Geochemistry of metamorphosed basaltic and sedimentary rocks from the Smolník Cu-pyrite deposit (Gemeric Superunit, Western Carpathians): a reappraisal of older geochemical data

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Geochémia metamorfovaných bazaltov a sedimentárnych hornín z Cu-pyritového ložiska Smolník (Gemerikum, Západné Karpaty): prehodnotenie starších geochemických údajov

Abstract: Stratiform chalcopyrite-pyrite deposit of Smolník is located in the low-grade metamorphosed Early Palaeozoic volcano-sedimentary Gelnica Group. Various types of phyllites, mostly sericite and graphite-sericite phyllites with metadolerite bodies build up proximate vicinity of the deposit. The imminent host rocks of sulphide pods are chlorite phyllites with subordinate chlorite-sericite phyllites intercallations. Metadolerites previously interpreted as effusive rocks are probably subvolcanic in origin. Original igneous mineral association of clinopyroxene, plagioclase, ilmenite and probably also olivine were transformed to association of amphiboles, albite, clinozoisite/epidote, titanite ± calcite by metamorphic alteration. Composition of metadolerites is close to basaltic liquids although indices of some fractionation of plagioclase, olivine/chrom-spinelide or clinopyroxene exist. Trace element distribution points to their similarity to within-plate continental tholeiites (CT) and probable relation to the beginning of rifting in the Lower Devonian time. Three possible sources of sedimentary material have been identified in the sedimentary host rocks of the Smolník deposit: *(i)* basalts generated from enriched mantle reservoir; *(ii)* less fractionated calc-alkaline volcanic rocks and *(iii)* fractionated calc-alkaline rhyolites. An additional hydrothermal source for silica and iron is supposed for chlorite phyllites and allows classified them as metaexhalites. The sulphide ores were directly precipitated in the exhalite environment due to reaction hydrothermal solution with hydrogen sulphide produced by thermochemical reduction of the marine sulphate. Geochemical data on metamorphosed dolerites and sediments in combination to other geological characteristics of the Smolník deposit support its classification as the Besshi-type deposit.

Key words: metadolerites, phyllites, geochemistry, pyrite deposit, Besshi-type

1. INTRODUCTION

Cu-pyrite stratiform deposit of Smolník belongs to numerous ore deposits and mineralizations located in the Early Palaeozoic Gelnica Group – the most extended lithostratigraphic unit of the Gemeric Superunit, which is without doubt the most important metallogenic area of the Western Carpathians. Many of siderite, siderite-sulphide, gold-antimonite, iron and manganese oxides and polymetallic veins, metasomatic or volcanic-hosted stratiform deposits were mined in the past, some of them for several centuries, and their economic potential seems not to be still exhausted (Grecula et al., 1995). For that reason, any data concerning these abandoned and inaccessible deposits preserve permanently their own distinctive interest. Quality of whole-rock analyses advanced towards contemporary level in respect to major elements several centuries ago and trace element analyses especially performed by INAA method at least 40 years ago in the former Czechoslovakia. Ilavský & Bajaník (1981) published in their paper the data on chemical composition of the mineralization-hosted metamorphosed sediments and adjacent basic volcanic rocks from the Smolník deposit practically without any interpretation of them. Moreover, many formal errors (used incorrect form of measured values, misprinted values and some clue trace elements omitted as well) made these data unusable in their presented form. The aim of our paper is the correction and completing of the above mentioned data based on original laboratory protocols and their application for the obtaining of new knowledge concerning the origin of host rocks of the Smolník Cu-pyrite deposit in combination with our original data.

2. GEOLOGY

Stratiform chalkopyrite-pyrite Smolník deposit is located in the central part of the Early Palaeozoic Gelnica Group (Gemeric Superunit, central Western Carpathians). The Gelnica Group

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is build up by two types of rocks complexes: *(i)* volcanogenic, where the low-grade metamorphosed rhyolite tuffs of various granularities labelled by local term as "porphyroids" are intercalated by phyllites originally representing fine-grained acid volcaniclastic material and effusive acid metavolcanics occur only in subordinary amounts, and *(ii)* flysh-like sedimentary complexes composed of the alternated metamorphosed psammitic and pelitic sediments, locally also with subordinated black shales, black metacherts (lydites) or crystalline limestones (Ivanička et al., 1989). Rare small intercalations of acid metavolcaniclastics are also present there. Both mentioned types of rocks complexes contain also small mostly subvolcanic metabasalt bodies (Ivan, 1993, 2009) and are intruded by small bodies of the Permian S-type granites (Uher & Broska, 1996; Finger & Broska, 1999). Metamorphosed rhyolites and their tuffs are Ordovician in age (two age groups – ca. 490 and 465 Ma; Vozárová et al., 2010), whereas micropaleontological dating of metasediments (metacherts) indicates also two different age groups – Upper Cambrian/Lower Ordovician and Upper Silurian/Lower Devonian (Snopková & Snopko, 1979; Soták et al., 2002). There are several concepts of the more detailed stratigraphic division of the Gelnica Group (Grecula, 1982; Bajaník et al., 1983; Ivanička et al., 1989; Grecula et al., 2011) but all of them reflect rather present-day tectonic structure of the group than real stratigraphy.

The Smolník deposit is situated in the sedimentary rocks complexes of Gelnica Group in an area among Smolník and Smolnícka Huta villages and Lastovičí vrch hill (1064 m a.s.l.). It is oriented in W–E direction with declination ca. 70° to S (Fig. 1). The length of deposit exceeds 2 km and 10 to 11 pod-like ore bodies several metres in thickness form this deposit (Ilavský, 1993). Ore bodies are represented by massive, disseminated and sporadically also banded ores dominated by pyrite. Less amounts of chalcopyrite and subordinately also sphalerite, galenite, tetrahedrite, arsenopyrite and pyrrhotite are also present (Kantor & Rybár, 1970). Ore pods are embedded in the series of strata composed mainly by chlorite phyllites locally with thin interbeds of sericite-chlorite to sericite phyllites. Rarely intercalations of metacarbonates, quartzites or quartzose phyllites also occur (Ilavský & Bajaník, 1981; Fig. 2). The hanging wall of the deposit is build up by dark sericite phyllites with intercalations of graphitic phyllites and metacherts (lydites). In the metacherts microfossils (acritarchs, spores, kerogen) indicating their

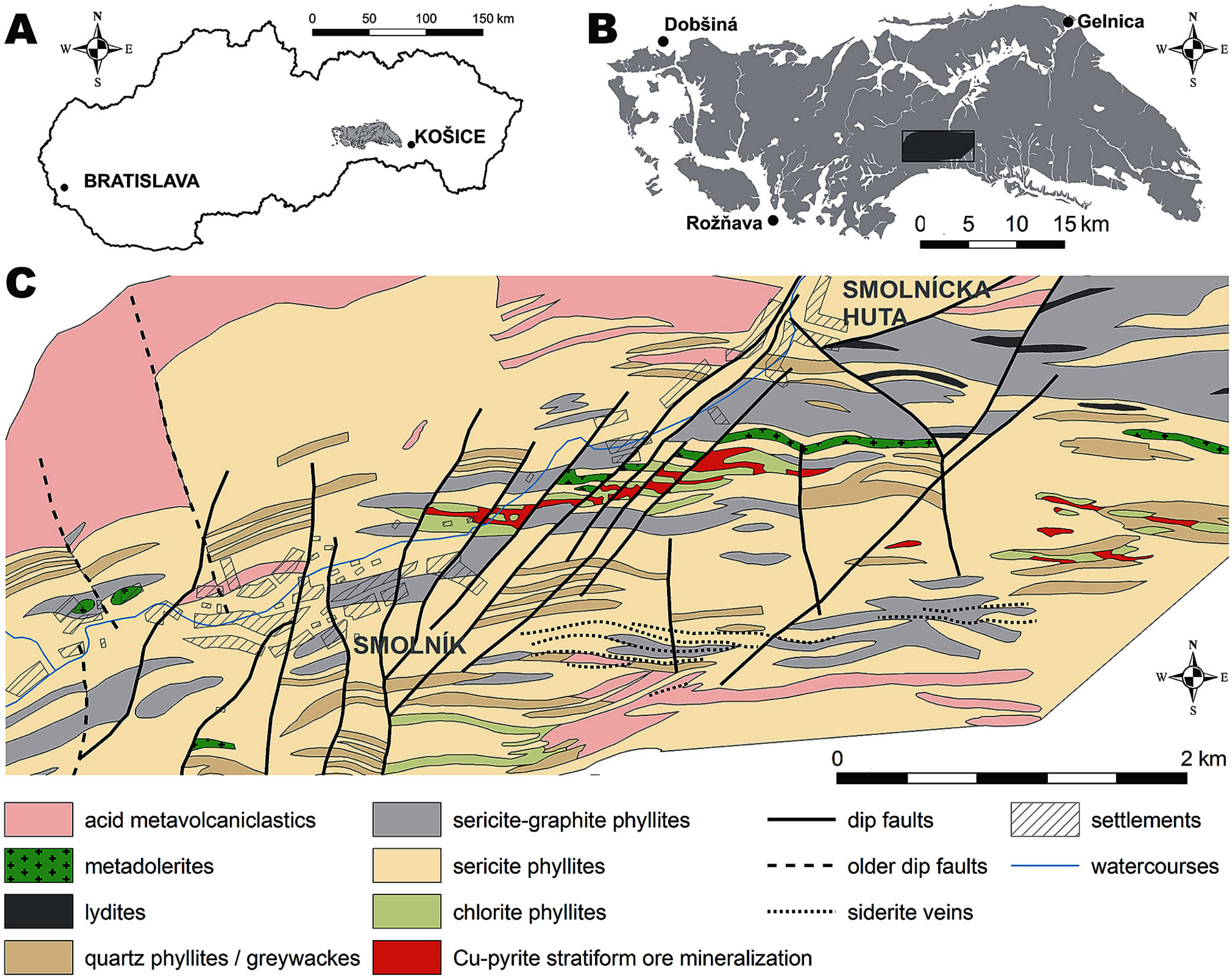

Fig. 1. A) Geographical position of the Gelnica Group deposits in the Slovak Republic; B) Location of the studied area within the Gelnica Group; C) Geological sketch-map of the vicinity of stratiform chalcopyrite-pyrite deposit of Smolník (modified after Ilavský & Bajaník, 1981).

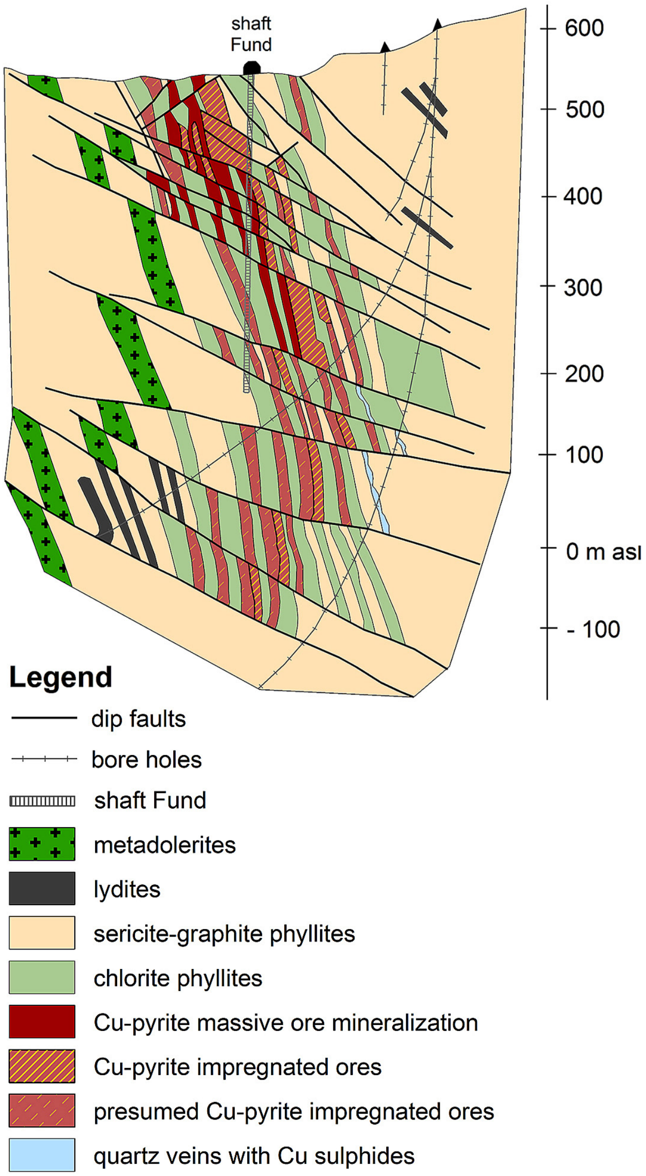

Fig. 2. Schematic section of the stratiform chalcopyrite-pyrite deposit of Smolník (modified after Ilavský, 1964)

Upper Silurian to Lower Devonian age have been found (Ilavský et al., 1985). Similar rocks are also known from the lying wall of deposit. An elongated body of the relatively coarse-grained metabasalt (metadolerite) is embedded in the dark phyllites denoted as graphitic parallel in orientation with ore pods at the distance of ca. 100 m. Thickness of the body varies between 3 and 5 metres and it diminishes with increasing depth, its length exceeds 2 km (Chmelík & Ilavský, 1965). The body is split tectonically into several segments, some segments are duplicated and the interbed of dark phyllite separates them. Small metadolerite lenses as its potential continuation to the west and east have been found near Smolník village and at the Lastovičí vrch hill and Porče valley. Intrusive origin was originally supposed for metabasic rocks from the Smolník deposit, later Chmelík & Ilavský (1965) and Ilavský & Bajaník (1981) proposed their volcanic, effusive character. Crucial role of these rocks for the genesis of the Smolník deposit seems to be generally accepted, formation of chalcopyrite-pyrite ores is supposed to be close related just to this volcanic activity and host chlorite phyllites would be originally basaltic tuffs.

3. PETROGRAPHY

Three petrographic types of rocks closely related to the Smolník deposit ores were the object of our geochemical study: *(i)* metabasic rocks; *(ii)* chlorite phyllites; and *(iii)* chlorite-sericite phyllites. All metabasic rock samples except two were taken from the profile across ca. 6 metres thick metabasite body. Chlorite phyllite and also chlorite-sericite phyllite samples were collected from two individual sedimentary beds, the synthetic scheme of whole lithostratigraphic sequence in the Smolník deposit together with sample locations is depicted in Fig. 3. Detailed sample location schemes can be found in Ilavský & Bajaník (1981).

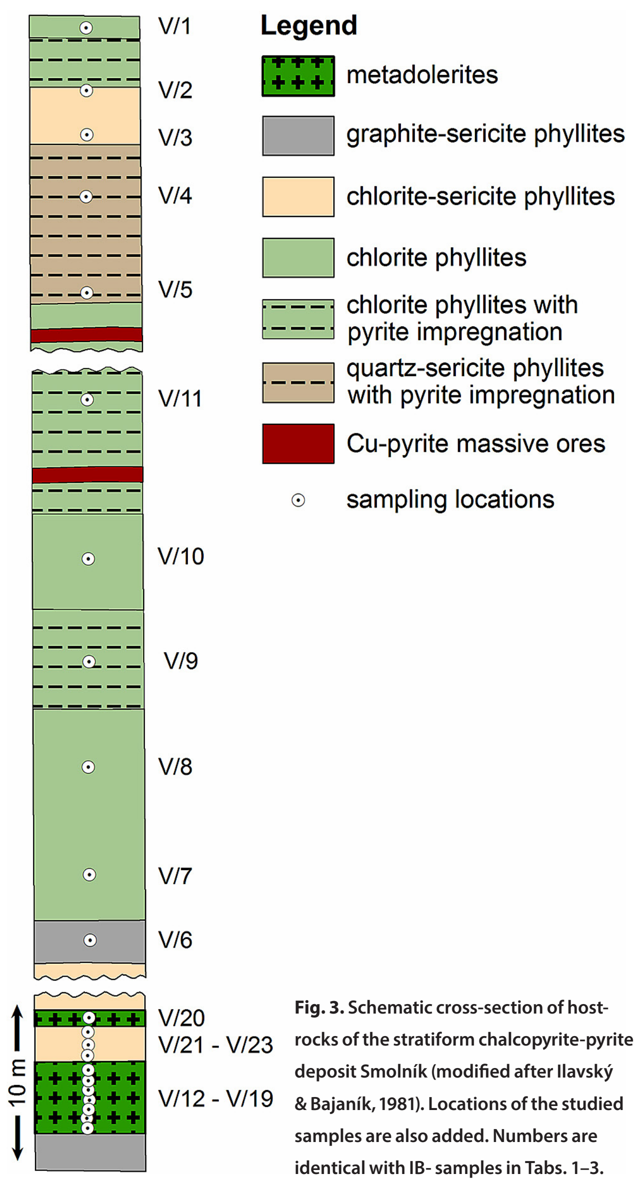

Fig. 3. Schematic cross-section of host-rocks of the stratiform chalcopyrite-pyrite deposit Smolník (modified after Ilavský & Bajaník, 1981). Locations of the studied samples are also added. Numbers are identical with IB- samples in Tabs. 1–3.

Metabasic rocks are typically massive, mostly coarse-grained, deep green in colour reminding of amphibole gabbros or amphibolites. Microscopically they show blastodoleritic to blastogabbrodoleritic texture and a multi-stage metamorphic evolution is obvious from the observed mineral associations (Fig. 4A,B). Originally they were represented by gabbrodolerites to dolerites with typical doleritic texture with clinopyroxene, basic plagioclase and some euhedral ilmenite and olivine(?) as main mineral constituents. Grain size in the central part of bodies was around 4 mm, fine-grained varieties occurred near to boundaries. Ilmenite and rarely also clinopyroxene are only preserved original magmatic mineral phases. As a result of metamorphic alteration clinopyroxene was transformed to magnesian chlorite variously replaced by amphiboles whereas plagioclase was replaced by albite with small aggregates of clinozoisite, rarely epidote crystals. Some of the magnesian chlorite aggregates remind of pseudomorphoses after olivine phenocrysts. Ilmenite crystals are variously replaced from rims by leucoxene (titanite). Three amphibole types different in colour and composition reflect changing p,T,X-conditions in the course of metamorphic evolution.

Chlorite phyllites are oriented massive to shaly rocks dark-green to black-green in colour frequently containing pyrite veining or impregnation. They form intercalations between massive chalcopyrite-pyrite ore pods or they directly represent the environment where disseminated ores were precipitated (cf. Kantor & Rybár, 1970). Oriented lepidoblastic to granolepidoblastic textures are typical under microscope. Iron chlorite is the main mineral component together with less amounts of small (0.02–0.08 mm) irregular grains and aggregates of quartz and small flakes of sericite (Fig. 4C,D). Pyrite, Fe-Ti-oxides and carbonate are also present (Ilavský & Bajaník, 1981).

Chlorite-sericite phyllites are characterized by similar structures and textures as chlorite phyllites. Phyllosilicates are the dominant component, occasionally also alternation of the sericite and quartz-chlorite strips can be observed. Pyrite and Fe-Ti oxides are less significant components only.

4. ANALYTICAL METHODS AND CHECKING OF ANALYTICAL DATA

Major element concentrations in the studied samples were performed by classic wet method in the laboratories of the Geological Survey (Geologický prieskum) in Spišská Nová Ves town. Results

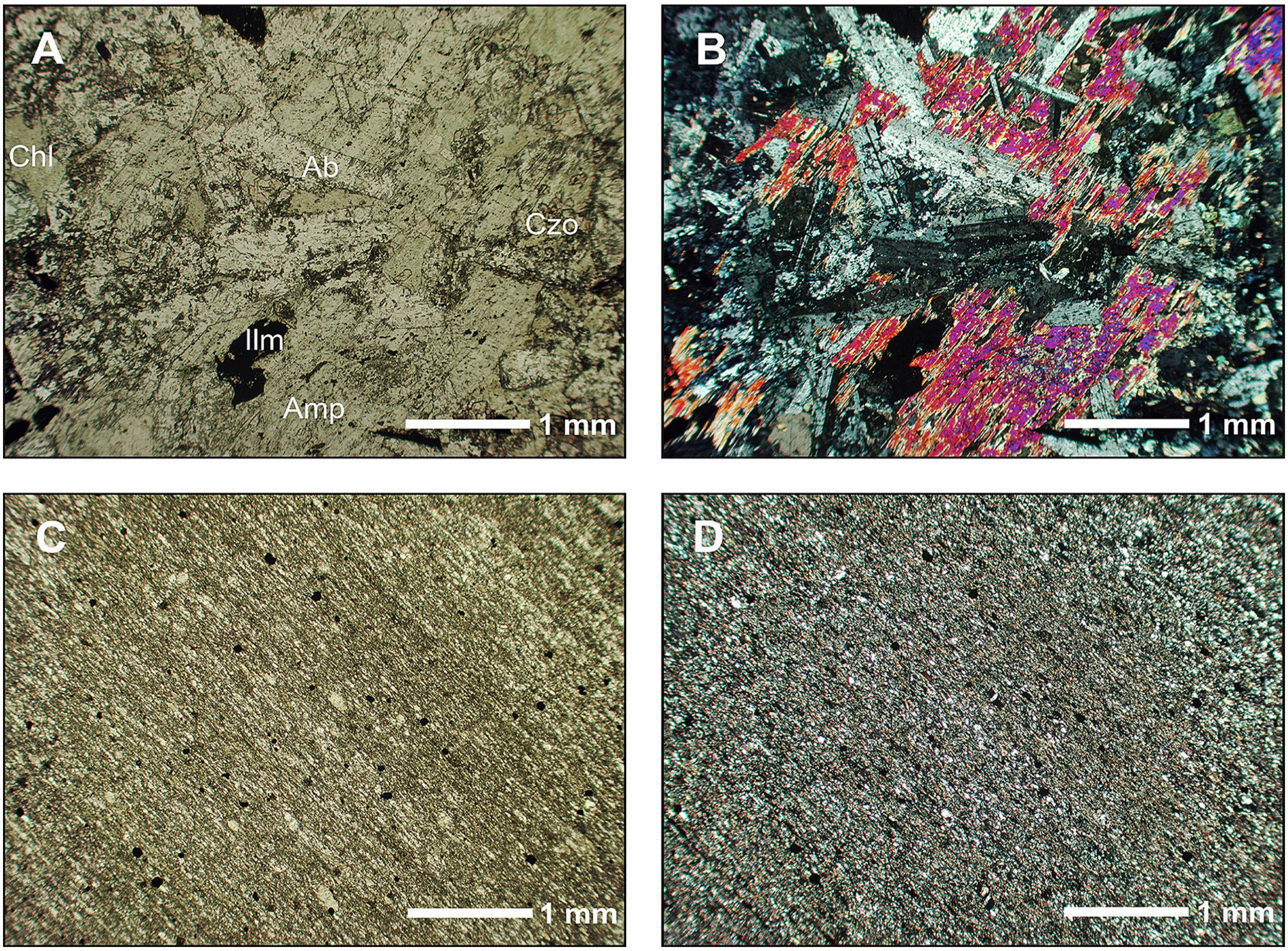

Fig. 4. Microscopic view on the typical metadolerite and chlorite phyllite from the stratiform chalcopyrite-pyrite deposit Smolník. (A) metadolerite with relic ophitic (doleritic) texture, sample VSM-3, PPL; (B) the same, XPL; (C) chlorite phyllite, sample VSM-4, PPL; (D) the same, XPL. Chlorite phyllite is composed mostly of chlorite with small amount of sericite and fine-grained quartz.

of these analyses are presented erroneously in the original paper of Ilavský & Bajaník (1981) because values for $Fe_2O_3^t$ were misinterpreted as Fe_2O_3, moreover total iron content in analyses 5 to 11 (labelled in our paper as IB-5 to IB-11) estimated as Fe was not recalculated for $Fe_2O_3^t$ by mistake. As for trace elements a part of them (V, Zn, Pb, Cu, and Sn) were performed in the same laboratories by AAS method, all other by INAA method in the Institute of Raw Materials (Ústav nerostných surovin) in Kutná Hora town (analyst J. Lenk). The INAA analyses in comparison to the original paper of Ilavský & Bajaník (1981) are presented in corrected and completed form according to the original analytical protocol. The reliability of all corrected data summarized in our paper has been tested by their comparison to our original data from the rock complexes of the Smolník deposit and its vicinity.

Tab. 1. Distribution of major and trace elements in the metadolerites from the Smolník stratiform chalcopyrite-pyrite deposit and their analogues from the Gelnica Group in the spatial continuation of the deposit. *Note: values with asterisk – loss on ignition, Fe(%) was performed by INAA method. Samples 10–12 Ivan (2009): VSM-3 – the Smolník deposit, Pech shaft, fifth horizon, cross-cut to ventilation funnel, 17m from the point no.142; FMZ-6 – Zadné Porče valley ca. 4,5 km to the E from the Pech shaft of the Smolník deposit; FMZ-10 – Jedľovec hill (953.6 m a.s.l.) ca. 5 km to the E from the Pech shaft.*

	1	2	3	4	5	6	7	8	9	10	11	12
Sample	**IB-12**	**IB-13**	**IB-14**	**IB-15**	**IB-16**	**IB-17**	**IB-18**	**IB-19**	**IB-20**	**VSM-3**	**FMZ-6**	**FMZ-10**
SiO_2	44.51	47.43	48.30	47.29	39.51	45.93	44.70	46.52	47.33	47.59	47.71	47.78
TiO_2	1.40	1.51	1.48	1.50	1.72	1.61	2.01	1.63	1.96	1.16	1.22	1.22
Al_2O_3	11.25	15.65	16.32	17.18	11.51	16.48	13.91	14.42	17.21	16.09	17.27	16.53
$Fe_2O_3^t$	15.26	11.16	11.22	11.95	10.50	11.18	13.55	14.17	11.93	11.62	9.33	9.59
MnO	0.21	0.19	0.16	0.16	0.31	0.16	0.28	0.32	0.34	0.22	0.18	0.14
MgO	10.15	8.52	7.81	7.71	4.28	6.90	6.10	7.37	9.37	8.01	6.74	7.72
CaO	7.30	7.79	7.14	7.28	20.92	10.21	12.72	9.01	2.48	8.46	10.45	9.11
Na_2O	3.90	4.94	4.71	4.37	4.10	4.70	3.58	3.56	4.26	3.07	3.38	3.50
K_2O	0.13	0.18	0.13	0.13	0.13	0.13	0.18	0.18	0.22	0.05	0.01	0.03
P_2O_5	0.28	0.29	0.22	0.24	0.16	0.23	0.33	0.30	0.29	0.15	0.16	0.15
H_2O^+	5.39	2.65	2.48	1.86	6.32	2.12	2.45	2.32	4.35	*4.91	*3.30	*4.49
H_2O^-	0.29	0.37	0.46	0.38	0.31	0.48	0.36	0.34	0.38	0.09	0.23	0.09
SO_3	0.04	0.03	0.03	0.04	0.08	0.05	0.10	0.04	0.05			
Total	100.11	100.70	100.47	100.11	99.85	100.19	100.27	100.17	100.17	101.42	99.98	100.35
Cs	0.2					0.6	0.3					
U	0.2	0.2	0.5	0.5		0.2	1.1	0.61	0.85			
Hf	2.6	1.8	2.2	2.3	1	1.8	2.8	1.8	3.2	1.9	1.9	2.2
Th			0.89	0.88		0.2		2	0.81	1.75	1.6	2.1
Ta	0.66	0.49	0.54	0.48	0.4	0.48	0.83	0.88	0.8	0.82	0.72	0.86
La	11	8.8	10.1	7.2	6	8	13	12	16	10.9	10.2	12.1
Ce	34	23	22	30	15	18	26	28	37	24.4	24.6	28.6
Nd	16	14	21	13	12	16	21	18	32	11.8	9.5	16.8
Sm	3.8	3.1	3.1	2.8	2.3	2.7	4.6	3.7	5	3.2	2.7	2.9
Eu	1.45	1.27	1.14	1.2	1.04	1	1.93	1.49	1.03	1.05	1.1	1.1
Tb	0.39	0.4	0.35	0.4	0.27	0.38	0.58	0.48	0.45	0.35	0.47	0.45
Yb	1.6	1.2	1.4	1.2	1	1.1	1.2	1.5	1.5	1.05	0.95	1.3
Lu	0.16	0.14	0.23	0.14	0.077	0.15	0.16	0.16	0.17	0.275	0.237	0.176
Cr	380	270	340	520	500	610	280	55	500	330	525	445
Ni	132	110	112	118	49	91	85	29	178	332	87	312
Co	54	44	52	53	24	41	51	45	102	41	48	41
Sc	39	44	40	38	40	54	56	39	45	21.4	30.5	26.9
V	200	186	159	191	145	240	302	246	240	163	168	207
As								25	155	43	5	13.8
Sb	1.7	1.3	1.6	1.9	2	1.5	4.4	2.5	5.2	5.3	4.5	4.2
Zn	240	124	108	130	74	116	158	100	188		78	
Pb	80	83	28	48	72	26	36	65	17			
Cu	50	88	77	122	102	68	38	25	38			
Ga	22	20	23	20	11	22	32	18	30			19
Fe (%)	10.1	7.7	9	9.4	5.4	8.1	11	8.9	13.3	7.6		6.75

5. GEOCHEMISTRY

The concentrations of major and trace elements in the metamorphosed basic rocks (metadolerites) from the Smolník chalcopyrite-pyrite deposit and its surroundings are summarized in Tab. 1, the data on chlorite and sericite phyllites from the same area in Tab. 2 and 3.

Major element distribution in metabasites fully reflects their primary petrographic character corresponding to coarse-grained basalts (dolerites or also gabbrodolerites) and they are in accordance with the composition of our samples from this area. In some cases, the original composition is modified by intensive secondary carbonatization (cf. data in paper Chmelík & Ilavský, 1965). As follows from the diagram TiO_2 vs. Al_2O_3 (Pearce, 1983;

Tab. 2. Distribution of major and trace elements in the chlorite and chlorite-sericite phyllites representing the direct host-rocks of chalcopyrite-pyrite ore pods in the Smolník deposit.

	1	2	3	4	5	6	7	8	9
Sample	IB-1	IB-4	IB-5	IB-6	IB-7	IB-8	IB-9	IB-10	IB-11
SiO_2	61.96	66.36	71.87	68.19	58.09	63.45	55.25	53.20	59.70
TiO_2	0.46	0.19	0.31	0.19	0.37	0.47	0.38	0.62	0.64
Al_2O_3	9.66	7.17	6.08	8.51	9.56	8.58	10.44	10.45	11.25
$Fe_2O_3^t$	21.78	21.07	15.40	16.27	23.22	20.23	24.51	25.75	20.79
MnO	0.10	0.11	0.12	0.11	0.13	0.15	0.15	0.21	0.19
MgO	3.74	3.69	2.26	3.39	4.30	3.18	4.28	4.52	3.49
CaO	0.40	0.20	0.53	0.39	0.57	0.38	0.38	0.38	0.57
Na_2O	0.04	0.01	0.01	0.04	0.01	0.02	0.04	0.01	0.04
K_2O	0.52	0.11	0.09	0.76	0.10	0.33	0.23	0.10	0.96
P_2O_5	0.16	0.05	0.13	0.06	0.13	0.13	0.13	0.17	0.15
H_2O^+	1.29	1.01	1.68	1.61	1.78	1.90	2.90	2.58	1.16
H_2O^-	0.20	0.09	0.25	0.17	0.17	0.22	0.25	0.21	0.20
SO_3	0.92	0.93	1.00	0.32	0.54	0.34	0.16	0.37	0.11
Total	101.23	100.99	99.73	100.02	98.98	99.38	99.11	98.57	99.26
Cs	1.4	1.1		2.5	0.47	1.4	1.2		0.97
U	1.9	5	1.5	3.4	3.6	3.4	2.7	2.7	2.6
Hf	7.1	5.4	3.6	5.5	6.2	2.5	3.8	4.7	2.5
Th	13	15	7.8	14	12	4.8	7	5.2	4
Ta	0.47	0.66	0.27	0.83	0.73	0.29	0.5	0.32	0.3
La	28	22	25	33	34	21	23	20	14
Ce	75	55	63	79	80	45	55	70	35
Nd	38	31	36	41	42	31	30	32	31
Sm	5	4.6	5.7	8.4	7.7	4.8	5.6	5.2	3.2
Eu	0.86	0.61	0.68	1.11	1.14	0.87	1.02	1.19	0.78
Tb	0.75	0.83	0.58	1.3	0.9	0.51	0.65	0.5	0.42
Yb	2.2	3.9	1.5	4.8	2.8	1.9	2.2	2.8	1.6
Lu	0.42	0.51	0.26	0.55	0.42	0.31	0.3	0.43	0.35
Cr	13	0	3	3	12	10	3	40	9
Ni	8	7	5	5	8	5	5	8	8
Co	28	38	7.9	14	14	19.4	41	43	28
Sc	15.5	12.6	5.5	18.7	16.5	31	20	30	24
V	32	10	10	10	19	32	25	50	56
As	55	76	20	260	200	65	130	41	34
Sb	1.6	2.1	0.84	9	1.4	1.5	3	1.5	1
Zn	68	142	46	134	270	188	405	400	184
Pb	20	72	30	28	40	20	63	20	28
Cu	190	1500	34	80	125	87	392	58	52
Ga	28	28	17	21	38	22	32	30	20
Sn	74	66	35	110	42	71	71	52	132
Fe (%)	13.6	14.8	10.4	11	19.2	13.7	17.6	18.6	11.5

Fig. 5C), the composition of metadolerites is in concordance with basaltic liquids although some indices of small fractionation of plagioclase and possibly also ilmenite are obvious. As for trace elements, variability in chromium content (55 to 610 ppm) without any correlation to other compatible elements is notable. Chondrite normalised REE patterns (Fig. 5A,B) indicate enrichment in LREE (L_n = 25.32–67.51) together with the differentiated LREE/HREE enrichment (La_n/Yb_n = 4.08–7.35) and positive Eu-anomaly (Eu/Eu* = 1.13–1.44). Slightly different seems to be the composition of metadolerite from the small body parallel-oriented to the main one with the highest total REE content and negative Eu-anomaly (Eu/Eu* = 0.69). In the Hf/3-Th-Ta discriminating diagram (Wood, 1980) metadolerites plot in the area of enriched mid-ocean ridge basalt (E-MORB) field close to calc-alkaline basalt (CAB) and alkaline within-plate basalt (WPB) fields, whereas in the 3Tb-Th-2Ta diagram (Cabanis & Thieblemont, 1988; Fig. 5D) they plot within the field of continental tholeiites (CT). There is no difference in geochemical signature between metabasic rocks from the Smolník deposits and the same rocks from the Gelnica Group in the vicinity of deposit studied by Ivan (2009) except of the signs of plagioclase fractionation.

For the study of low-grade metamorphosed sediments (chlorite and chlorite-sericite phyllites) from the Smolník deposit we used also the comparison with analogical or similar rocks – (chlorite)-sericite phyllites and hematite phyllites from the Gelnica Group (Ivan & Méres, 2005). Major element distribution in the metamorphosed sedimentary rocks is essentially related to the main rock-forming mineral abundance, observed variations seems to be caused by changeable content of quartz and sericite or the presence/absence of feldspar in some cases. Remarkable increased iron contents ($Fe_2O_3^t$ = 16.72–27.52 wt%) and lower contents of alumina (Al_2O_3 = 7.10–11.19 wt%) at stable Fe/Al ratio and variable silica contents (SiO_2 = 52.95–71.54 wt%) are typical for the composition of chlorite phyllites. These facts also follow from the testing in several diagrams based on atomic ratios of elements e.g., Fe+Mg/Al vs. Si/Al, K/Al vs. Si/Al or K/Al vs. Fe/Al (Fig. 6A,B). Moreover, the diagrams support similarity in composition between chlorite-sericite phyllites from the Smolník deposit and their analogues including also hematite phyllites from the other parts of the Gelnica Group. Hematite phyllites seem to be close also to metabasic rocks in some parameters (Si/Al, Fe/Al). Rocks resembling chlorite phyllites occur just between sulphide ore pods and they frequently belong to special rock types designate as exhalites and metaexhalites, respectively, originated as a mixture of the volcaniclastic and chemical sedimentary components. From the diagram Al-Fe-Mn (Fig. 6C) follows that in sulphide deposits really exist

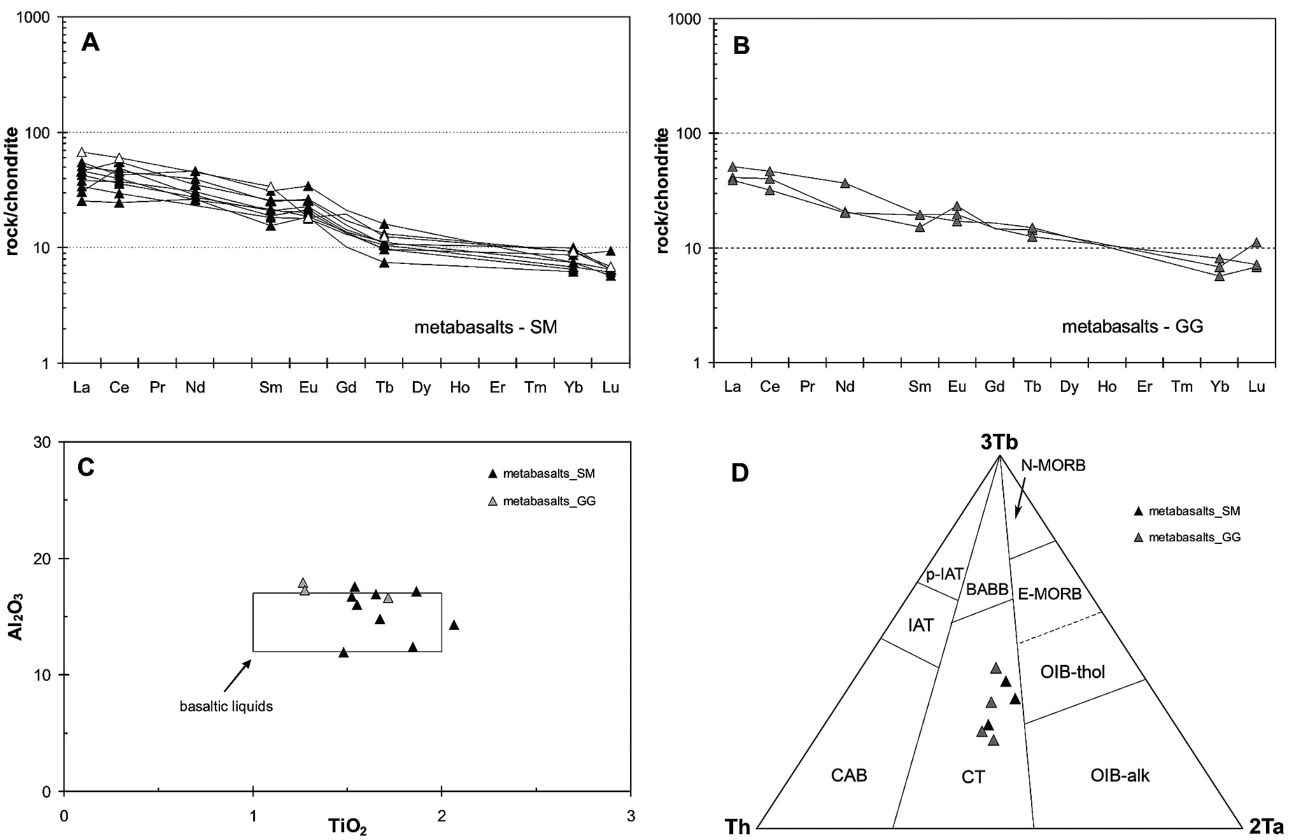

Fig. 5. **(A) Chondrite normalized REE patterns of metadolerites from the Smolník deposit; (B) Chondrite normalized REE patterns of metadolerites from the Gelnica Group of the vicinity of the deposit; (C) Diagram TiO_2 vs. Al_2O_3 (Pearce, 1983) for metadolerites from the stratiform chalcopyrite-pyrite deposit Smolník (SM) and from the Gelnica Group (GG) from the vicinity of deposit; (D) Discrimination diagram 3Tb-Th-2Ta (Cabanis & Thiéblemont, 1988) for the same metadolerites, all of them plot in the continental tholeiite (CT) field. Data sources: Tab. 1; Vozárová & Ivanička (1993), Ivan (2009) and unpublished data; normalization by McDonough & Sun (1995)**

exhalites compositionally similar to chlorite phyllites which are plotted in this diagram within fields of the hydrothermal and non-hydrothermal origin as well (cf. Spry et al., 2000).

Trace element distribution in the studied metamorphosed sediments seems to be different not only between the chlorite and sericite-chlorite phyllites but also divides sericite-chlorite phyllites into two sub-groups and remarkable variability can be observed inside the chlorite phyllites group as well. Chondrite normalized REE patterns for all these rocks show enrichment in LREE (L_n = 59.07–303.79) and also differentiated LREE/HREE enrichment (3.83–16.87), although the HREE depletion rate is lower for some chlorite phyllites (Fig. 7). Negative

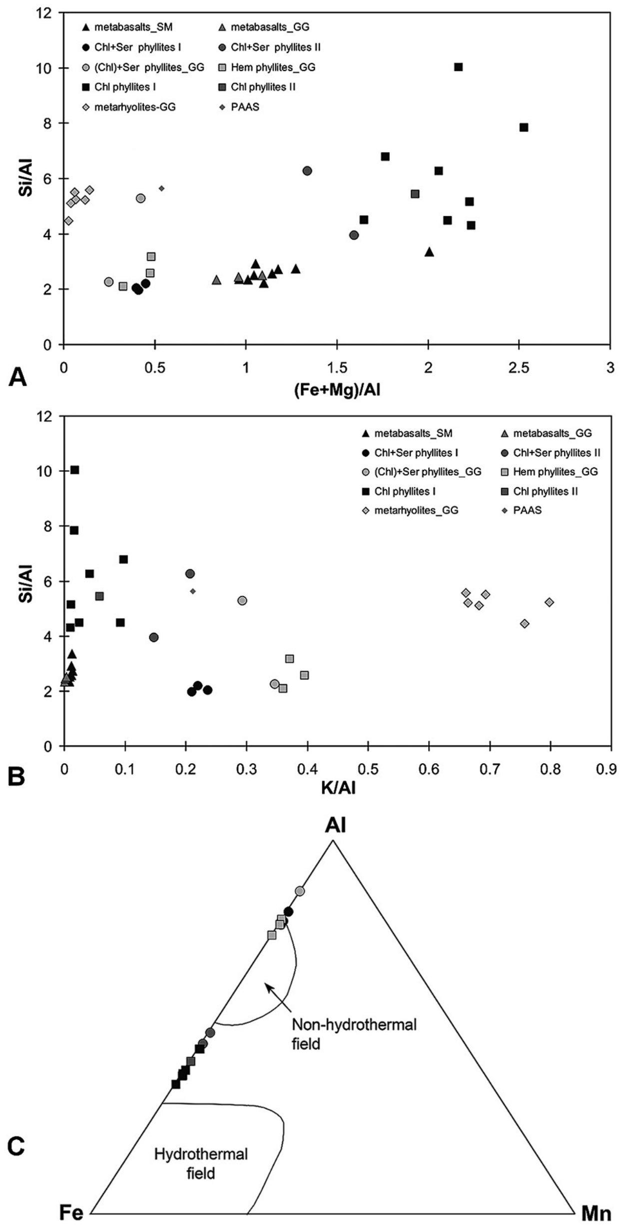

Fig. 6. (A) Diagram Si/Al vs. Fe/Al (atomic %) for the metamorphosed dolerites and sediments from the Smolník deposit. Analogical rocks from the Gelnica Group are added for comparison; (B) Diagram K/Al vs. Fe/Al (atomic %) for the metamorphosed dolerites and sediments from the Smolník deposits. Analogical rocks from the Gelnica Group are added for comparison; (C) Chlorite phyllites from the Smolník deposit in the diagram Al-Fe-Mn with fields for metaexhalites from various types of ore deposits (Spry et al., 2000). Explanations: Chl – chlorite, Ser – sericite, Hem – hematite, SM – Smolník deposit, GG – Gelnica Group, I and II subgroups – see text. Data sources: Tab. 1 and 2; Vozárová & Ivanička (1993), Ivan (2009), Ivan & Méres (2005) and unpublished data.

Tab. 3. Distribution of major and trace elements in the chlorite-sericite phyllites representing the direct host-rocks of chalcopyrite-pyrite ore pods (anal. 1–2) or metadolerites (anal. 3–5) in the Smolník deposit.

Sample	IB-2	IB-3	IB-21	IB-22	IB-23
SiO_2	56.79	69.49	55.07	53.72	56.21
TiO_2	0.91	0.57	1.14	1.29	1.20
Al_2O_3	12.18	9.40	22.91	23.08	21.71
Fe_2O_3	22.60	15.50	8.32	9.72	9.67
MnO	0.18	0.12	0.16	0.25	0.23
MgO	3.94	2.12	3.02	2.60	2.84
CaO	0.40	0.30	0.60	0.90	0.61
Na_2O	0.07	0.07	1.45	0.31	0.46
K_2O	1.66	1.80	5.00	4.47	4.41
P_2O_5	0.23	0.14	0.32	0.25	0.34
H_2O^+	1.24	1.31	2.00	1.87	2.20
H_2O^-	0.20	0.15	0.33	0.37	0.25
SO_3	0.91	0.14	0.30	0.29	0.16
Total	101.31	101.11	100.60	99.13	100.29
Cs	3.3	4.5	7	6.1	7.5
U	1.2	1.3	2.4	3.3	2.2
Hf	9.4	6.3	3.4	4.3	3.3
Th	9.6	9.9	16	17	19
Ta	0.65	0.38	1	1.2	1.04
La	35	30	57	60	72
Ce	84	72	128	127	144
Nd	43	33	76	79	87
Sm	6.9	6.1	10.8	11.2	12.4
Eu	0.97	0.73	2.3	2.3	2.5
Tb	0.85	0.65	0.99	1.1	1.1
Yb	2.5	1.9	3	3.5	2.9
Lu	0.3	0.33	0.3	0.52	0.42
Cr	30	11	110	89	110
Ni	12	8	46	55	52
Co	27	11.8	29	35	18.8
Sc	42	20	31	31	28
V	91	32	118	118	110
As	62	24	80	40	28
Sb	1.2	1.1	11		1
Zn	70	48	66	60	74
Pb	16	20	15	20	21
Cu	22	10	50	48	60
Ga	30	23	38	35	35
Sn	129	257	8	8	8
Fe (%)	14	9.3	6	7.8	6.8

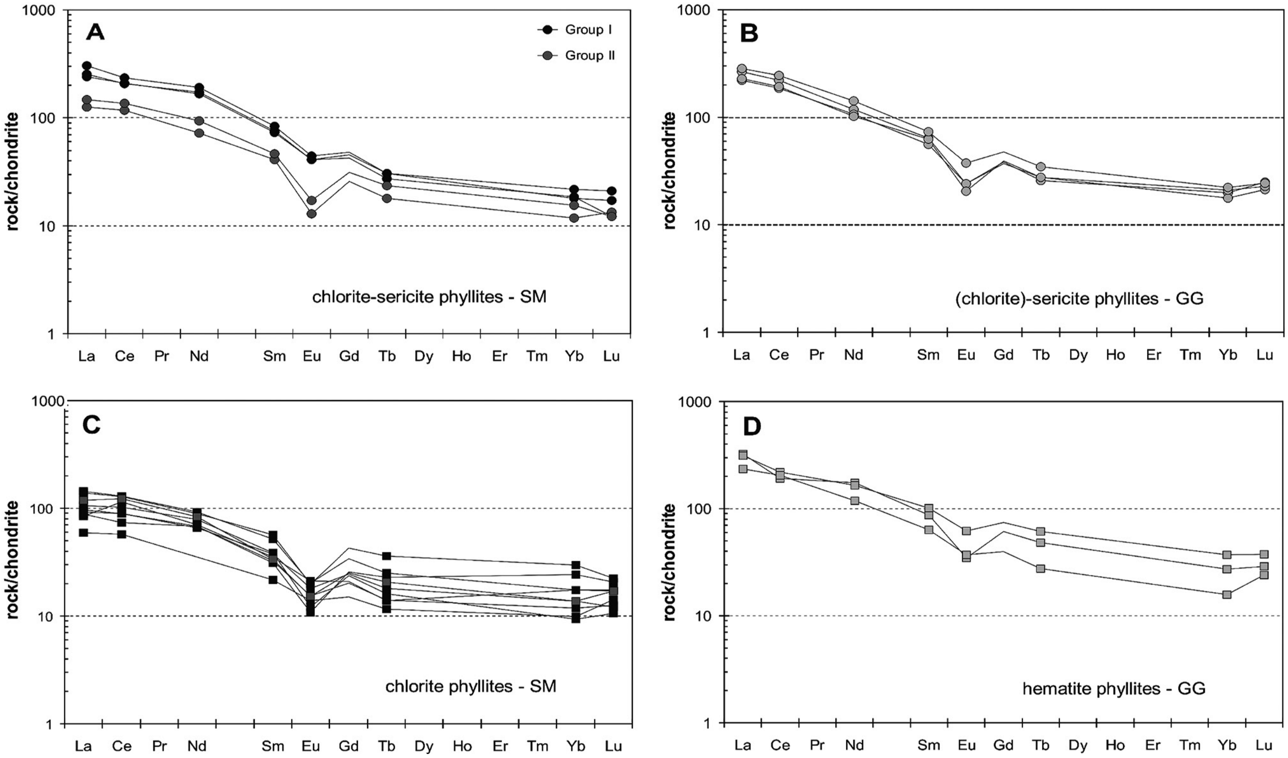

Fig. 7. Chondrite normalized REE patterns for the metamorphosed sediments from the Smolník deposit and their analogues from the other areas of the Gelnica Group: (A) chlorite-sericite phyllites from the Smolník deposit; (B) (chlorite)-sericite phyllites from the Gelnica Group; (C) chlorite phyllites from the Smolník deposit; (D) hematite phyllites from the Gelnica Group. Normalization by McDonough & Sun (1995). Data sources: Tab. 2; Ivan & Méres (2005) and unpublished data.

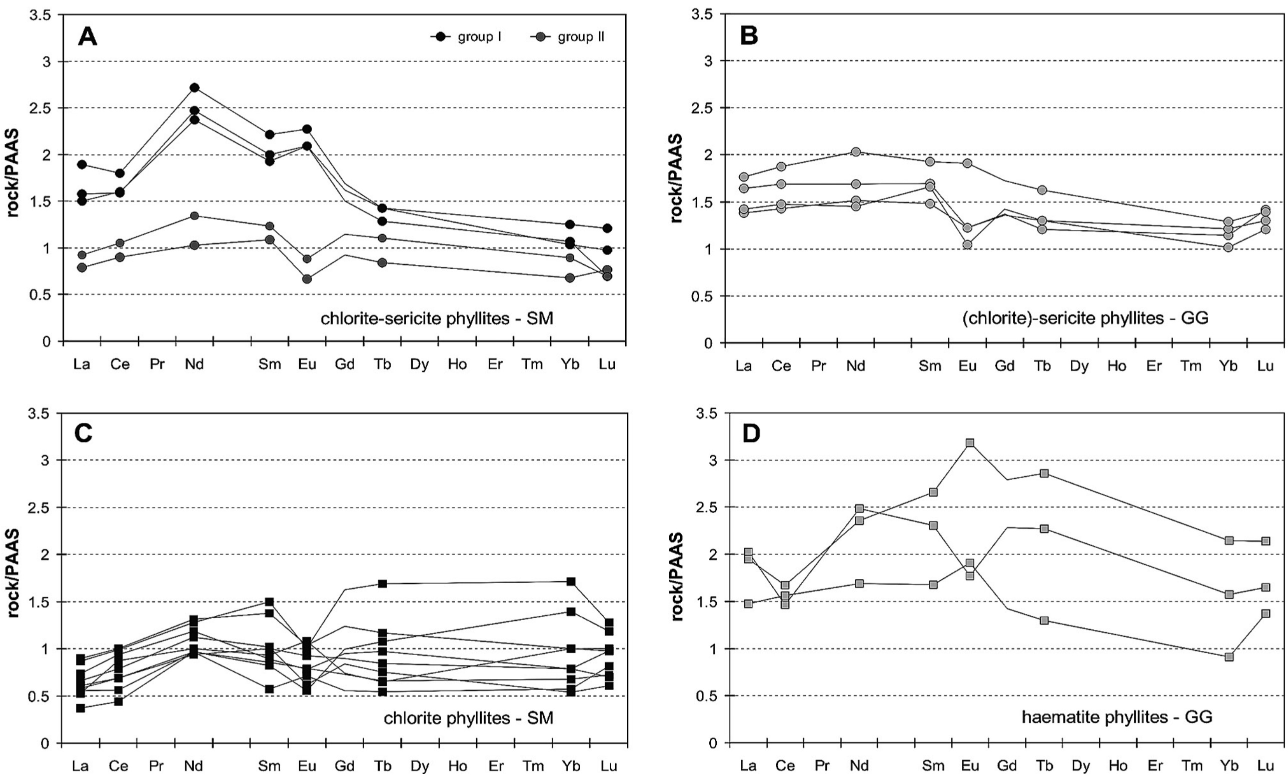

Fig. 8. PAAS normalized REE patterns of the metamorphosed sediments from the Smolník deposit and their analogues from the other areas of the Gelnica Group: (A) chlorite-sericite phyllites from the Smolník deposit; (B) (chlorite)-sericite phyllites from the Gelnica Group; (C) chlorite phyllites from the Smolník deposit; (D) hematite phyllites from the Gelnica Group. Normalization by Taylor & McLennan (1985). Data sources: see Fig. 7.

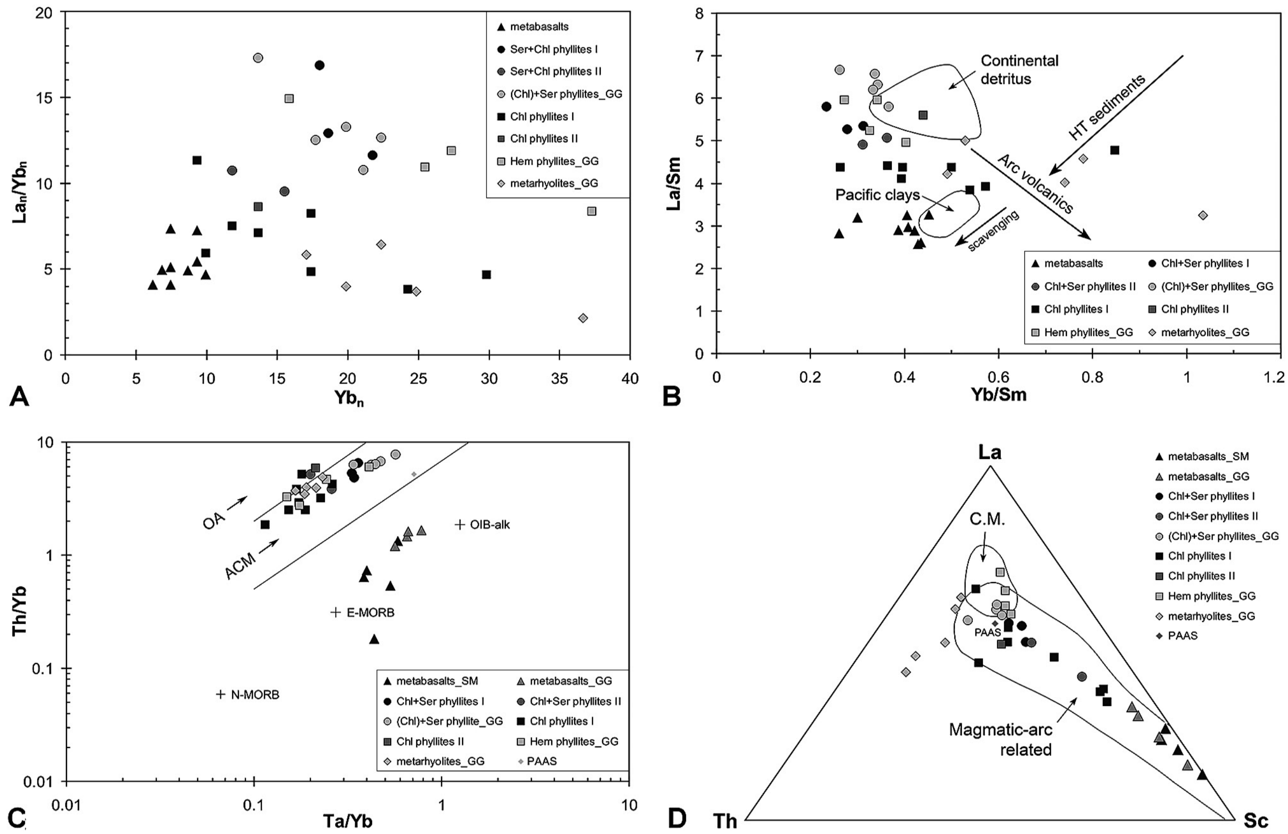

Fig. 9. (A) Lan/Ybn vs. Ybn diagram for the metamorphosed dolerites and sediments from the Smolník deposit and their analogues from other localities in the Gelnica Group; (B) La/Sm vs. Yb/Sm diagram (Plank & Langmuir, 1998) diagram for the metamorphosed dolerites and sediments from the Smolník deposit and their analogues from other localities in the Gelnica Group; (C) Ta/Yb vs. Th/Yb diagram (version by Gorton & Schandl, 2000) for the metamorphosed dolerites and sediments from the Smolník deposit and their analogues from other localities in the Gelnica Group; (D) Metamorphosed dolerites and sediments from the Smolník deposit and analogous rock types from other localities in the Gelnica Group in the diagram La-Th-Sc (Girty et al., 1993). Explanations: OA – oceanic arcs, ACM – active continental margin, C.M. – continental margin; other explanations and data sources: see Fig. 7.

Eu-anomaly (Eu/Eu* = 0.21–0.78) also belongs to common features. Chlorite-sericite phyllites associated with chlorite phyllites display REE patters more similar to these ones. Despite of the similarity of chondrite normalized REE patterns to argillaceous schists, normalization to PAAS (post-Archean average Australian shale) shows considerable differences (Fig. 8). Especially one of two groups of chlorite-sericite phyllites is remarkably enriched in the medium REE (MREE) similarly to hematite phyllites from the Gelnica Group. However, similar trends at lower REE contents can be observed also for a part of chlorite phyllites, whereas others, similarly to a part of chlorite-sericite phyllites, display intensive Eu-anomaly and LREE/HREE enrichment in comparison to PAAS. In the diagrams La_n/Yb_n vs. La_n and La_n/Yb_n vs. Y_n (Fig. 9A) the metadolerites, a part of chlorite-sericite phyllites together with their analogues from the Gelnica Group and metarhyolites plot into three different areas, while chlorite phyllites and other part of chlorite-sericite phyllites plot in the place among these areas. Similar distribution of projection points can be seen in the La/Sm vs. Yb/Sm diagram (Plank & Langmuir, 1998) where majority of studied metamorphosed sedimentary rocks come outside of the continental detritus field (Fig. 9B). In diagram Ta/Yb vs. Th/Yb (version by Gorton & Schandl, 2000) these rocks fall mostly into the field of active continental margin volcanics, a part of them lie beyond the boundary of the field of island arcs acid volcanics (Fig. 9C). Metamorphosed sediments projected in the La-Th-Sc ternary diagram (Girty et al., 1993) form continual row between composition of metadolerites and metarhyolites from the Gelnica Group, whereby they mostly plot in the fields of arc volcanics and PAAS partly overlapped (Fig. 9D). Similar position of metamorphosed sediments from the Smolník deposit can be observed also in the diagrams Eu/Eu* vs. La_n/Yb_n and Th/Sc vs. La_n/Yb_n (Fig. 10A,B) with higher La_n/Yb_n ratio for chlorite-sericite phyllites. In diagram Hf vs. La/Th (Floyd & Leveridge, 1987) chlorite-sericite phyllites likewise chlorite phyllites plot in the field of acid arc sedimentary source as well as mixed acid-basic arc source (Fig. 10C).

6. DISCUSSION

Testing of corrected and completed geochemical data from the paper by Ilavský & Bajaník (1981) in several geochemical diagrams gave the proof of their internal consistency, relation to presented mineral composition and comparable characteristics with our original samples of analogical types.

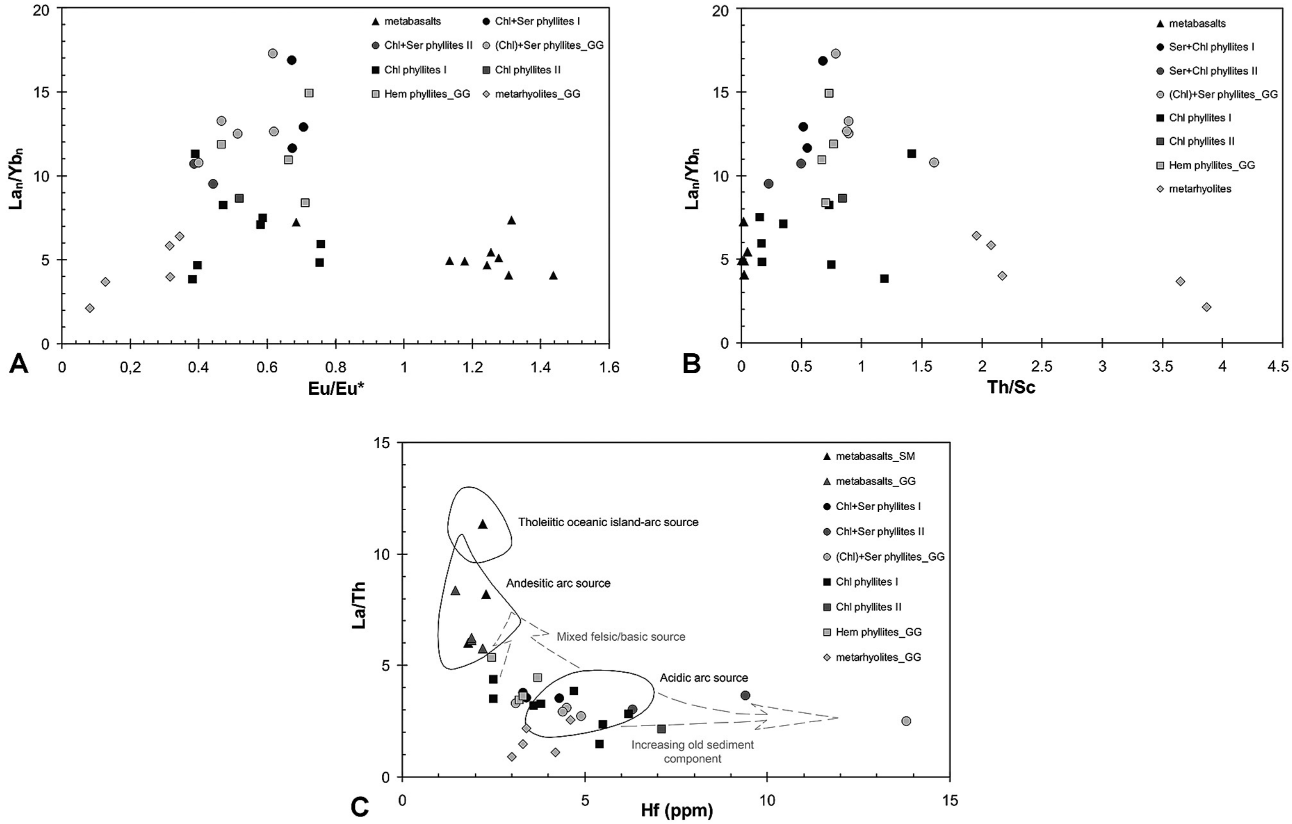

Fig. 10. (A) Eu/Eu* vs. Lan/Ybn diagram for the metamorphosed dolerites and sediments from the Smolník deposit and their analogues from other localities in the Gelnica Group; (B) Th/Sc vs. Lan/Ybn diagram for the metamorphosed dolerites and sediments from the Smolník deposit and their analogues from other localities in the Gelnica Group. Data sources and explanations; (C) Hf vs. La/Th (Floyd & Leveridge, 1987) for the metamorphosed dolerites and sediments from the Smolník deposit and their analogues from other localities in the Gelnica Group. Data sources and explanations: see Fig. 7.

Metadolerites from the Smolník deposit were considered by Chmelík & Ilavský (1965) and Ilavský & Bajaník (1981) as effusive rocks and their bodies as lava flows. However, effusive character of these rocks was not supported by any reliable evidence and by our opinion their interpretation as subvolcanic sills seems to be more conformable with field data on the Smolník deposit and its vicinity. Major element distribution in metadolerites is generally in accordance with the composition of basaltic liquids although the manifestation of some fractionation of plagioclase (Eu-anomalies), olivine with chromspinel (variability in Mg and Cr content) and likely also clinopyroxene (Sc variability) is obvious. Primary magmatic mineral association was represented mostly by plagioclase and clinopyroxene together with some ilmenite and maybe olivine arranged into dolerite or gabbrodolerite textures. Metamorphic minerals (three generation of amphiboles, albite, clinozoisite/epidote, and titanite) are products of multistage metamorphic alteration in p,T conditions not exceeding greenschist facies except a short period just after solidification, when some brown amphibole (edenite/pargasite) typical for amphibolite facies conditions was created (cf. Ivan, 2009). Chloritization, carbonatization and pyrite formation seem to be mostly products of hydrothermal alteration. Trace element distribution in metadolerites, especially enrichment in LREE and differentiated LREE/HREE enrichment (Fig. 5) points to generation from the enriched mantle source. Position of these rocks in relevant discrimination diagrams indicate the geochemical type close to E-MORB with affinity to alkaline oceanic island basalt (OIB) and also to CAB (Hf/3-Th-Ta diagram) what is typical for oceanic island tholeiites (OIT) maybe with some contamination of continental crust (Ta/Yb vs. Th/Yb diagram, Fig. 9C) or CT (3Tb-Th-2Ta diagram, Fig. 5D) respectively. Basic metavolcanics with identical geochemical signature are present in the Gelnica Group not only in the lateral continuation of studied metadolerite body in the Smolník deposit (Lastovičí vrch hill, Jedľovec hill, Zadné Porče valley) but they form a northerly located belt of individual occurrences between Vyšná Slaná and Helcmanovce villages (Ivan, 2009). All these metavolcanic rocks are geotectonically related to the inicial stage of within-plate extension and rifting which was followed by more intensive OIT-type volcanism (without signs of continental crust contamination) preserved in the Rakovec Group adjacent to the Gelnica Group from north and which finally led to the ocean opening in Late Devonian (Ivan, 2009; Ivan & Méres, 2012).

Two petrographic types of metamorphosed sediments are close spatially related to the chalcopyrite-pyrite stratiform Smolník deposit: *(i)* chlorite phyllites, and *(ii)* chlorite-sericite phyllites. Chlorite phyllites occur directly between individual pods of massive or impregnation types of ores. Studied samples were taken from the continual profile and their subdivision into two subgroups follows from their separation in profile by intercalation of chlorite-sericite phyllite. A bed of chlorite phyllite enriched in quartz is also a component of the profile (Fig. 3). Chlorite-sericite phyllites are divided into two subgroups as well, because the samples of one subgroup come from an intercalation between two metadolerite bodies, whereas samples of the second subgroup were taken from the bed in the chlorite phyllites mentioned above. Fundamental mineral composition and their variability of all types of studied phyllites are well reflected by diagrams based on atomic ratios as Fe+Mg/Al vs. Si/Al, K/Al vs. Si/Al or K/Al vs. Fe/Al (Fig. 6A,B). Chlorite phyllites display stable Fe/Al ratio what seems to be a result of the bonding of iron in Fe-chlorite but variable Si/Al ratio that is caused by variable content of quartz. Strong enrichment in Fe, as follows from the position in the Al-Fe-Mn ternary diagram (Fig. 6C), is probably a consequence of contribution from hydrothermal source (cf. Spry et al., 2000; Lode et al., 2016).

Trace elements as REE, Th or Sc are generally accepted as little fractionated during the weathering and sedimentary processes and can be used as sedimentary source material tracers (e.g., Taylor & McLennan, 1985; McLennan et al., 2003). In the case of domination of volcaniclastic source material also relatively immobile elements as Nb, Ta, Zr or Hf can be important for its further genetic characterization (e.g., Clift et al., 2005). Chondrite-normalized REE patterns of the both types of metamorphosed sediments (Fig. 7) remind of acid metavolcanics typical for the Gelnica Group. While chlorite-sericite phyllites form two well-defined subgroups different in La_n/Yb_n and Eu/Eu* ratios that reflect their different lithostratigraphic position, REE patterns of the chlorite phyllites show greater variability. Increasing La_n/Yb_n ratio with increase of Yb_n value in all types of studied rocks (Fig. 9A) excludes a variation in quartz content as the only cause. Normalization for PAAS indicates that all metamorphosed sediments from the Smolník deposit are variably enriched in LREE and variability in both directions is observable also for intensity of Eu-anomaly. Chlorite-sericite phyllites occurring in association with metadolerites are markedly enriched in MREE in comparison with PAAS, what could be interpreted as a mixing of the acid source material with calc-alkaline characteristics with material related to basalts generated from enriched mantle source (cf. Girty et al., 1993). Although some variable enrichment in MREE is observable also for other studied rocks, similar degree of such enrichment in the Gelnica Group has been found only in hematite phyllites (Fig. 8). Testing studied sedimentary rocks mainly in La-Th-Sc (Girty et al., 1993), Eu/Eu* vs. La_n/Yb_n and Th/Sc vs. La_n/Yb_n diagrams (Figs. 9D and 10A,B) indicate that besides the hydrothermal source for chlorite phyllites also three other sources of sedimentary material could participate in variable proportions on the formation of sedimentary host rocks in the Smolník deposit: *(i)* basalts generated from enriched mantle reservoir (the same as for metadolerites), *(ii)* less fractionated calc-alkaline volcanic rocks, and *(iii)* fractionated calc-alkaline rhyolites. Such interpretation, with respect mainly to the contribution of arc-related calc-alkaline volcanic material, is supported also by testing in diagrams Hf vs. La/Th (Floyd & Leveridge, 1987; Fig. 10C) and Ta/Yb vs. Th/Yb (Gorton & Schandl, 2000; Fig. 9C), where former one points to their active continental margin provenance. Although presence of any fraction of an argillaceous material connected with deep weathering of old crystalline rocks cannot be fully excluded, the preserved morphological attributes of volcaniclastic admixture in sediments make it rather improbable.

The formation of sulphide ores in the Smolník deposit is directly related to chlorite phyllites representing originally probably the beds of smectite-rich clay. Relic colloform, spherulitic or framboidal textures preserved mostly in the banded pyrite ores, euhedral pyrite crystals in impregnation ores, in all cases with inclusions of chlorite, sericite, quartz. Other sulphides (Kantor & Rybár, 1970) are also the indications of direct in situ precipitation from hydrothermal solutions (e.g., Wilkin & Barnes, 1997; Craig, 2001; Rickard, 2012). Precipitation was probably controlled by the reaction of hydrothermal solutions with hydrogen sulphide produced by the reduction of oceanic sulphate in the zone of oceanic water-solution mixing in the upper part of unconsolidated sediment. Such reaction mechanism is supposed based on sulphur isotopic composition in pyrite $\delta^{34}S$ = 10.1–16.3 ‰ (Kantor & Rybár, 1970). Two possible causes have been ascribed to the sulphate reduction within the Smolník deposit: *(i)* bacterial activity (Kantor & Rybár, 1970), or *(ii)* inorganic reduction (Grecula et al., 1993). Although occurrence of the framboidal pyrite is supposed to be related mostly with bacterial activity (Wacey et al., 2015), narrow $\delta^{34}S$ interval for disseminated and massive pyrite and the finding of colloform iron carbonate in association with pyrite indicate rather thermochemical sulphate reduction by carbonaceous compounds (cf. Machel, 2001), moreover a potential source of these compounds – sediments rich in organic matter – was a component of stratigraphic sequence.

Subvolcanic dolerite bodies served as the thermal source for hydrothermal system and together with related volcaniclastic material also as an important metal source (Fe, Cu) for ores. Rock-water interaction shortly after solidification is supported by the preserved relics of relatively high-temperature brown pargasitic amphibole in metadolerites. Close genetic relations to basaltic magmatic activity, position in sedimentary sequence, forms and mineral composition of ore bodies classify the Smolník chalcopyrite-pyrite deposit as Besshi-type (cf. Kase & Yamamoto, 1988; Dergatchev et al., 2011). Common occurrence of chlorite phyllites with metadolerite bodies seems to be the key attribute which could be necessary to take into account for the further prospection of this deposit type in the Gelnica Group.

7. CONCLUSIONS

Interpretation of corrected and completed geochemical data originally published by Ilavský & Bajaník (1981) combined with our original data and some new pieces of knowledge on the Gelnica Group led to these new findings:

• metadolerites from the stratiform chalcopyrite-pyrite deposit of Smolník are geochemically close to within-plate basalts (continental tholeiites) which occur also at the further localities of Gelnica Group and they are the products of extension related to rifting;

• source of sedimentary material for the host rocks of ore pods in the Smolník deposit is probably combination of following partial sources: *(i)* volcanogenic material with the same geochemical signature like metadolerites, *(ii)* calc-alkaline volcanogenic material originally generated in a continental arc, and *(iii)* hydrothermal precipitates as additional source for chlorite phyllites;

• chlorite phyllites were originally the environment, where sulphide ores were precipitated by the reaction of hydrothermal solutions with hydrogen sulphide produced by the thermochemical reduction of marine sulphate;

• the Smolník chalcopyrite-pyrite deposit can be classified as Besshi-type deposit.

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