSA), gneisses (G) and from contact metamorphosed rocks (CMR) from various lithostratigraphic units of the Malé Karpaty Mts. (sensu Cambel l.c.) are depicted in Fig. 14. Plot (A) shows phyllites (MPEL&MPSA) connected with the Bratislava massif and the Pezinok-Pernek crystalline basement and plot (B) shows phyllites (MPEL&MPSA) outcropping in the Harmónia Series. The plots of both A and B phyllites depict also pairing of samples from neighbouring beds with differing grain-sizes. In the case of phyllites (A) these are the samples RMK5a (=metapsammite) and RMK5b (=metapelite), in the case of phyllites (B) these are samples RMK36a (=metapelite) and RMK36b (=metapsammite). The small differences in patterns of normalized REE between MPEL and MPSA indicate in both cases the mineralogically and chemically non-mature less sorted protolith, differing mainly by the grain-size (greywackes, lithic arenites). The finer-grained protolith from coarser-grained one differed besides the grain-size only by the relative higher content of clay minerals. In the REE contents it was demonstrated by the relatively higher ΣREE in MPEL, which is typical for the fine-grained fractions (Taylor and McLennan, 1985). The normalization for PAAS (lower ΣREE, positive Eu/Eu*) confirms about the important presence of plagioclases in protolith.

The chondrite-normalized REE patterns from phyllites (A) and from phyllites (B) have the same characteristics: They are enriched by LREE, have negative Eu-anomaly and form relatively tight spectrum of patterns. The PAAS-normalized REE patterns from phyllites (A) and gneisses (B) show also the same characteristics: lower ΣREE as PAAS, positive Eu-anomaly as well as they form relatively tight spectrum of patterns. The normalized REE patterns from the contact metamorphosed schists (CMR) have similar characteristics as phyllites and gneisses, though they form wider spectrum of patterns (Fig. 14).

The same REE characteristics in phyllites and gneisses tied to Bratislava massif and the Pezinok-Pernek crystalline basement (A) and phyllites and gneisses outcropping in the Harmónia Series (B) and in CMR confirm the same source area and protolith in both cases. The higher ΣREE in the case of CMR can be in the context of further until found geochemical characteristics explained as a result of the higher ratio of clays in finer-grained fractions of the protolith and lower ΣREE can be explained by the higher presence of quartz in the protolith of CMR.

Tectonic setting

HFS elements and some trace elements in sedimentary rocks effectively discriminate various types of tectonic settings of sedimentary basins (Bhatia and Crook, 1986). The first geochemical group of metamorphosed sedimentary rocks of MK has a range of La, Th and Sc values characteristic for continental island arcs (Fig. 16). The range of values for La, Th and Sc from the second geochemical group are similar to rocks from oceanic island arcs and they indicate the oceanic sedimentary environment (Fig. 17).

Metamorphic effect

During geochemical analysis we also observed the distribution of all studied chemical elements from the viewpoint of influence of regional and contact metamorphism. The immobility of these chemical elements is confirmed by their comparable contents (range of values, ratios, trends) in differently metamorphosed metamorphosed sedimentary rocks of the first geochemical group:

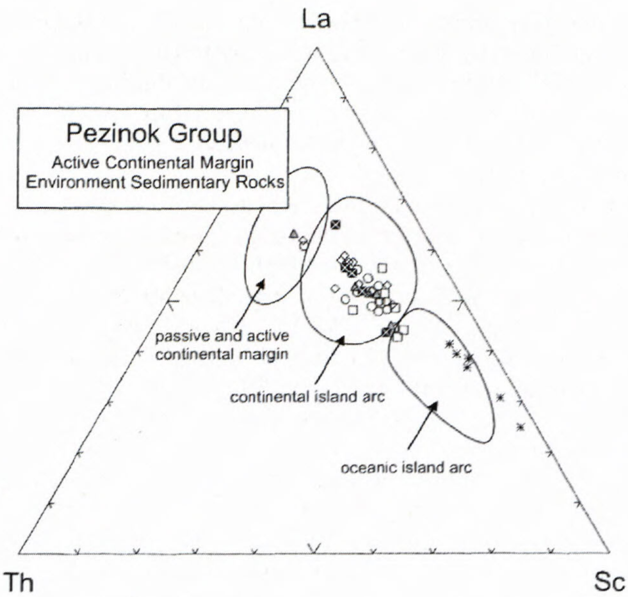

Fig. 16. Plot of the metamorphosed sedimentary rocks of the Pezinok Group in the tectonic discrimination plot La–Sc–Th for discrimination of the tectonic setting of sandstones (after Bhatia and Crook, 1986). Explanations in Figs. 3 and 11.

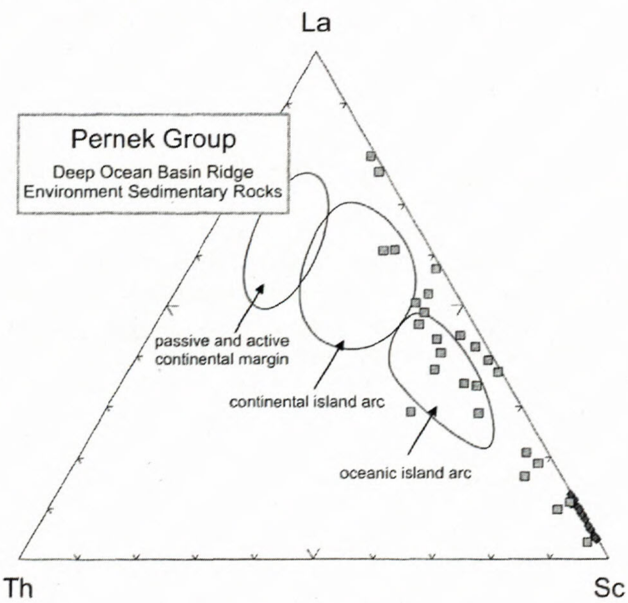

Fig. 17. Plot of the metamorphosed sedimentary rocks of the Pernek Group in the tectonic discrimination plot La–Sc–Th for discrimination of the tectonic setting of sandstones (after Bhatia and Crook, 1986). Explanations in Figs. 3 and 11.

in phyllites, gneisses and contact metamorphosed rocks. In all plots the differently metamorphosed rocks have always position in the whole range of values. It shows on it, that these geochemical parameters express the pre-metamorphic distribution. As an exception there would be CMR with relatively high K_2O content, which could be expressed also by biotitization, which is typical for CMR. The most probable reason of high K_2O contents in CMR is probable the higher ratio of clays in fine-grained protolith. In favour of such interpretation is also the petrographic character of these samples: they represent in all cases the very fine-grained rocks (Fig. 2D).

Synthesis and conclusions

The paleoreconstruction of pre-metamorphic development of metamorphosed sedimentary rocks is complex due to great petrographic and geochemical variability. Among the most important of variables are the composition of parental rocks, type and intensity of weathering in the source area, transport, sorting, environment of sedimentation, and mobility/immobility of chemical elements during diagenesis and metamorphism. The complex chemical analyses of metamorphosed sedimentary rocks (main oxides, trace elements and REE) provided objective qualification and quantification of these processes. For the paleoreconstruction of metamorphosed sedimentary rocks from the Malé Karpaty Mts., we used only those geochemical characteristics which were not significantly affected by element mobility during regional or contact metamorphism. The petrographic characteristics of metamorphosed sedimentary rocks of MK indicate the variability in protolith composition in individual lithological members. Only the petrographic characteristic of the metamorphosed sedimentary rocks generally, without more detail geochemical analysis, does not serve precise identification about variable origin of theese rocks. It is very well confirmed by the black schists (BS1 and BS2) from the Malé Karpaty Mts. Their differing protolith and origin was investigate only by detail geochemical study.

In the Early Paleozoic crystalline basement of the Malé Karpaty Mts. the geochemical study of metabasites and part of metamorphosed sedimentary rocks allows the definition of two pre-metamorphic lithostratigraphic groups: Pezinok and Pernek Groups (Ivan et al., 2001). In this work, we divided these metamorphosed sedimentary rocks by petrographic study, geological position and geochemical study, and also into two principal geochemical groups. The metamorphosed sedimentary rocks of the first geochemical group are a part of the Pezinok Group and metamorphosed sedimentary rocks of the second geochemical group are a part of the Pernek Group (in the sense of Ivan et al., 2001). These geochemical groups differ by the source area, protolith and the sedimentary environment.

Metamorphosed sedimentary rocks of the Pezinok Group protolith evidently came from the same source area. This protolith represented the Active Continental Margin Environment Sedimentary Rocks (ACMESR). The weak chemical weathering of the source area (low range of CIA and PIA values), accelerated transport (geochemical and mineralogical non-mature weakly sorted protolith) and rapid burial (the presence of organic matter) show that protolith of ACMESR was similar to greywackes and lithic arenites ± organic matter. The geochemistry of parent rocks in the source area resembled tonalite-granodiorite (or dacite–rhyodacite) respectively. The geochemical composition ACMESR is variable, values of ratio Th/U (>1), negative Eu anomaly (0.5-0.9), ratio Th/Sc (0.3-0.8), values La_N/Yb_N (> 5) and values Eu/Eu^+ (0.6-0.9) La_N/Yb_N indicate the components derived from the Young Differentiated Arc provenance type (YDA, McLennan et al., 1993; Girty et al., 1996). The YDA province included the young (derived from the mantle) volcanic and plutonic rocks from the island and continental arcs, which underwent significant intracrustal differentiation (they have negative Eu anomalies). The geochemical classification of the type of tectonic position of the sedimentary basin (Bhatia and Crook, 1986) indicates the sedimentary basin in a continental island arc (Fig. 16). The sedimentation took place on the continental slope of the active continental margin locally accompanied with synchronous mafic volcanism producing the basalts of E-MORB type (Ivan et al., 2001).

The protolith of metamorphosed sedimentary rocks of Pernek Group rocks represent the Deep Ocean Basin Ridge Environment Sedimentary Rocks (DOBRESR). From a petrographic viewpoint, the DOBRESR are very fine-grained schists with fine laminations and variegated quantitative proportion of quartz, sericite, amphibole and organic matter ± chlorite ± epidote ± sulphides ± carbonate. The petrographic variability of DOBRESR is also reflected in geochemical variability. The geochemistry indicates that DOBRESR represent the metamorphosed, originally pelagic sediments, outcropping together with the stratiform hydrothermal sulphidic bodies. The protolith of black schists (BS2a) was represented by pelagic shales with organic matter, while the protolith of metacherts (BS2b) was represented by pelagic siliceous deposits with organic matter. The quartz in chemogenous sediments BS2b can be of hydrothermal, hydrogenous or biogenous origin. In metacherts, all of these quartz sources were present by some proportion. Protolith of actinolite schists and chlorite-actinolite schists with admixture of organic matter (BS2c) was formed by basalts with halmyrolytic alteration and their hyaloclastites ± organic matter. The sedimentary environment of DOBRESR was the ocean floor and sedimentation was accompanied with rift volcanism producing basalts of N-MORB type (Ivan et al., 2001). The geochemical characteristic of a part of DOBRESR (BS2c - halmyrolytic mudstone) are: variable composition, low ratio Th/U (<1), value of Eu anomaly (around 1) and ratio Th/Sc (<0.25), La_N/Yb_N (<6) and values $Eu/Eu^*(\sim 1)$ indicate components derived from the Young Undifferentiated Arc provenance type (YUA, McLennan et al., 1993; Girty et al., 1996). YUA was represented by the young effused arc material (volcanic or plutonic), which has not undergone significant intracrustal differentiation (i.e., it has not undergone the plagioclase fractionation and therefore it has no Eu-anomalies). The values La, Th and Sc from halmyrolytic mudstone (BS2c) resemble rocks from oceanic island arcs (Fig. 17) with typical extremely low La and Th contents, and high Sc content. The general contents of La, Th and Sc in DOBRESR document the common oceanic sedimentary environment with mixing of four principal compounds of protolith: pelagic shales, pelagic cherts, halmyrolytically altered basalts/hyaloclastites and organic matter.

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