Geochemistry of amphibolites and related graphitic gneisses from the Suchý and Malá Magura Mountains (central Western Carpathians) — evidence for relics of the Variscan ophiolite complex

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Abstract: Three small bodies of amphibolites and associated graphitic gneisses from the Suchý and Malá Magura Mountains (Tatric Megaunit, central Western Carpathians) have been studied by petrographic and geochemical methods. Isolated, fault-bounded bodies first hundreds of meters in size are located in the complex of the Early Paleozoic paragneisses and migmatites intruded by the Lower Carboniferous granitoid rocks. Amphibolites (locally actinolite schists) were formed from effusive basalts, dolerites or isotropic gabbros hydrothermally altered and veined before the regional metamorphic transformation. Distribution of the trace elements relatively immobile during the metamorphic alteration (HFSE, REE, Cr, V, Sc) is similar to E-MORB type in the Malá Magura Mountain or to N-MORB/E-MORB types in the Suchý Mountain. Graphitic gneisses to metacherts are rich in silica (up to 88 wt. %) and C^{tot}, poor in other major element contents and display negative Ce-anomaly, enrichment in HREE, V, Cr and U. They were probably originally deposited as non-carbonate and silica-rich deep-sea sediments in anoxic conditions. The oceanic provenance of amphibolites and related graphitic gneisses clearly indicates their oceanic crust affinity and identity with the uppermost part of the ophiolite sequence. Ophiolite bodies from the Suchý and Malá Magura Mountains are supposed to be relic fault blocks identical with the Upper Devonian Pernek Group which represents a Variscan ophiolite nappe preserved to large extent in the Malé Karpaty Mountains located in the Tatric Megaunit further to the southwest. All these ophiolite relics are vestiges of the original ophiolite suture created by oceanic closure in the Lower Carboniferous.

Key words: Western Carpathians, Variscides, Suchý and Malá Magura Mts, ophiolites, metabasites, graphitic gneisses, geochemistry.

Introduction

Ophiolite sutures, thin belts with specific rock associations, are relics of the oceanic crust displaced into continental crust as a result of the closure of former oceanic basins. In orogenic belts they represent fossil boundaries between lithospheric paleoplates. They are thus very important for the reconstruction of the geological history of orogens (e.g. Dilek 2003; Dilek & Furnes 2011, 2014; Nicolas 2012). Because the majority of orogenic belts are formed as a consequence of multiple collisions, several generations of ophiolite sutures can occur (Ollier & Pain 2000; Frisch et al. 2011). Identification of older sutures is, as a rule, very problematic due to tectonic splitting, thinning and dismembering of former ophiolite nappes in the course of their reworking by younger orogenic activities (e.g. Zhang et al. 2008). In the following paper we would like to show that even relatively small relics of an ancient high-grade metamorphosed oceanic crust can be reliably identified by geochemical methods if metamorphic equivalents of basalts together with related deep-sea sediments are still preserved. We demonstrate such identification using an example of amphibolites associated with graphitic gneisses from the Suchý and Malá Magura Mts in the Western Carpathians.

Geology

The Suchý and Malá Magura Mts (SE part of the Strážovské vrchy Mts) belong to the so called core mountains in the Tatric megaunit of the central Western Carpathians (Plašienka et al. 1997). An Early Paleozoic crystalline core and Late Paleozoic-Mesozoic cover form these mountains (Mahel' 1985). The crystalline core of the Suchý and Malá Magura Mountains is formed by two structural parts (the western part - Suchý core, the eastern part - Malá Magura core) separated by the N-S trending Diviaky fault but both parts contain genetically identical rock complexes (Fig. 1). Several typical features characterize the geological structure of this crystalline core: (1) alternation of paragneiss, migmatite and granitoid belts, (2) petrographic variability of granitoids together with widespread aplite-pegmatite granites and plenty of aplite and pegmatite veins and (3) the absence of retrogression and Alpine schistosity (Kahan 1979; Mahel' 1986 and references herein). Granitoid rocks display S-type signature (Petrík et al. 1994) and similarly to other such granitoids in the central Western Carpathians are of lowermost Carboniferous age (356±9 Ma, Kráľ et al. 1997, U-Pb zircon evaporation technique). Metamorphic rocks are products of the progressive Variscan metamorphism (Korikovsky et al. 1987). Two stages of the

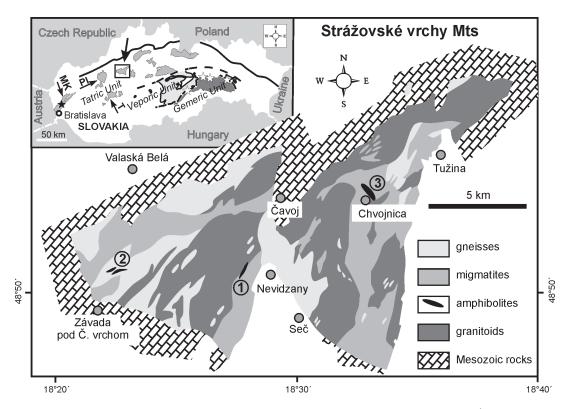


Fig. 1. Geological sketch-map of the crystalline complexes of the Suchý and Malá Magura Mts. After Mahel et al. (1982) — modified. MK — Malé Karpaty Mts, PI — Považský Inovec Mts, SMM — Suchý and Malá Magura Mts. 1-3 — studied amphibolite bodies (1 — Nevidzany, 2 — Železná dolina valley, 3 — Chvojnica). full star — location of the Pernek and Pezinok Grps., empty stars — locations of the Zlatník and Ochtiná Grps. (see discussion).

pre-Alpine metamorphic evolution were described in the study area (Méres & Hovorka 1989; Vilinovičová 1990; Hovorka & Méres 1991), the former one was probably caused by heat related to the granitoid magmatic activity and their intensity decrease to the west. According to Čík & Petrík (2014) peak metamorphic conditions reached T=670-765 °C, and P~600-820 MPa. Besides widespread paragneisses and their migmatitized analogues, quartzose biotite gneisses to biotite quartzites are also comprised in the Suchý and Malá Magura crystalline complexes occasionally also with intensive pyrite impregnation and graphitic paragneisses (Kahan 1980). Metabasic rocks (amphibolites) are scarce and mostly form small bodies (first several meters) embedded in all main rock types (cf. geological map 1:50,000 — Mahel' et al. 1982). In addition they also occur in granitoid rocks usually accompanied by gneiss relics. Our study has been focused especially on the three largest metabasic bodies: (1) the body near Nevidzany village in the valley of the Krstenica brook (Suchý Mts), (2) the body in the Żelezná dolina valley N of the village of Závada pod Čiernym vrchom (Suchý Mts) and (3) the body near Chvojnica village, the largest of three, about 1500 m long and 500 m wide (Fig. 1). Boundaries between these bodies and the surrounding gneisses and migmatites are formed by faults and frequently injected by veins of pegmatitoid granites, pegmatites and aplites. Metamorphosed veinlets with sulphide mineralization and local sulphide impregnation are typical. With the exception of the body near Nevidzany village the metabasite bodies closely associate

with metamorphosed carbonaceous pelitic and silicic rocks interlaid by thin laminas of sulphide ore. The direct spatial relationship of the metabasic rocks with the above mentioned rocks and sulphide mineralization is illustrated by a schematic profile across the Chvojnica metabasite body (Fig. 2).

Petrography

Metamorphosed basic rocks from the Suchý and Malá Magura Mts crystalline complexes have generally been described as typical plagioclase amphibolites without any peculiar petrographic features. However, our detailed study indicates that several petrographic types could be discerned here. The variability in such types is partly observable macroscopically as differences in grain size mostly inherited from magmatic protolith or the intensity of pre-metamorphic pervasive seafloor hydrothermal alteration. Microscopically the metabasites are composed mostly of aggregates of amphibole and plagioclase grains. Ilmenite, titanite and occasionally biotite, clinozoisite and sulphides are also present in subordinate amounts. Diopside in association with albite, quartz and sulphides are components of metamorphosed hydrothermal veins. Scarce young veinlets contain prehnite and smectite. Metabasites from the Suchý and Malá Magura Mts could be classified into two groups based on mineral association as well as amphibole compositions: (1) actinolite schists (transitional rock type between greenschists and amphibo-

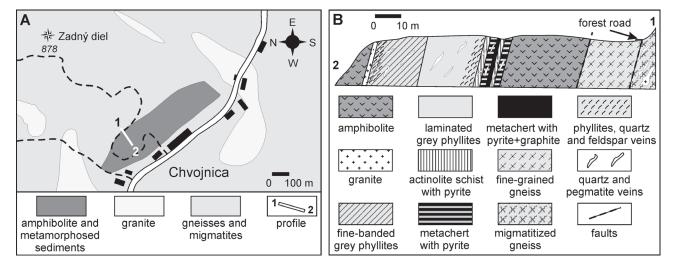


Fig. 2. A — Geological sketch-map of the amphibolite body near Chvojnica village with location of the geological profile depicted in Fig. 2B. Modified after Mahel et al. (1982); B — Schematic geological profile across zone of the metamorphosed sedimentary rocks with sulphide mineralization located in the amphibolite body near the Chvojnica village (Malá Magura Mts). Profile follows morphological ridge between the NW border and central part of the NW-SE oriented amphibolite body.

lites) and (2) amphibolites. The samples with still discernible magmatic protolith are of four types: (1) metabasalts, (2) metadolerites, (3) metagabbros and (4) strongly veined and hydrothermally altered basaltic rocks. Metabasalts were originally the most widespread rock type at both most significant localities - Železná dolina valley (Suchý Mts) and Chvojnica village (Malá Magura Mts). The former locality is mostly represented by actinolite schists composed of oriented aggregate of acicular pale green to green actinolite and plagioclase with subordinate amount of ore minerals and small titanite grains. The composition of plagioclase varies in a wide range (An₀₄-An₄₇). Rarely preserved phantom textural relics point to effusive fine-grained to glassy basalts with hyaloporphyric and/or intersertal textures (Fig. 3A,B), massive basalts likely with ophitic texture were also present. Some clinozoisite and diopside together with pyrite are concentrated in albite veins. At the Chvojnica locality basalts were transformed to amphibolites composed of fine-grained mosaic aggregate of anhedral or subhedral brown amphibole (magnesiohornblende) and plagioclase (ca. An₅₀). Impregnation by ore minerals (predominantly pyrite) of variable intensity is common as well as veining by network of mostly albitic veins also containing diopside, amphibole and ore minerals. Some metabasites, originally intensively hydrothermally altered, comprise diopside not only in veins, but also in surrounding rock with decreasing quantity away from the veins.

Metadolerites display still preserved indices of ophitic/doleritic texture in the form of alternation of almost monomineralic sub-aggregates of brown amphibole with sub-aggregates of the mosaic plagioclase including small amounts of fine amphibole crystals and following orientations of the original magmatic plagioclase laths (Fig. 3C). Metadolerites have been identified at localities Železná dolina valley (in a small isolated body) and Chvojnica village.

Amphibolites formed from the flaser gabbro protolith could be revealed based on the specific texture represented by alternation of attenuated lenses composed of the brown amphibole monomineralic aggregate with lenses of mosaic amphibole-plagioclase aggregates displaying variable ratio of both minerals. Rare lens-shaped clusters of titanite/ilmenite grains, sporadic crystals of dark mica and impregnation with sulphides are also present. Metagabbros form the body near Nevidzany village (Suchý Mts) and rarely occur in the body near Chvojnica village (Malá Magura Mts), where types with relic granular texture have also been found (Fig. 3F).

Metamorphosed carbonaceous sedimentary rocks closely spatially related to metabasic rocks are generally present as graphitic gneisses. They macroscopically form dark grey to black rocks, mostly siliceous, with schistose structure locally intercalated by light grey belts with intensive sulphide impregnations.

Microscopically the lepidogranoblastic and granoblastic textures are dominant (Fig. 3E,F). Plagioclase, white micas, metamorphosed organic matter and quartz, are common mineral components, while tourmaline, garnet, sillimanite and ore minerals are relatively rare. Vanadium-rich aluminosilicates, such as goldmanite (Bačík et al. 2012), V-rich tourmaline (Bačík et al. 2011) and V-rich mica — roscoelite (Méres & Ivan 2007) have also been found in these rocks. They were locally formed in the course of regional metamorphism from the originally vanadium-rich protolith represented by sediment rich in organic matter. Metacherts are compositionally similar to graphitic gneisses only with comparatively high content of quartz and lower content of plagioclase. Layers of quartz-sericite phyllites with variable content of tremolite/actinolite, carbonaceous matter and sulphides are also present in this sequence of the metamorphosed sedimentary rocks.

All the types of metamorphosed basic and carbonaceous sedimentary rocks identified in the Suchý and Malá Magura Mts are petrographically very similar to those from the Pernek Group in the Malé Karpaty Mts (cf. Ivan et al. 2001; Méres 2005; Ivan 2009).

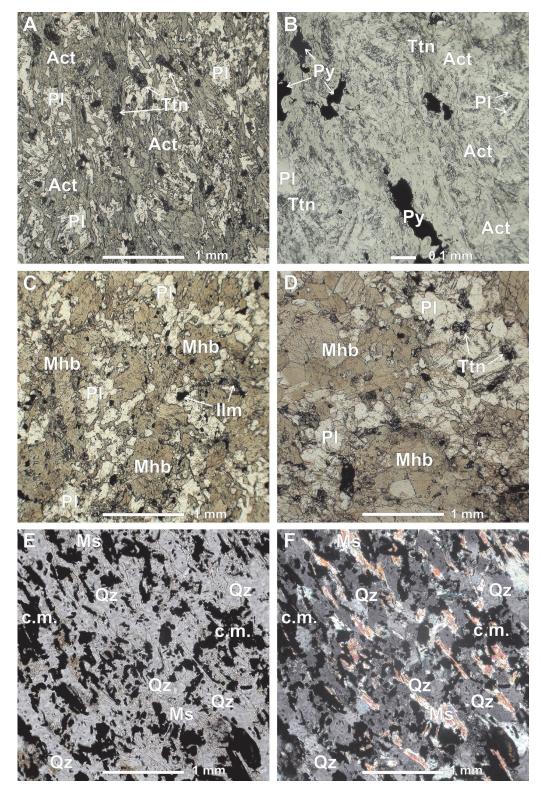


Fig. 3. Thin-section photomicrograph of metabasic rocks and graphite gneiss from the Suchý and Malá Magura Mts. A — Actinolite schist containing actinolite (Act), albitic plagioclase (Pl), titanite/ilmenite (Ttn) and clinozoisite/epidote. Locality: Železná dolina Valley, Suchý Mts, sample ASU-13; B — Phantom intersertal texture preserved in actinolite schist with pyrite (Py). Locality: Železná dolina Valley, Suchý Mts, sample ASU-10; C — Relic ophitic texture in amphibolite composed mostly of brown magnesiohornblende (Mhb) and plagioclase (Pl). Locality: Chvojnica village, Malá Magura Mts, sample AMM-15; D — Relic granular texture in amphibolite with the brown magnesiohornblende (Mhb). Locality: Chvojica village, Malá Magura Mts, sample AMM-19; E — Graphitic gneiss composed of muscovite (Ms), carbonaceous matter (c.m.) and quartz (Qz) with some plagioclase and pyrite. Locally also vanadian muscovite (roscoelite) is present. Locality: Chvojnica village, Malá Magura Mts, sample MM-05-4; F — The same, crossed nicols.

Analytical methods

The chemical composition of the rocks was determined at the ACME Analytical Laboratories (Vancouver, Canada).

Total abundances of major element oxides were determined by inductively coupled plasma — emission spectrometry (ICP-ES) following lithium metaborate-tetraborate fusion and dilute nitric acid treatment. Loss on ignition (LOI) was calculated from the difference in weight after ignition to 1000 °C. For the total carbon (TOT/C) and sulphur analysis (TOT/S) by LECO analysis, the samples were heated in an induction furnace to >1650 °C which caused the volatilization of all C and S bearing phases. Vapours were carried through an infrared spectrometric cell wherein the concentrations of C and S were determined by the absorption of specific wavelengths in the infrared spectra (ORG/C=TOT/C minus graphite C and carbonate). Concentrations of trace elements and rare earth elements were determined by ICP mass spectrometry (ICP-MS). Further details

are accessible on the web page of the ACME Analytical Laboratories (http://acmelab.com/).

Geochemistry

Major and trace elements distribution in selected samples of metabasic rocks from the Suchý and Malá Magura Mts is demonstrated in Table 1.

Major element concentrations in the studied rocks fully reflect their basic basaltic character. The basaltic composition of these rocks is also supported by their position in diagrams Zr/TiO₂ vs. SiO₂ (Winchester & Floyd 1977) or Nb/Y vs. Zr/Ti (Pearce 1996; Fig. 4), falling into the field of non-alkaline basalts. Their tholeitic character is revealed by a Zr/Y vs. Th/Yb discrimination diagram (Ross & Bédard 2009). Compositions mostly compatible with primary basaltic liquids, less frequently also with more differentiated Fe-Ti basalts, are indicated by TiO₂ vs. Al₂O₃ diagram (Pearce 1983; Fig. 5).

Table 1: Major and trace element analyses of the metamorphosed basic rocks from the Suchý and Malá Magura Mts. Note: Samples labelled AMM — Malá Magura Mts, ASU — Suchý Mts. Location and GPS coordinates of samples — see appendix.

	AMM-					ASU-						
Sample	10	11	14	15	15A	1	5	6	7	8	12	13
SiO ₂	46.71	48.20	49.59	49.39	49.00	46.13	46.20	48.65	48.80	48.50	48.53	46.72
TiO ₂	1.72	1.84	2.12	1.84	1.89	1.53	1.87	1.18	1.35	2.26	2.23	2.55
Al ₂ O ₃	14.23	16.01	16.75	15.11	15.23	14.22	14.37	14.29	16.13	15.78	15.64	15.75
Fe ₂ O _{3tot}	12.02	10.84	9.18	10.77	11.05	10.44	12.12	10.27	10.36	10.90	10.28	11.34
MnO	0.13	0.12	0.11	0.15	0.14	0.15	0.13	0.17	0.16	0.18	0.13	0.15
MgO	8.68	5.73	5.51	7.24	7.55	12.72	8.54	8.62	6.72	7.70	6.72	6.26
CaO	11.25	12.49	11.94	10.36	10.49	10.05	12.24	11.10	10.65	9.11	10.37	11.91
Na ₂ O	2.75	3.30	3.28	2.97	2.99	2.42	1.70	2.85	3.09	3.71	4.07	2.98
K ₂ O	0.55	0.29	0.18	0.44	0.31	0.18	0.55	0.44	0.87	0.15	0.12	0.28
P ₂ O ₅	0.17	0.18	0.20	0.18	0.17	0.15	0.20	0.07	0.18	0.22	0.23	0.31
LOI	1.40	0.70	0.80	1.20	0.80	1.60	1.60	2.00	1.40	1.20	1.30	1.40
C_{tot}	< 0.02	0.02	0.04	0.03	0.04	0.03	0.03	0.04	0.07	0.03	< 0.02	< 0.02
S _{tot}	< 0.02	0.11	< 0.02	0.03	< 0.02	< 0.02	0.05	< 0.02	< 0.02	< 0.02	0.76	0.04
Total	99.72	99.77	99.75	99.68	99.67	99.67	99.69	99.73	99.77	99.72	99.73	99.73
Zr	108	112	140	115	127	99	136	73.8	65.5	155	154	186
Y	28.3	29.3	34	30.9	30.5	23.3	29	20.6	28.2	34.5	33.6	40.8
Hf	3	3.2	3.9	3.4	3.3	2.7	3.6	1.9	2	4.5	4	4.9
Th	0.7	0.8	0.7	0.6	0.7	< 0.2	0.5	0.2	< 0.2	0.3	0.3	0.3
U	0.3	0.3	2.3	0.2	0.2	0.1	0.7	0.1	0.9	0.1	0.2	0.8
Ta	0.5	0.5	0.6	0.6	0.5	0.2	0.4	0.1	< 0.1	0.4	0.3	0.6
Nb	7.9	8.1	9.8	9	9.5	2.1	6.2	2.1	0.4	5	5	7.4
Cr	479	335	328	274	294	657	910	390	411	267	404	185
Co	48.3	46.4	57.6	40.3	45.8	57.6	60.2	31.8	39.5	35.3	48.7	39.9
Ni	228	150	125	116	111	273	376	52	59	87	178	63
Sc	34	36	40	36	36	35	33	42	51	40	41	40
V	276	295	331	294	305	229	259	269	295	317	299	367
La	6.6	7.2	8.8	7.9	7.8	3.1	6.5	2.9	1.5	6.4	6.6	8.9
Ce	16.7	17.5	22	19.8	19.7	9.8	18	8.3	5.3	18	19.1	25.8
Pr	2.74	2.85	3.48	3.04	3.04	1.88	3.02	1.48	1.16	3.14	3.23	4.23
Nd	14.2	14.9	17.8	15.7	14.6	10.9	16.2	8.3	7.4	17.5	16.6	20.8
Sm	4.12	4.25	5.25	4.5	4.62	3.39	4.51	2.66	2.97	4.95	4.99	5.82
Eu	1.3	1.53	1.6	1.51	1.47	1.2	1.81	0.92	1.15	1.63	2.03	2.02
Gd	4.81	5.09	6.02	5.1	5.36	4.18	5.2	3.34	4.23	6.04	5.91	6.9
Tb	0.88	0.92	1.1	0.92	0.97	0.74	0.92	0.64	0.83	1.1	1.07	1.2
Dy	5.14	5.45	6.1	5.52	5.81	4.34	5.39	3.92	5.13	6.38	6.38	7.04
Но	1.04	1.15	1.31	1.17	1.17	0.92	1.09	0.81	1.13	1.31	1.32	1.46
Er	2.88	3.07	3.55	3.05	3.17	2.51	3.12	2.27	3.09	3.74	3.63	4.23
Tm	0.45	0.47	0.55	0.46	0.48	0.37	0.48	0.35	0.49	0.6	0.58	0.61
Yb	2.75	2.83	3.22	2.89	2.98	2.41	2.75	2.2	2.91	3.5	3.4	3.78
Lu	0.4	0.43	0.47	0.44	0.43	0.34	0.4	0.31	0.44	0.52	0.5	0.57

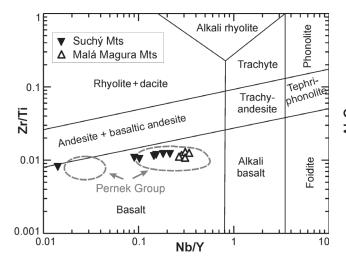


Fig. 4. Nb/Y vs. Zr/Ti diagram (Pearce 1996) for metabasic rocks from the Suchý and Malá Magura Mts. Fields for their analogues from the Pernek Group (Malé Karpaty Mts) were added for comparison. Data for fields: Ivan et al. (2001), Ivan (2009) and unpublished data.

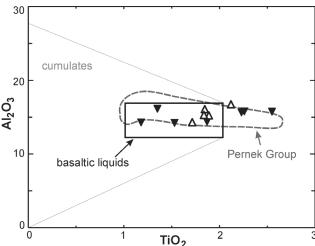


Fig. 5. ${\rm TiO_2}$ vs. ${\rm Al_2O_3}$ diagram (Pearce 1983) for metabasic rocks from the Suchý and Malá Magura Mts indicating similarity of their composition to the mantle basaltic liquids or fractionated basalts. Symbols and field — see Fig. 4.

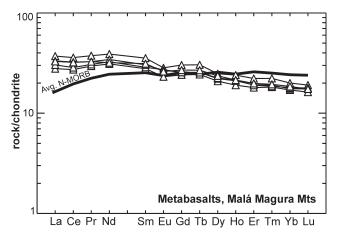


Fig. 6. Chondrite normalized REE patterns for metabasic rocks from the Malá Magura Mts. Normalization by McDonough & Sun (1995), average N-MORB by Niu et al. (2002).

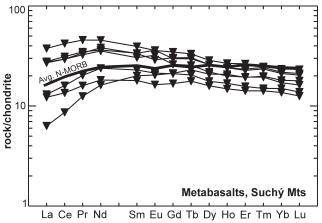


Fig. 7. Chondrite normalized REE patterns for metabasic rocks from the Suchý Mts. Normalization by McDonough & Sun (1995), average N-MORB by Niu et al. (2002).

Magnesium number varies in the narrow interval 45-53 for the metamorphosed basalts, elevated values, up to 65, are typical for metagabbros/metagabbrodolerites. Titanium concentrations as a whole are low, not exceeding 2 wt. % TiO2 in the majority of samples do (max. 2.55 %). Furthermore, they decrease with an increasing magnesium number, where chromium contents increase. In the case of nickel, however, the positive correlation with magnesium number is weak. Potassium contents are low (<0.2 wt. % K₂O), slightly elevated concentrations (max. 0.88 wt. %) are related to the weak secondary biotitization. We used trace elements generally accepted as immobile during the metamorphic alteration, namely REE, HFSE, Cr, V or Sc for reconstruction of the geochemical signature of the metabasalts and geodynamic setting of their generation. Chondrite normalized REE patterns for metabasalts from the Malá Magura Mts (Fig. 6) are uniformly mildly sloped ($La_N/Yb_N = 1.63-1.86$) and enriched in LREE in

comparison to mean oceanic N-MORB (La_N=27.85-37.13; $La_N/Sm_N = 1.00-1.10$) resembling E-MORB types. The majority of them also display a small Eu-anomaly (Eu/Eu*=0.84-0.98). The REE patterns for metabasalts from the Suchý Mts are more variable (Fig. 7). Types similar to N-MORB with low total REE contents, depletion in LREE and flat form of HREE patterns ($La_N = 6.33-37.55$; $La_N/Sm_N = 0.32-0.96$; $La_N/Yb_N=0.87-1.61$) can also be found there besides the types identical to those from the Malá Magura Mts. However, all these rocks with such different REE patterns belong petrographically to metagabbros or metadolerites. Eu-anomalies are absent or small (0.89-1.12). Geochemical signature close to MORB for the metabasic rocks from the Suchý and Malá Magura Mts can be deduced from the several traditionally used discrimination diagrams such as Zr vs. TiO₂ (Pearce 1982), Ti vs. V (Shervais 1982) or Y vs. Cr (Pearce 1982). The more detailed specification of the geochemical type of these rocks

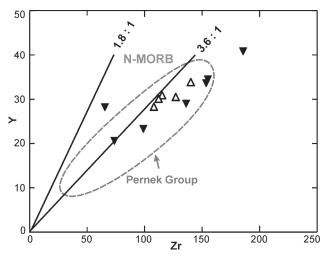


Fig. 8. Zr vs. Y diagram (Le Roex et al. 1983) for metabasic rocks from the Suchý and Malá Magura Mts. Field for their analogues from the Pernek Group (Malé Karpaty Mts) was added for comparison. Symbols and data for field — see Fig. 4.

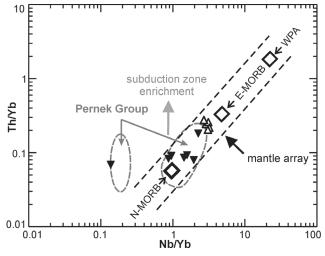


Fig. 9. Nb/Yb vs. Th/Yb diagram (Pearce & Peate 1995) for metabasic rocks from the Suchý and Malá Magura Mts. Symbols and fields — see Fig. 4.

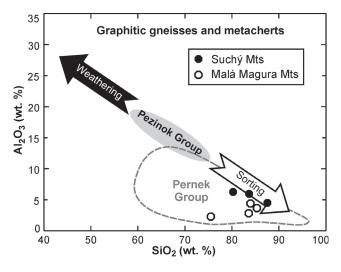


Fig. 10. The Al_2O_3 vs. SiO_2 plot (Méres 2007) indicating an absence of the chemical weathering and high contents of the SiO_2 in the protolith of the graphitic gneisses and metacherts from the Suchý and Malá Magura Mts. Fields for metamorphosed sedimentary rocks of the Pernek and Pezinok Groups from the Malé Karpaty Mts were added for comparison (see discussion for more details). Data for graphitic gneisses and metacherts are taken from Table 2, fields are based on data from Méres (2005, 2007).

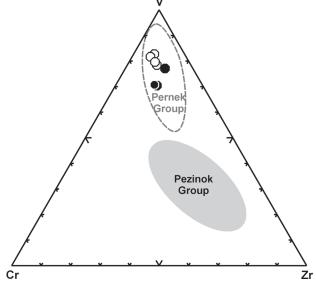


Fig. 11. V-Cr-Zr diagram (Méres 2007) illustrating relatively high content of V in the studied rocks similar to its analogues in the Pernek Group and different composition of metamorphosed sedimentary rocks in the Pezinok Group (both groups — the Malé Karpaty Mts). Symbols and fields — see Fig. 10.

in the Zr vs. Y diagram (Le Roex et al. 1983; Fig. 8) indicates that they are more similar to E-MORB than to N-MORB. This fact is fully supported by the Nb/Yb vs. Th/Yb diagram (Pearce & Peate 1995; Fig. 9) which also clearly displays some geochemical differences between metabasic rocks from both crystalline cores — samples from the Malá Magura Mts are more similar to typical E-MORB than those from the Suchý Mts. The same results can be obtained using Hf/3-Th-Ta (Wood 1980), Th-3Tb-2Ta (Cabanis & Thiéblemont 1988) or La/10-Y/15-Nb/8 (Cabanis & Lecolle 1989) discrimination diagrams. Comparison of the studied rocks with their

petrographic analogues from the Pernek Group (Malé Karpaty Mts) displays identity or close similarity in all tested diagrams.

Major and trace element distributions in selected samples of the metamorphosed carbonaceous sedimentary rocks from the Suchý and Malá Magura Mts are presented in Table 2. High contents of SiO₂ (75–88 wt. %) and C_{tot} (3.5–11 wt. %, including C_{org} 0.9–2.7 wt. %) as well as low contents of Al₂O₃ (<7 wt. %), Fe₂O₃^{tot} (<1.8 wt. %), MgO (<0.7 wt. %), CaO (<0.1 wt. %), Na₂O (<1 wt. %) and K₂O (1.8 wt. %) are typical for graphitic gneisses and metacherts. Their position in the

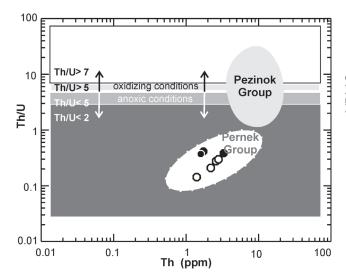


Fig. 12. Plot Th/U vs. Th (Méres 2007) indicates strong anoxic sedimentary environment of the graphitic gneisses and metacherts from the Suchý and Malá Magura Mts. Symbols and fields — see Fig. 10.

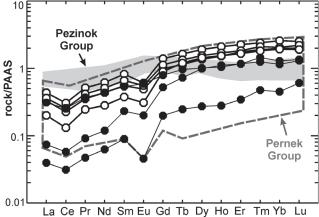


Fig. 14. PAAS-normalized REE patterns of the graphitic gneisses and metacherts from the Suchý and Malá Magura Mts. Fields for the metamorphosed sedimentary rocks from the Pernek and Pezinok Groups (both Malé Karpaty Mts) were added for comparison. Symbols and fields — see Fig. 10. **PAAS** — Post-Archean average Australian Shale (Taylor & McLennan 1985).

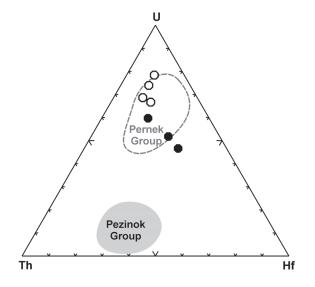


Fig. 13. U-Th-Hf diagram (Méres 2007) indicated relatively high uranium content in the graphitic gneisses and metacherts from the Suchý and Malá Magura Mts. Similarity of these rocks to their analogues in the Pernek Group and difference to metamorphosed sediments of the Pezinok Group is obvious. Symbols and fields — see Fig. 10.

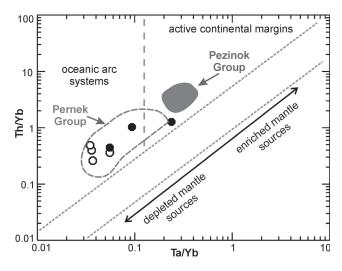


Fig. 15. Th/Yb vs. Ta/Yb diagram for the graphitic gneisses and metacherts from the Suchý and Malá Magura Mts. Fields for the metamorphosed sedimentary rocks from the Pernek and Pezinok Groups (both Malé Karpaty Mts) were added for comparison. Symbols and fields for Pezinok and Pernek Groups — see Fig. 10. Others fields after Cluzel et al. (2001).

Al₂O₃ vs. SiO₂ diagram (Fig. 10) indicates an absence of the chemical weathering of the protolith. The high vanadium content (Fig. 11) provides important clues for evaluation of the original petrography and sedimentary environment of these rocks. The enrichment in U (Fig. 12) and depletion in Th, Sr, Ti and LREE as well are characteristic features of the studied graphitic gneisses and metacherts in comparison with other types of gneisses in the Suchý and Malá Magura Mts (Table 2, Fig. 13) thought to be an equivalent of the Pezinok Group from the Malé Karpaty Mts (Méres & Ivan 2008). Vanadium and uranium contents positively correlate with Ctot content. Low CaO and Sr contents suggest an ab-

sence of carbonates in the protolith and provide evidence of non-carbonate sedimentary environments. Moreover, the low Sr content together with low Ti content in metacherts is an indication of the chemical/biochemical origin of their protolith. PAAS normalized REE patterns display negative Ce-anomaly, negative Eu-anomaly, low LREE/HREE ratio and high HREE content (Fig. 14).

The occurrence of V-bearing minerals and U, Th, Cr and V enrichment in metacherts together with the specific REE distribution (including negative Ce anomaly, McLennan 1989; Sholkovitz & Schneider 1991; Holser 1997; Cullers 2002; Kato et al. 2002), Th/U ratio (McLennan et al. 1993; Asiedu

Table 2: Major and trace element analyses of the metacherts and graphitic gneisses from the Suchý and Malá Magura Mts. Note: Samples labelled MM — Malá Magura Mts, body near the Chvojnica village; S — Suchý Mts, body in the Železná dolina valley.

MM-05-1 MM-05-2 MM-05-3 MM-05-4 S-03-9 S-05-1 S-05-2 Sample 80.27 87.55 83.46 SiO₂ 83.58 83.95 85.32 75.53 TiO_2 0.18 0.29 0.25 0.180.4 0.29 0.33 4.41 6.28 Al_2O_3 2.83 3.67 2.3 4.51 6.13 Fe₂O_{3tot} 0.26 0.25 0.04 0.13 1.78 0.25 0.18 MnO 0.01 0.01 0.01 0.01 0.02 0.01 0.01 ΜσΩ 0.17 0.25 0.18 0.27 0.68 0.26 0.28 CaO 0.01 0.01 0.01 0.01 0.07 0.02 0.07 Na₂O 0.26 0.07 0.1 0.21 0.85 0.27 1.4 1.48 K₂O 0.83 1.49 1.36 1.71 1.43 0.61 P_2O_5 0.04 0.01 0.02 0.02 0.17 0.01 0.03 LOI 11.8 9.2 8.9 9.3 5.3 6.5 7.5 99 97 99 94 99.86 88 57 99.73 99.9 99.87 Total \mathbf{C}_{tot} 10.9 9.13 8.92 8.93 6.13 3.57 5.99 C_{org} 1.21 1.43 1.2 1.23 2.66 2.18 1.1 TOT/S 0.03 0.02 0.05 0.08 0.02 0.01 0.04 Cr 150 140 190 110 110 120 90 4.5 1.9 21.2 Ni 2.0 2.3 2.6 1.4 Co < 0.5 < 0.5 0.6 < 0.5 < 0.5 1.4 0.5 10 12 9 10 13 14 Sc 12 1051 950 756 733 V 1279 498 522 36.2 36.2 36.2 Rb 23.6 38.9 37.9 35.1 1041 274 Ba 387 752 464 830 1246 Sr 9.3 3.5 5.4 7.7 24.1 10.7 33.5 Ta 0.2 0.4 0.2 0.2 0.3 0.2 0.3 Nb 3.1 3.5 2.8 2.6 3.1 2.4 3.4 Hf 2.1 1.5 1.3 2.4 3.1 1.5 2.5 85.3 121 97.4 83.2 99.6 96.6 128 Zr Y 64.8 82.1 68.7 61.1 38.6 39.2 10.7 Th 2.2 2.6 2.8 1.4 3.3 1.6 1.6 9.4 10.5 9.4 IJ 9.8 8.6 4.3 4.1 Th/U 0.21 0.28 0.30 0.14 0.38 0.37 0.39 Th/Sc 0.22 0.22 0.23 0.16 0.33 0.12 0.11 12.5 2.8 La 16.5 13.7 7.6 11.8 1.5 Ce 18.1 24.5 20.4 10.5 20.2 4.6 2.5 0.81 0.42 Pr 3.14 4.57 3.71 2.18 3.29 14.0 19.7 16.3 9.0 14.0 3.8 Nd 2.0 4.6 2.1 3.0 1.3 0.5 Sm 3.1 3.7 0.61 Eu 0.54 0.67 0.34 0.65 0.22 0.05 4.64 6.54 4.23 3.72 2.46 0.93 Gd 5.3 0.88 1.26 1.03 0.92 0.74 0.56 0.19 Th Dy 6.01 8.39 6.81 6.33 4.44 4.34 1.2 1.54 0.28 Но 1.52 2.1 1.69 1.05 1.11 6.53 5.32 4.81 3.39 1.00 Er 3.37 5.1 Tm 0.76 0.96 0.84 0.73 0.5 0.58 0.19 Yb 5.54 7.21 5.75 5.39 3.21 3.6 1.26 1.08 0.56 0.58 Lu 0.86 0.95 0.82 0.26 La_N/Yb_N 1.52 1.54 1.61 0.95 2.48 0.52 0.80 Eu/Eu* 0.44 0.37 0.42 0.35 0.57 0.37 0.23

et al. 2000; Dypvik & Harris 2001) are generally interpreted as evidence for deposition in an extremely anoxic sedimentary environment (Figs. 12 to 14). Taking into account additional geochemical ratios (Th/U, La/Sc, La/Y, La/Ce, Th/Sc) and position in Th/Yb vs. Ta/Yb diagram (Fig. 15) lends further support to a deep oceanic provenance of the sedimentary protolith of the studied graphitic gneisses and metacherts. As follows from the presented diagrams, all geochemical features of the studied rocks are fully comparable with their petrographic analogues from the Pernek Group but they are distinctly different from the paragneisses and phyllites form-

ing the Pezinok Group — an adjoining lithostratigraphic unit found in the Early Paleozoic of the Malé Karpaty Mts.

Discussion

The crystalline complexes of the Suchý and Malá Magura Mts together with the crystalline complexes of the two other core mountains - the Malé Karpaty Mts and Považský Inovec Mts, all located on the NW margin of the Tatric megaunit, differ from the rest of the Tatric megaunit in some aspects of their geological structure and evolution. Presence of relatively lower-grade metamorphic rocks, clearly intrusive relations of granitoids with surrounding rocks or a common occurrence of metamorphosed basic igneous rocks and sedimentary rocks rich in organic matter are among the most distinctive features of the mentioned area, sometimes designated as the Infratatric unit (e.g. Plašienka et al. 1997). The most pronounced manifestations of all these peculiarities are concentrated in the crystalline core of the Malé Karpaty Mts. Two different lithostratigraphic units have been discerned - (1) the ophiolitic Pernek Group and (2) the volcano-sedimentary, riftogeneous Pezinok Group. They form an integral part of the Variscan and Alpine nappe structures (Ivan et al. 2001; Ivan & Méres 2006).

Tectonically restricted bodies of the metabasic rocks associated with the carbonaceous metamorphosed sedimentary rocks at the studied localities in the Suchý and Malá Magura Mts represent small relics of specific lithologies preserved in the complex mosaic of the present structure of this area. Integrity of these domains is indicated not only by the local preservation of original stratification (Fig. 2) but also by the conformity of fundamental rock parameters. Metabasic rocks can be petrographically

classified as actinolite schists or amphibolites reflecting differences in their metamorphic grade. Preserved relic textures indicate that the starting rocks were a variegated association of basic igneous rocks from effusive basalts through subvolcanic dolerites to intrusive gabbros (Fig. 3). As could be inferred from the presence of stockwork of the metamorphosed hydrothermal veins, an intensive hydrothermal alteration preceded regional metamorphism of all these rocks. Some rocks, mostly gabbros, underwent strong deformation at that time. Major element distribution in the metabasalts and their deep-seated equivalents indicate that they crystal-

lized from mostly less fractionated subalkaline tholeiitic basaltic magmas (Fig. 4). Evidence of limited fractionation of only olivine and plagioclase were detected, while all the identified metagabbros belonged to the isotropic type (Fig. 5). The distribution of trace elements generally accepted as immobile in metamorphic processes (HFSE, REE) indicates that original basaltic magmas had a geochemical signature close to the MORB-type. Metamorphosed basaltic rocks from the Malá Magura Mts appear more uniform and close to the E-MORB type (Figs. 6 and 9), whereas those from the Suchý Mts with variable trace element distribution are much more similar to the typical N-MORB (Figs. 7 and 9). The MORB-type geochemical signature of all these metabasic rocks indicates an oceanic floor geotectonic setting.

Graphitic gneisses and metacherts are closely spatially related to metabasic bodies and do not occur isolated outside of these bodies. As follows from a preserved lithological sequence in the metabasic body near Chvojnica village (Fig. 2), the metamorphosed sedimentary rocks form the belt with the stratiform sulphide mineralization a couple of dozens of meters in thickness. This belt is embedded in metabasic rocks originally represented by the strongly hydrothermally altered basalts. The geological situation is very similar to that in the Pernek Group, where several analogous belts with Cyprustype sulphide mineralization are present (Cambel 1962; Chovan et al. 1992; Ivan et al. 2001). Although graphitic gneisses rich in carbonaceous matter and quartz are the most widespread petrographic type of metamorphosed sediments (Fig. 3E and F), related types such as metacherts or quartzsericite rocks with variable content of carbonaceous matter and/or tremolite/actinolite are also present. Impregnation by sulphide minerals (pyrite, rarely sphalerite) is ubiquitous in all these rock types. The chemical composition of graphitic gneisses and metacherts points to a non-carbonate, mostly silica dominated sedimentation in strongly anoxic conditions with variable supply of organic matter and clastic material of the pelitic fraction. Such sedimentation is typical for a deepsea environment below CCD and the close spatial relations to metabasalts of MORB signature localize it on the ocean floor close to an active oceanic volcanic spreading center. The contributions of several sources of sedimentary material can be inferred on the basis of trace element distribution. Negative Ce-anomaly and relative enrichment in HREE (Fig. 14) reflect participation of an ancient seawater source (cf. Kato et al. 2002), whereas values of other geochemical parameters (Th/U<1, Th/Sc<0.25, La_N/Yb_N<6) and Ta/Yb vs. Th/Yb diagram (Fig. 15) indicate a supply from the terrigenous source resembling YUA (Young Undifferentiated Arc; McLennan et al. 1993; Girty et al. 1996). The graphitic substance (with partly preserved organic compounds) is a product of transformation of the organic matter accumulated in sediments due to anoxic conditions which is also responsible for enrichment in V, Cr and U (Figs. 11 to 13).

As mentioned above, the petrographic and geochemical features of metabasic rocks as well as graphitic gneisses and metacherts from the Suchý and Malá Magura Mts are fully comparable with those from the Pernek Group in the Malé Karpaty Mts. The Pernek Group has recently been identified as a tectonically reduced Variscan ophiolite nappe incorpo-

rated in the modern Alpine nappe structure, representing dismembered remnants of the uppermost part of the oceanic crust profile (Ivan et al. 2001; Ivan & Méres 2003, 2006). The Pernek Group was preliminarily dated as ca. 370 Ma old (Putiš et al. 2009) and together with neighbouring Pezinok Group (Devonian) they were intruded and metamorphosed by the ca. 350 Ma old granitoid plutons (Kohút et al. 2009). The bodies of metabasic rocks associated with graphitic gneisses and metacherts in the Suchý and Malá Magura Mts probably represent fault blocks of a Variscan ophiolite nappe identical to that in the Malé Karpaty Mts. Such interpretation is also supported by the existence of a similar fault block in the Malé Karpaty Mts, located in the granitoid rocks on the northernmost margin of the crystalline complex (geological map 1:50,000; Mahel' et al. 1970). A further additional support also follows from the similarity of other lithologies adjacent to the ophiolite nappe in both areas - granitoids or paragneisses. The geochemistry and intrusive age of the granitic rocks from the Suchý and Malá Magura Mts are close to the Bratislava granitoid massif in the Malé Karpaty Mts (Vilinovičová 1990; Kráľ et al. 1997; Kohút et al. 2009) and paragneisses of the studied area strongly resemble those from the Pezinok Group in the Malé Karpaty Mts in all significant parameters (Méres 2007). Any amphibolitic rocks as banded amphibolites or retrogressed eclogites typical for complexes of the lower crustal origin (leptynite-amphibolite complexes — LACs; e.g. Hovorka et al. 1997) have not been found there. The presence of ophiolitic rocks of the Pernek Group in the Suchý and Malá Magura Mts is an important additional argument for the specific geological structure of the "Infratatric unit".

Domination of a geochemical signature close to E-MORB-type among metabasalts of the Pernek Group as well as its occurrence in the Suchý and Malá Magura Mts enables classification of this ophiolite nappe as a relic of the P-type (Pearce 2008) or CM-type (CM — continental margin; Dilek & Furnes 2011) of ophiolites. Such ophiolite type indicates as a rule opening of the oceanic basin along the rifted continental margins. This mechanism probably acted in the case of the studied rocks because of the spatial and time relations existing between the Pernek Group and the Pezinok Group including the typical rift-related volcanic rocks (Ivan et al. 2001).

Ophiolites of the same geochemical type, similar in age and lithology to the Pernek Group have also been found in the Zlatník and Ochtiná Groups on the northern margin of the Gemeric Superunit in the inner Western Carpathians (Fig. 1). They probably represent, together with the Pernek Group, relics of a single Variscan ophiolite suture tectonically dismembered in the Alpine era. This suture was created as the last evolutionary stage of an oceanic basin termed as the Pernek Ocean, which was opened as a result of rifting probably in the Early Devonian and closed in the Late Devonian/EarlyCarboniferous time (Ivan & Méres 2012, 2014). The suture can be interpreted as a fossil boundary separating two lithospheric paleoplates with different Variscan tectonothermal evolution where the southern plate (in present day coordinates) was spared extensive plutonic activities and metamorphic reworking. On the other hand, the northern plate displays a different history — the magmatic activity related to the subduction of the Pernek Ocean and formation of a magmatic arc also led to an intensive metamorphic alteration in the upper crust mainly due to increased thermal flow and related granitoid plutonism. Late Devonian/Early Carboniferous (365–350 Ma) I- and S-type granitoids in the Veporicum and Tatricum Superunits of the Western Carpathians could be the products of this plutonism (cf. Kohút et al. 2009; Broska et al. 2013).

The Variscan ophiolites identified in the Suchý and Malá Magura Mts and in other areas of the Western Carpathians were formed during the oceanic basin opening and spreading immediately before the main phase of the Variscan orogeny in the Mississippian. Their analogues are known from several localities in the European Variscides. Variscan ophiolites Devonian in age have been described from NW Spain (Arenas et al. 2007; Sánchez Martínez et al. 2007), Cornwall (Great Britain — Clark et al. 1998), Giessen (Germany — Pin 1990), Vosges (France — Skrzypek et al. 2012) or from the French Massif Central (Berger et al. 2006).

The paleogeographic position of the Pernek oceanic basin still remains obscure and it could be solved in future by comparative studies of adjoining terrains concerning the place of Pre-Miocene docking of the ALCAPA block (Eastern Alps + Western Carpathians) somewhere in the vicinity of the French Massive Central (e.g. Michalík 1994; Stampfli & Hochard 2009). The Pernek Ocean, in conformity with the existing global tectonic schemes, can be interpreted as a small oceanic basin formed by the active volcanic rifting in the leading edge of the Galatian superterrane as a result of roll-back of the retreating Rheic Ocean (Stampfli et al. 2013). Another possibility, based on a new interpretation of the Variscan orogeny in the Eastern Alps, is its creation as an embayment of the Paleotethys Ocean progressively scissorlike widening to the east in the present-day coordinates (Frisch et al. 2011).

Conclusions

The metamorphic rocks from the Suchý and Malá Magura Mts previously known as amphibolites and graphitic gneisses have been studied by field, petrographic and geochemical methods. Interpretation of the results led us to the following conclusions:

- Small bodies composed of both mentioned rocks represent a specific lithology genetically different from the surrounding crystalline rock complex;
- Amphibolites, locally also actinolite schists, were formed from effusive basalts, dolerites and isotropic gabbros by hydrothermal and following metamorphic alteration;
- Metamorphosed basic igneous rocks display N- to E-MORB geochemical signature typical for the oceanic floor igneous rocks;
- Graphitic gneisses to metacherts represent metamorphosed equivalents of non-carbonate siliceous sediments with variable amount of organic matter;
- Geochemical characteristics of metamorphosed sediments indicate a deep-sea sedimentary environment and a combined oceanic water/terrigenous source of the sedimen-

- tary material with the specific organic matter contribution (enrichment in V, Cr, U) as a result of anoxic conditions;
- The oceanic provenance of the studied rocks is a proof of their ophiolitic character and oceanic crust affinity;
- All relevant parameters correlate the studied rocks with the ophiolitic Pernek Group, Devonian in age, widespread in the Malé Karpaty Mts;
- The small ophiolite bodies in the Suchý and Malá Magura Mts could be interpreted as fault blocks created by tectonic disintegration of the same Variscan ophiolite nappe as that preserved in the Malé Karpaty Mts;
- All the preserved Variscan ophiolites in the Western Carpathians including those from the Suchý and Malá Magura Mts belong to the continental margin type usually generated by spreading in the rifted continental margin environment;
- All the Variscan ophiolites in the Western Carpathians originally formed an integrated suture as a vestige of the Pernek Ocean subducted in the Lower Carboniferous and a fossil boundary between two lithospheric paleoplates with different geological evolution in Variscan times.

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Appendix

Location of samples presented in the paper:

AMM-10: amphibolite, Malá Magura Mts, Chvojnica village. GPS coordinates: N 48°53.598', E 018°33.065', 562 m a.s.l.

AMM-11: amphibolite, Malá Magura Mts, Chvojnica village. GPS coordinates: N 48°53.598', E 018°33.074', 562 m a.s.l.

AMM-14: amphibolite, Malá Magura Mts, Chvojnica village. GPS coordinates: N 48°53.389', E 018°33.344', 646 m a.s.l.

AMM-15: amphibolite, Malá Magura Mts, Chvojnica village. GPS coordinates: N 48°53.394′, E 018°33.328′, 644 m a.s.l.

AMM-15A: amphibolite, like AMM-15, 1 m to the N, GPS coordinates: N 48°53.394′, E 018°33.328′, 644 m a.s.l.

AMM-19: amphibolite, Malá Magura Mts, Chvojnica village. GPS coordinates: N 48°53.503′, E 018°33.209′

ASU-1: amphibolite, Suchý Mts, Nevidzany village, valley of the Krstenica brook.

GPS coordinates: N 48°53.503', E 018°33.209'

ASU-5: amphibolite, like ASU-1 GPS coordinates: N 48°53.503′, E 018°33.209′

ASU-6: amphibolite, Suchý Mts, Závada pod Čiernym vrchom village, Železná dolina valley (valley of the Závada brook).

GPS coordinates: N 48°50.270', E 018°21.906'

ASU-7: amphibolite, Suchý Mts, Závada pod Čiernym vrchom village, Železná dolina valley.

GPS coordinates: N 48°50.240', E 018°21.844'

ASU-8: amphibolite, Suchý Mts, Závada pod Čiernym vrchom village, Železná dolina valley.

GPS coordinates: N 48°50.631', E 018°22.339'

ASU-10: actinolite schist, Suchý Mts, Závada pod Čiernym vrchom village, Železná dolina valley.

GPS coordinates: N 48°50.587', E 018°22.252'

ASU-12: actinolite schist, Suchý Mts, Závada pod Čiernym vrchom village, Železná dolina valley.

GPS coordinates: N 48°50.584′, E 018°22.586′, 437 m a.s.l.

ASU-13: actinolite schist, Suchý Mts, Závada pod Čiernym vrchom village, Železná dolina valley.

GPS coordinates: N 48°50.581', E 018°22.308', 489 m a.s.l.

MM-05-1: metachert, Malá Magura Mts, Chvojnica village. GPS coordinates: N 48°53.490′, E 018°33.209′

MM-05-2: metachert, like MM-05-1

MM-05-3: metachert, Malá Magura Mts, Chvojnica village. GPS coordinates: N 48°53.522′, E 018°33.280′

MM-05-4: metachert, like MM-05-3

S-03-9: graphitic gneiss, Suchý Mts, Závada pod Čiernym vrchom village, Železná dolina valley.

GPS coordinates: N 48°50.654', E 018°22.210'

S-05-1: metachert, Suchý Mts, Závada pod Čiernym vrchom village, Železná dolina valley.

GPS coordinates: N 48°50.479′, E 018°22.375′

S-05-2: metachert, like S-05-1.