

Geochemical properties of selected Paleozoic formations – bearers of stratiform mineralization in Veporicum and Tatricum

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Abstract. The investigation of selected formations in metallogenetic zones of Veporicum and Tatricum in the mountain ranges Slovenské rudohorie, Nízke Tatry, Malé Karpaty and Považský Inovec, was focussed on appraisal of their possible elevated metal content according to the suggestion of the project IGCP 254 definition “the black schists and metalliferous black schists” (sensu Huyck, 1991). The element contents in investigated rocks (complete chemical analysis of 16 major elements and 47 microelements) were normalized according to USGS standard SDO-1, according to the Geochemical atlas of Finland as well as the clark contents. The content of C_{org} , the bitumen type, origin and source of hydrocarbons, conditions of sedimentation, carbonification metamorphism, migration, etc. are presented. Besides known deposits and mineralizations in investigated formations, according to normalized values for standards and clarks and further criteria we indicated their possible metal content and perspective.

Key words: geochemistry, metalliferous black schists, organic matter, mineralization

Introduction

Presented work is focussed on metallogenetic zones of Veporicum and Tatricum (according to Ilavský and Sattran, 1980). It reviews the occurrences of ore and non-ore sedimentary mineralizations in particular formations, the influence of epigenetic mineralization processes connected with magmatic, volcanic and tectonic activity influencing the evolution of sedimentation as well as the later processes.

The main formations geochemical characteristics and information about anomalously increased contents compared to standards and clarks in the Earth crust are based on complete chemical analyses (16 main and 28–47 microelements).

The C_{org} content, its composition, the bitumen type, origin and source of hydrocarbons, sedimentation conditions, carbonification metamorphism, migration etc. are stated in studied formations. The metalliferous potential of uranium-bearing and copper-bearing formations was detected. Next there was investigated the ratio of K_2O/Na_2O , showing the degree of sediments maturity as well as the tuffitic admixture indicating the possible volcanosedimentary mineralization.

The evaluation of metalliferous capacity of sedimentary formations was done according to the suggestion of definition “black schists and metalliferous black schists” (sensu Huyck, 1991) in the frame of the project IGCP 254. The metalliferous sediments have contents of $C_{org} > 0.5\%$ (some samples did not reach this value) at twice or multiple enrichment by any of metals in comparison with standard (according to Vine & Tourtelot, 1970), for Be, Co, Mo and U already at the same level of enrichment. We used the well defined USGS standard SDO-1 (Devo-

nian metalliferous black schists of Appalachian basin), based on analyses results from 32 laboratories (including the laboratory of Geological Survey of Slovak Republic - ŠGÚDŠ). For normalization of some next elements the values by Belinda Arbogast and Joel Leventhal (letter from 29. 1. 1989, later published in Kane et al., 1990) and from Geochemical atlas of Finland (6. schists and crystalline schists FNB). The clark value of particular elements is from the Geochemical atlas of Slovak Republic - rocks (Marsina et al., 1995) and from work by Sláma et al. (1999), where it was used for characteristic of geochemical types of the file of various rocks and contrast sources.

The substantial part of samples was analysed in following laboratories: Geological Survey, national enterprise, Spišská Nová Ves and Turčianske Teplice, Geological Survey of Slovak Republic, Bratislava, UNIGEO, state enterprise, Ostrava, laboratories Brno, GEL Spišská Nová Ves, EL Ecological laboratories Ltd. Spišská Nová Ves, GÚ PriF UK Bratislava, GÚ SAV Bratislava, ÚÚG Brno, laboratories Stráž pod Ralskem and ěernošice. The samples of organic matter were analysed by Geological-chemical department, Moravské naftové doly Comp. Hodonín. [The following analytical methods were used: Atomic emission spectrometry with inductively coupled plasma (AES-ICP); Automatic mercury analyser (Hg-AAS); Flame atomic absorption spectrometry (F AAS); Gravimetric analyses (VA, GA); Ion selective electrode (ISE); Flameless atomic absorption spectrometry (AAS-ETA); Optical emission spectrometry (OES); Radiometric gamaspectrometry (RAD); Pyrolysis (PYR); Neutron activation analysis (INAA)]. The majority of used analyses was performed in Ecological laboratories Ltd. in Spišská Nová Ves.

Because of limited extent of this contribution we do not treat the results of the study of mutual relation of steady and weakly reacting elements (La, Th, Sc, Hf, Co, Rb, Ta, Yb), being demonstrated in diagrams and graphs (according to Pearce et al., 1984; Taylor and McLennan, 1985). The study of mutual relations aimed to reveal the source of volcanic and granitic clastic material in investigated sediments. The comprehensive results are accessible in the final report (Slavkay, 2003). This report from the Slovenské rudohorie Mts. characterizes parallelly with Veporicum also some Paleozoic to Triassic rocks and their metamorphic equivalents in next neighbouring tectonic units (Hronicum, Meliaticum, Turnaicum and Silicicum). The characteristic rock analyses in table form with corresponding recomputations and figures we display only from Veporicum of Slovenské rudohorie Mts. (besides main elements). From further areas they are stated preferably in works by Molák et al. (1993), Slavkay (2003) and further works cited in further text.

Veporicum

Slovenské rudohorie Mts.

Proterozoic? – Lower Paleozoic

From metamorphic rocks (protolith: prevailingly pelitic-psammitic sediments) the samples rich in carbon matter were investigated (the sample numbers are indicated in brackets). Two samples attacked by hydrothermal processes (Nos. 8 and 48) were taken. Further samples from macroscopically non-attacked rocks were used for finding of differences.

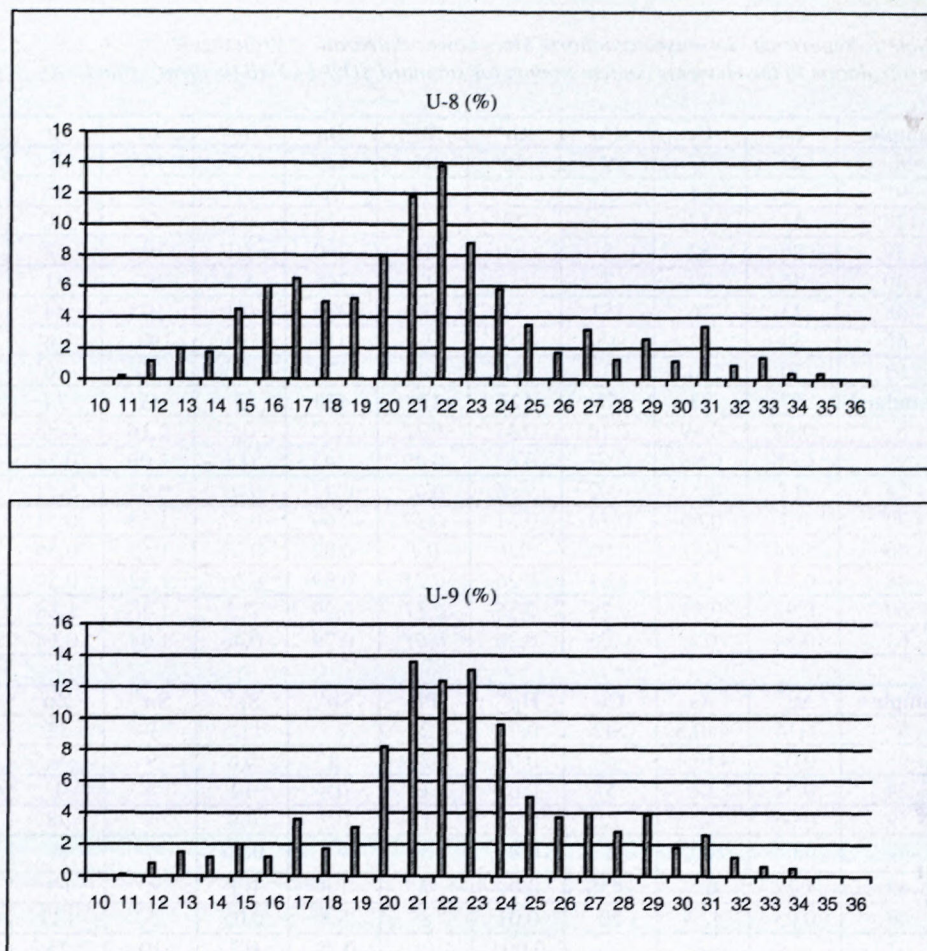
- Metaquartzite forming intercalations in chlorite-sericite schists of Sinec Complex from locality Hnúšťá-Mútnik (8) approximately 1.2 km to NE from the enterprise Talcum, near road to Polom.
- Schist with carbon matter from the Ostrá micaschist complex (9). Outcrop at forest road 1.2 km to NE from Talcum enterprise, app. 300 m to north from the road to Polom.
- Muscovite and graphite metaquartzites from the Ostrá micaschist complex (24). Outcrop 0.8 km to WNW from the Krížna poľana altitude point (1018 m), near forest hut.
- Black schist to phyllite (39). Sample from mining space of Cerberus occurrence (Mútnik, Balantky).
- Dark-grey schist from the Ostrá micaschist complex (40). Outcrop above forest road 350 m northward from the Cerberus occurrence (Mútnik, Balantky).
- Schist from paragneisses from Filier (48) altered by hydrothermal processes, bearing the fine-scattered pyrite-chalcopryrite sulphidic mineralization. Outcrop 750 m to NW of Filier, at junction of two small streams in altitude point 485 m.
- Quartzite paragneiss with graphite (60). Open pit in Kozlovo local part, 1.6 km to NW from the railway stop Rohozná,
- Graphitic gneiss from the micaschist of the Ostrá complex, trench RMT-1 at village Muránska Dlhá Lúka.

The normalizing of samples (8 and 48) altered by hydrothermal solutions using standards SDO-1 + FNB shows the multiple increase of element content: Co - 2.65; Cr - 2.16; V - 3.46 and 3.06; Ag - 59.63; As - 4.24; Cu - 7.32 and 33.19; Se - 38.33; Ni - 6.8. The differences between both rocks are in the content of Co, Cr, Ag, As, Se and Ni, which confirms diversity of their mineralization types (Tab. 1). The contents of Co and Ni above standard are caused by the presence of pentlandite in the Cerberus deposit. The vanadium is one of elements enriching the surrounding of supplying channels of hydrothermal solutions. The differences are visible also in behaviour of REE (Fig. 2). The increase of HREE contents in altered rocks can be explained by oxidation of mineralized zone, when the disintegration of sulphides has increased the acidity of environment where the LREE are unstable, easily transferred to solution and flushed away. At the same time the rocks were enriched by HREE, being stable in this environment. Besides above stated rocks, further ones of higher multiplication (24, 63) do not indicate any mineralization. According to 1/3 standard these are Co, B, Be, Hg, Pb and U. The manifold increase of As can be possibly assigned to original sedimentary mineralization.

The maturity of fine-grained sediments with C_{org} 1.74–3.76 % is demonstrated by the high K_2O/Na_2O ratio, besides the rocks with very low content of C_{org} (0.03 and 0.01) where samples 48 and 60 manifest the low ratio (1.60 and 0.8). All remaining rocks have higher content of C_{org} (1.74–3.76 %), but regarding the standard SDO-1 + FNB its part do not overreach 0.30. The evaluation of organic substance from samples 8 and 9 was presented by Slavkay and Širáňová (1993; in Molák et al., 1993). The content C_{org} in sample 8 is 2.9 %, in sample 9 it is 3.76 %, the average content is 3.38 %. In the carbon balance the same content was found in the case of C_{bit} (0.5 %), C_{hum} (0.7 %) and C_{resid} (98.8 %), which shows the substantial presence of metamorphosed component of organic substance - kerogene. When comparing with the standard SDO-1 + FNB the C_{org} ratio is low (0.28x and 0.37x). According to the component analysis (Tab. 3) the presence of oil, pitch and asphaltenic component is unbalanced. According to IR spectrometry and the ratio of absorption strips $1460/1735\text{ cm}^{-1}$ in samples, the absorbance of carbonyl strip prevails, so samples can be arranged among the remanent ones. According to the ratio of absorption strips $720/1610\text{ cm}^{-1}$ the bitumens have distinct preponderance of aliphatic component above aromatic, the bitumens are therefore of remnant sapropel type. According to distribution of hydrocarbons GC samples analyses (Fig. 1), the maxima C_{22} , C_{23} show the organic substance of marine provenance. According to the low bitumen content and not-fulfilling the condition $n-C_{15} > n-C_{17} > n-C_{19}$ the bitumens are not migrated. The ratio $pristan/phytan > 1$ expresses the oxidizing conditions during sedimentation.

Between Muránska Dlhá Lúka and Klenovec villages three main micaschist types with the intercalations of quartzite and schist with organic matter are spread (samples 9, 24, 40, 63): 1. garnet-chloritoid, 2. garnet-chlorite

Fig. 1. Abundance of *n*-alkanes in sample U-8 and U-9 in %.



and 3. garnet-biotite micaschist with plagioclase. The quartz and muscovite are present in the same amount, in the third type quartz is prevailing and plagioclase is more often. The pseudomorphoses of chloritoid with sericite, porphyroblasts of staurolite and garnet, accessory ilmenite, clinozoisite, zircon, apatite, tourmaline, magnetite, pyrrhotite and pyrite were found in these samples. They show the high content of Al_2O_3 (19.8–30.43 %), low SiO_2 (43.84–60.84 %), K_2O prevails above Na_2O in the ratio 2:1. In the majority of samples beneath the level of 1/3 of clark (Tab. 1a) remained Co, Sr, Zr, Cu, Hg, Pb, Zn, moderately increased are Ce, Y, Li, Sn and Ni (1.2–2.91x), triple to fivefold clark content is overreached by As, Sb and Se, but both elements in several samples reach even anomalous contents (6.38–1243.3 multiple).

The succession of muscovite-chlorite schists with metabasites, metacarbonates, graphite quartzites, metaconglomerates, metaarkoses and chlorite-sericite schists is variegated (Slavkay, 1996, in Sláma et al., 1999). The C_{org} content (1.19 %) represents 66.25-fold of clark, oxides are close to clark values, only MgO and MnO are lower and Fe_2O_3 , CaO and Na_2O are scarce. The SiO_2 content varies from 58.34 to 83.36 %, Al_2O_3 from 5.92 to 20.61 % and ratio $\text{K}_2\text{O}/\text{Na}_2\text{O}$ is very variable and highly in favour to K_2O . The higher than triple to quintuple of clark was registered in Sr, V, As, Cu, Sb, Se, Ni and U. The sample 8 is mineralized, but in sample 39 no

ore minerals were found. The scarce elements ($< 1/3$ multiple of clark) are Ba, Be, Sr, Zr, Hg, Pb and Zn.

Mineralization

We suppose, that during sedimentation of former rocks of pre-Hercynian age in oxidic environment of the basin also lepto-chlorite and hematite ores with organic matter have sedimented. During regional metamorphism (later possibly also contact metamorphism, Gubač, 1957) they were replaced to magnetite ore of the deposit Kokava nad Rimavicou, Hrabina and organic matter was changed to graphite. The deposit is formed by several lenses in the zone of migmatitized micaschist paragneisses in hybridic granitoids. As a protolith of ores Radvanec (2000) supposes the well sorted pelitic-psammitic sediments with content of organic substance and Fe carbonatic beds, bodies and veins, being metamorphosed at the boundary of lower crust in the field of normal geothermic gradient 25 °C/km. According to Kováčik (2000) the assemblage of magnetite-grunerite-garnet-biotite-quartz originated probable at temperature 600 °C in medium-pressure conditions. The presence of magnetite influences the high content of iron and more pelitic petrographic character (higher content of Al_2O_3 , K_2O), with higher content of Fe^{3+} (differing from quartz-grunerite types). The deposit represents the formation of metamorphic Fe ore of pre-Hercynian to Hercynian phase (Slavkay and Petro, 1993).

Table 1. Veporicum, Slovenské rudohorie Mts., Lower Paleozoic, ? Proterozoic
Recalculation of the elements content in ppm for standard SDO-1+FNB (content : standard)

Sample	La	Ce	Co	Rb ¹⁾	B ²⁾	Ba	Be ²⁾	Cr	Sr	V	Y	Zr	Li ²⁾
U - 8	23	37	9	46	16	139	0,9	145	26	554	32	57	0
U - 9	29	51	4	79	64	187	0,9	71	25	169	10	45	0
U - 24	11	17	1	20	4	176	0,2	58	8	575	10	28	2
U - 39	26	52	8	64	16	290	1,1	106	38	260	17	84	35
U - 40	46	98	3	113	13	345	1,7	102	41	146	49	101	22
U - 48	13	16	151	32	32	373	0,1	102	44	489	50	101	28
U - 60	34	62	15	70	14	416	0,9	97	139	147	28	193	42
U - 63	20	30	3	32	9	332	1,38	70	10	383	22,7	25	4
Standard	37	75	57	125	130	420	3	67	74	160	36	120	60
U - 8	0,62	0,49	0,16	0,37	0,12	0,33	0,3	2,16	0,35	3,46	0,89	0,48	0
U - 9	0,78	0,68	0,07	0,63	0,49	0,45	0,3	1,06	0,34	1,06	0,28	0,38	0
U - 24	0,3	0,23	0,02	0,16	0,03	0,42	0,07	0,87	0,11	3,59	0,28	0,23	0,03
U - 39	0,7	0,69	0,14	0,51	0,12	0,69	0,37	1,58	0,51	1,63	0,47	0,7	0,58
U - 40	1,24	1,31	0,05	0,9	0,1	0,82	0,57	1,52	0,55	0,91	1,36	0,84	0,37
U - 48	0,35	0,21	2,65	0,26	0,25	0,89	0,03	1,52	0,59	3,06	1,39	0,84	0,47
U - 60	0,92	0,83	0,26	0,56	0,11	0,99	0,3	1,45	1,88	0,92	0,78	1,61	0,7
U - 63	0,54	0,4	0,05	0,26	0,07	0,79	0,46	1,04	0,14	2,39	0,63	0,21	0,07

Sample	Ag ²⁾	As	Cu	Hg ¹⁾	Pb	Sb ¹⁾	Se ²⁾	Sn ²⁾	Zn	Ga	Ni	U	Th
U - 8	0,14	440,5	542	0,01	2	7,1	11,5	9	12	9	85	7,4	4
U - 9	0,02	446,4	5	0,01	2	5	0,6	9	9	12	18	2,4	3
U - 24	0,02	1,6	5	0,01	1	0,4	0,1	4	1	4	24	1	2
U - 39	0,06	232,6	72	0,02	1	0,7	0,4	5	28	15	79	3	6
U - 40	0,08	1865	8	0,01	3	6,2	0,05	5	6	23	47	5	11
U - 48	4,77	0,5	2456	0,01	7	1,8	0,1	4	63	11	871	13	10
U - 60	0,05	32,4	20	0,01	8	5,8	0,05	5	133	19	62	0,5	6
U - 63	-	7	7	0,001	2	0,13	0,2	10	25	5	57	2	2
Standard	0,08	104	74	0,15	32	4	0,3	5	76	20	128	56	10
U - 8	1,75	4,24	7,32	0,07	0,06	1,78	38,33	1,8	0,16	0,45	0,66	0,13	0,4
U - 9	0,25	4,29	0,07	0,07	0,06	1,25	2	1,8	0,12	0,6	0,14	0,04	0,3
U - 24	0,25	0,02	0,07	0,07	0,03	0,10	0,33	0,8	0,01	0,2	0,19	0,02	0,2
U - 39	0,75	2,24	0,97	0,13	0,03	0,18	1,33	1	0,37	0,75	0,62	0,05	0,6
U - 40	1	17,93	0,11	0,07	0,09	1,55	0,17	1	0,08	1,15	0,37	0,09	1,1
U - 48	59,63	0,01	33,19	0,07	0,22	0,45	0,33	0,8	0,83	0,55	6,8	0,23	1
U - 60	0,63	0,31	0,27	0,07	0,25	1,45	0,17	1	1,75	0,95	0,48	0,01	0,6
U - 63	-	0,07	0,09	0,007	0,06	0,03	0,67	2	0,33	0,25	0,45	0,04	0,2

0.XX < 1/3 of standard; X.XX > double of the standard value; ¹⁾ – according to Belinda Arbogast, 29. 1. 1989; ²⁾ according to Geochemical atlas of Finland, column 6. schists

The pyrite-chalcopryrite ore of occurrence Revúca, Dolinský potok, has volcanosedimentary origin with regional metamorphic overprint in Lower Paleozoic. The mineralization is located at the contact of garnet micaschists of Ostrá complex with hybridic granitoids and migmatites. The minerals pyrite, marcasite, tetrahedrite and ankerite are related to younger remobilization. In occurrence Ratkovské Bystré, Filier in surrounding rocks with graphite the mineralization (quartz, pyrite, pyrrhotite, chalcopryrite) is developed in gneiss at the contact of migmatite with granite. Formerly it originated in anoxic environment of pre-Hercynian to Hercynian phase and belongs to formation of metamorphic pyrite ore (Slavkay and Petro, 1993).

The graphite in the occurrence Muránska Dlhá Lúka, Krížna Poľana forms larger concentrations with crystalline flakes disseminated in metaquartzite (about 3.5 %

C_{org}) and in intercalations of metabasite in garnet micaschists of the Ostrá complex. The graphite is of excellent quality and very well flotative (Očenáš, 1992). The graphite mineralization was found also in deposit Kokava nad Rimavicou, Zahrabina in the zone of biotite-albite paragneiss with quartzite bodies in hybridic granitoid with transitions to migmatite (Petro in Petro et al., 1998). The graphite originated by overheating of rocks rich in organic matter with following, most probable Hercynian regional metamorphic overprint (Radvanec, 2000; Kováčik, 2000). The gneisses with high graphite crystallinity occur in assemblage with high-iron gneisses (Pulec, 1989), which documents metamorphic conditions of amphibolite facies. Crystalline graphite is present also in occurrence Brezno, Kozlovo, in hybridic granitoid. The occurrences are enlisted to metamorphic deposits as products of regional (Hercynian resp. even pre-Hercynian) meta-

Table 1a. Veporicum, Slovenské rudohorie Mts., Lower Paleozoic, ? Proterozoic
Recalculation of the elements content in ppm for clark content in the Earth crust (content : clark)

Sample	La	Ce	Co	Rb	B	Ba	Be	Cr	Sr	V	Y	Zr	Li
U - 8	23	37	9	46	16	139	0,9	145	26	554	32	57	0
U - 9	29	51	4	79	64	187	0,9	71	25	169	10	45	0
U - 24	11	17	1	20	4	176	0,2	58	8	575	10	28	2
U - 39	26	52	8	64	16	290	1,1	106	38	260	17	84	35
U - 40	46	98	3	113	13	345	1,7	102	41	146	49	101	22
U - 48	13	16	151	32	32	373	0,1	102	44	489	50	101	28
U - 60	34	62	15	70	14	416	0,9	97	139	147	28	193	42
U - 63	20	30	3	32	9	332	1,38	70	10	383	22,7	25	4
Clark	30	64	10	112	15	550	3	35	350	60	22	190	20
U - 8	0,77	0,58	0,9	0,41	1,07	0,25	0,3	4,14	0,7	9,23	1,46	0,3	0
U - 9	0,97	0,8	0,4	0,71	1,27	0,34	0,3	2,03	0,7	2,82	0,46	0,24	0
U - 24	0,37	0,27	0,1	0,18	0,27	0,32	0,07	1,66	0,02	9,58	0,46	0,15	0,1
U - 39	0,87	0,81	0,8	0,57	1,07	0,53	0,37	3,03	0,11	4,33	0,77	0,44	1,75
U - 40	1,53	1,53	0,3	1,01	0,87	0,63	0,57	2,91	0,12	2,43	2,23	0,53	1,1
U - 48	0,43	0,25	15,1	0,29	2,13	0,68	0,03	2,91	0,13	8,15	2,27	0,53	1,4
U - 60	1,13	0,97	1,5	0,63	0,93	0,76	0,3	2,77	0,4	2,45	1,27	1,02	2,1
U - 63	0,67	0,47	0,3	0,29	0,6	0,6	0,46	2	0,03	6,38	1,03	0,13	0,2

Sample	Ag	As	Cu	Hg	Pb	Sb	Se	Sn	Zn	Ga	Ni	U	Th
U - 8	0,14	440,5	542	0,01	2	7,1	11,5	9	12	9	85	7,4	4
U - 9	0,02	446,4	5	0,01	2	5	0,6	9	9	12	18	2,4	3
U - 24	0,02	1,6	5	0,01	1	0,4	0,1	4	1	4	24	1	2
U - 39	0,06	232,6	72	0,02	1	0,7	0,4	5	28	15	79	3	6
U - 40	0,08	1865	8	0,01	3	6,2	0,05	5	6	23	47	5	11
U - 48	4,77	0,5	2456	0,01	7	1,8	0,1	4	63	11	871	13	10
U - 60	0,05	32,4	20	0,01	8	5,8	0,05	5	133	19	62	0,5	6
U - 63	-	7	7	0,001	2	0,13	0,2	10	25	5	57	2	2
Clark	0,05	1,5	25	0,09	20	0,2	0,05	5,5	71	17	20	2,3	8,1
U - 8	2,8	293,67	21,68	0,11	0,1	35,5	230	1,64	0,17	0,53	4,25	3,22	0,49
U - 9	0,4	297,6	0,2	0,11	0,1	25	12	1,64	0,13	0,71	0,9	1,04	0,37
U - 24	0,4	1,07	0,2	0,11	0,05	2	2	0,73	0,01	0,24	1,2	0,44	0,25
U - 39	1,2	155,07	2,88	0,22	0,05	3,5	8	0,91	0,39	0,88	3,95	1,3	0,74
U - 40	1,6	1243,3	0,32	0,11	0,15	31	1	0,91	0,09	1,35	2,35	2,17	1,36
U - 48	95,4	0,33	98,24	0,11	0,35	9	2	0,73	0,89	0,65	43,55	5,65	1,23
U - 60	1	21,6	0,8	0,11	0,4	29	1	0,91	1,87	1,12	3,1	0,22	0,74
U - 63	-	4,67	0,28	0,01	0,1	0,65	4	1,82	0,35	0,29	2,85	0,87	0,25

0.XX content beneath 1/3 of clark value; X.XX – content above triple of clark value; **X.XX** – content above quintuple of clark value.

morphism of rocks richer in organic matter, originating formerly in highly anoxic, Lower Paleozoic (? Proterozoic) environment.

The results of investigation and survey of carbonatic bodies in sedimentary rocks were summed up by Abonyi and Abonyiová (1980) and others. The limestones were suitable environment for later circulation of solutions and origin of magnesite and talc. The talc mineralization in deposit Hnúšťa, Mútnik (Kužvart, 1955; Lisý, 1971; Vitásek, 1988, 1990; Németh et al., 2004) bounds to intergranular spaces, joints and margins of magnesite bodies of quartz type in biotite-garnet micaschist of the Ostrá complex and muscovite-chlorite schist with metabasites of the Sinec complex. The main minerals are accompanied with dolomite, minerals of illite group, Mg and Mg, Fe chlorites. The sulphidic mineralization originated during younger mineralization processes (Trdlička, 1961). In veins of brown-red dolomite penetrating the

magnesite-talc body the sulphidic mineralization with disseminated uraninite was found (Varček, 1977), which explains also the multiple increase of the value of clark uranium content (Tab. 1a). Similar mineralization is developed in neighbouring occurrence Hnúšťa, Polom though with much weaker talc mineralization. Next deposits are Kokava baňa, Borovana, Sinec and Hnúšťa-Samobane (Suchár, 1974). In all these deposits the talc bodies are developed in the zone of sericite-chlorite schist with carbonate intercalations, being located at the contact with the biotite paragneiss of Klenovec complex (Slavkay and Lenárt, 1974). The talc in occurrence Muránska Dlhá Lúka forms the reaction rim of the serpentinite body in garnet micaschist of the Ostrá complex, which was caused by the metamorphic-recrystallization processes and hydrothermal activity.

Talc originated probable by reacting of hydrothermal solutions with limestone in Middle to Upper Cretaceous.

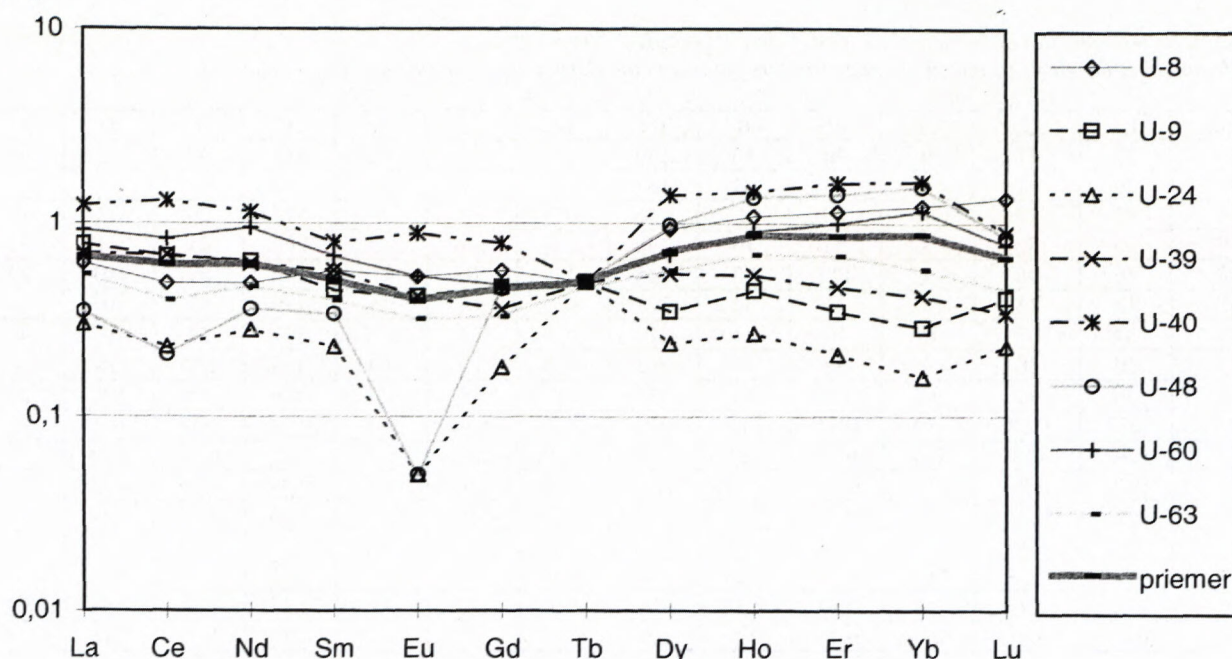


Fig. 2. Normalized REE values according to standard SDO-1. Slovenské rudohorie Mts., Veporicum, Lower Paleozoic - ? Proterozoic.

In the first phase there originated dolomite and magnesite, and in the second phase talc and next accompanying minerals from the solutions rich in SiO_2 , at the expense of a part of magnesite. The process is associated with the Alpine metallogenic phase and mineralization into magnesite-talc association of siderite formation (Slavkay in Slavkay et al., 2004).

The asbestos occurs in bodies of serpentinized ultrabasics in biotite paragneiss of the Klenovec complex. In the occurrence Uhorské the smaller bodies of antigoritic serpentinite are developed at the margin with carbonate-talc rim and fibroidal actinolite, less often chrysotile asbestos, similarly as in the deposit Muránska Dlhá Lúka (Hovorka, 1985). From the central part of the body the antigorite, actinolite and chlorite zone are developed, being a product of metasomatism of ultrabasic rock with surrounding rocks and fluids. This territory is perspective for similar raw-material types (Slavkay et al., 1997).

Nízke Tatry Mts.

Jánov grúň Formation (Devonian – Lower Carboniferous)

The formation is built with metasandstone, metagreywacke, metarhyodacite, metadacite and their volcanoclastics, less often are the products of basic volcanism altered to green schist and phyllite with admixture of organic matter ($C < 0.13\%$), ilmenite and tourmaline. The protolith of these rocks would be the clayey sediments with hydromicas. The metasandstone with the higher amount of quartz contains muscovite - phengite, biotite, chlorite, paragonite, K-feldspar, albite, carbonate, ilmenite and tourmaline. Rocks were metamorphosed in the middle part of the greenschist facies during Hercynian orogeny (Miko and Pulec in Molák et al., 1993; the cited work contains the complete rock analyses of stated samples and their description).

The Al_2O_3 content in phyllite varies in the range 20.67–23.12 %. The Fe and MnO contents are higher. The As, Ba and Ni have moderately increased contents comparing the clark composition. The metasandstone has increased SiO_2 and lowered TiO_2 , Al_2O_3 , MgO and K_2O . The fine-grained compact metapelite (ČB-22b) with black tourmaline has less SiO_2 , more Al_2O_3 and K_2O (abundant sericite) and significantly higher content Ba, Ce, Cs, F, Hg, La, Rb, Sn, Sr, Y and more elements of REE. Miko and Pulec, l. c., attribute this composition to influence of granite porphyries during intrusion into the rocks of this formation.

The organic matter with increased C_{org} and lower C_{bit} from the samples ČB-1 (phyllite), ČB-10 (metasandstone) from the lower part and ČB-22b (black metapelite) from the upper part of the formation was reviewed by Širáňová (in Molák et al., 1993). According to component analysis they represent the light hydrocarbons with oil component average in 87.7 %. According to IR spectrometry and the ratio of absorption strips $1460/1735\text{ cm}^{-1}$, samples ČB-1 and ČB-10 belong to remnant type (with prevailing absorbance of carbonyl strip). In sample ČB-22b the intensity of strips is comparable (comparable content of aliphatic and aromatic groups). Based on ratio of absorption strips $720/1610\text{ cm}^{-1}$ of samples ČB-1 and ČB-10 they represent the sapropel-humus type and sample ČB-22b (aliphatic component < aromatic component) represents the humus type of remnant bitumens. The distribution of hydrocarbons (GC analysis) in sample ČB-1 (max. C_{22} , C_{25}) shows mixed source of hydrocarbons of marine and terrigenous origins; in sample ČB-10 (max. C_{22}) the marine source of the hydrocarbons origin and in sample ČB-22b (max. C_{31}) the terrigenous source of hydrocarbons. According to distribution of n-alkanes they do not represent the migrated hydrocarbons. The values prist- $\text{phytan} < 1$ show reduction conditions.

Mineralization

It is supposed, that in sedimentary space and in oxidic environment the syngenetic iron ore originated in stratiform position with surrounding Paleozoic rocks. This ore was during Hercynian regional metamorphism replaced to magnetite iron ore in irregular comformable ore bodies, located in Bacúch - Biela skala locality in garnet-muscovite-biotite paragneiss, in localities Bacúch - Javorinka and Babiná in the strip of sericite-chlorite phyllites (Devonian - Lower Carboniferous). The ore contains also quartz, hematite, pyrite, pyrrhotite, chalcopyrite and sphalerite.

Further product of regional metamorphism is represented by pyrrhotite ore in deposit Heľpa. Originally it consisted from vulcanosedimentary pyrite mineralization (Precambrian?-Paleozoic) deposited in reduction environment of the basin. The ore bodies (pyrrhotite, pyrite, less ilmenite, chalcopyrite, sphalerite, calcite), conformable with schistosity, are present in paragneiss with intercalations of schist, phyllite, amphibolite, metarhyolite (away of the Jánov grúň Formation). Similar occurrences from the economic viewpoint are not interesting.

The more important anomalies in Veporic part of the Nízke Tatry Mts. were formed by younger mineralization processes preferably by ores of siderite formation. This group includes for example the occurrence Beňuš, Leňušská dolina valley (Fe-Cu ore) with quartz, ankerite, calcite, pyrite, pyrrhotite and chalcopyrite mineralization, disseminated in large area in Beňuš paragneisses. The quartz-siderite vein with chalcopyrite and pyrite in occurrence Jánov grúň - Adamov is developed in chlorite-sericite phyllite and in occurrence Sokolia dolina valley (Fe-Cu-Pb) the mineralization penetrates Mesozoic rocks (compare Slavkay et al., 1988; Slavkay, et al., 1994, Grečula et al., 1996).

Slovenské rudohorie Mts.

Slatviná Formation (Upper Carboniferous)

The complete analyses of characteristic samples of sedimentary rocks of psammitic-pelitic character (Tabs. 2 and 2a) are from various localities of the Slovenské rudohorie Mts. of following macroscopically moderately different types:

- Black schist (31) intercalation in fine-grained sandstone from the outcrop in the right slope of the road above railway station Slavošovce in direction to Čierna Lehota.
- Dark-grey sandy schist (32) in fine- to medium-grained sandstone from outcrop behind the waste dump of Slavošovce paper-factory, approximately 400 m west of gipsy settlement.
- Dark-grey strongly micaceous sandy schist (37) from outcrop in the forest road cut app. 1.5 km to NNE of village Rimavská Baňa, Klingové local part.
- Dark-grey brownish micaceous phyllite (38) from the outcrop in the road cut behind the public transport stop Hnúšť'a - Likier,

- Dark-grey phyllitic schist in sandstone (41) from the outcrop at gamekeeper's house Podlaz (Mokra Lúka) app. 250 m to W from the road from under the mine dump Lubeník.

- Dark-grey graphitic phyllite sericitized and disintegrated (44) from the forest road cut (behind the stream) app. 1 km to N of Turčok. Sample (45) is from the forest road cut app. 0.9 km to N of Turčok.

- Dark-grey graphitic phyllite (43) from the left slope of Uhliarska dolina valley app. 1 km to N of Turčok.

- Graphitic phyllite (54) from the cut of the left bank of the Blh stream app. 300 m to SE from Ratkovská Zdychava.

- Graphitic phyllite (55) from the cut of the road from Vyšná Burda to Krokava, abrupt turn of the road, 2.3 km to SSE from Krokava.

Relative large variability of the K_2O/Na_2O contents ratios (in two samples 0.36 and 0.65; in three samples 2.25–8.05, in five samples 1.03–1.67) indicates the tuffitic admixture. Oxides after normalization to standard SDO-1 + FNB (Tab. 2) prevailing fluctuate around its value. The double overreaching of its value was registered by MgO , MnO and Na_2O and deep beneath 1/3 are the contents of C_{org} (0.01–0.92 %). Co, B, As, Hg, Pb, Sb, Se and U have lower values than its 1/3, other elements vary tightly around the standard value. More than double values of Ag, Pb and Zn in sample 43 can be attributed to influence of hydrothermal processes, causing mineralization of the occurrences Turčok, Lipová dolina valley and Mokrú Lúka, Trešková. The REE in rocks, normalized according to SDO-1, do not show large variability and do not reach the standard values (Fig. 3). The schists of the Slatviná Fm. as a whole do not show metalliferous characteristics, so there is not expected the syngenetic sedimentary mineralization.

Vozárová (in Molák et al., 1993) supposes about this formation, that it represents the sequence of alluvial fans of small delta into the shallow water sedimentary basin. In calm poorly oxidized parts near continent the clay, organic matter and plant detritus were deposited in shallow water anoxic environment. The rocks have suffered the Alpine regional metamorphism in the greenschist facies.

Our geochemical study included also metasandstone, metaschist and phyllite (originally greywacke, sandstone, claystone), alternating in small cycles in the frame of two cycles of higher order (Vozárová and Vozár, 1988). The average modal composition from 6 analyses (in %): quartz 56; feldspars 4.5; biotite 7.5; muscovite 16.5; chlorite 10; epidote-zoisite 3; garnet 0.5, hydrothermal minerals 2. At the contact with granite the ratios of garnet, biotite and locally cordierite are increasing. Phyllites with intercalations of black schists are formed with following regional metamorphic minerals: quartz, muscovite, chlorite \pm albite + graphite. They contain the grains of ilmenite, leucosene, needles of tourmaline and rutile (Vozárová in Slavkay et al., 1995). In the places of contact metamorphism they have character of hornfels.

Oxides in clastic sediments have contents close to clark values, CaO is scarce. The ratio of average contents

Table 2. Veporicum, Slovenské rudohorie Mts., Slatviná Formation, Upper Carboniferous
Recalculation of the elements content in ppm for standard SDO-1+FNB (content : standard)

Sample	La	Ce	Co	Rb ¹⁾	B ²⁾	Ba	Be ²⁾	Cr	Sr	V	Y	Zr	Li ²⁾
U - 31	27	48	5	107	495	439	3.2	85	40	97	27	211	36
U - 32	19	38	15	51	22	447	1.1	94	161	121	17	179	34
U - 37	18	35	19	121	57	560	1.9	99	73	140	16	152	54
U - 38	28	54	16	62	23	419	1.2	102	148	147	26	138	41
U - 41	17	37	21	113	35	837	1.8	75	71	107	19	177	38
U - 43	32	60	10	93	42	831	1.5	105	70	144	26	162	41
U - 44	29	57	21	96	40	479	1.8	112	67	141	30	156	40
U - 45	30	61	15	98	62	513	1.3	106	62	147	28	171	42
U - 54	33	70	14	89	37	721	1.3	99	83	132	33	233	47
U - 55	20	37	8	64	20	538	1.4	96	76	135	21	147	38
Standard	37	75	57	125	130	420	3	67	74	160	36	120	60
U - 31	0.73	0.64	0.09	0.86	3.81	1.05	1.1	1.27	0.54	0.61	0.75	1.76	0.6
U - 32	0.51	0.51	0.26	0.41	0.17	1.06	0.4	1.4	2.18	0.76	0.47	1.49	0.57
U - 37	0.49	0.47	0.33	0.97	0.44	1.33	0.6	1.48	0.99	0.88	0.44	1.27	0.9
U - 38	0.76	0.72	0.28	0.5	0.18	1	0.4	1.52	2	0.92	0.72	1.15	0.68
U - 41	0.46	0.49	0.37	0.9	0.27	1.99	0.6	1.12	0.96	0.67	0.53	1.48	0.63
U - 43	0.86	0.8	0.18	0.74	0.32	1.98	0.5	1.57	0.95	0.9	0.72	1.35	0.68
U - 44	0.78	0.76	0.37	0.77	0.31	1.14	0.6	1.67	0.91	0.88	0.83	1.3	0.67
U - 45	0.81	0.81	0.26	0.78	0.48	1.22	0.4	1.58	0.84	0.92	0.78	1.43	0.7
U - 54	0.89	0.93	0.25	0.71	0.28	1.72	0.4	1.48	1.12	0.83	0.92	1.94	0.78
U - 55	0.54	0.49	0.14	0.51	0.15	1.28	0.5	1.43	1.03	0.84	0.58	1.23	0.63

Sample	Ag ²⁾	As	Cu	Hg ¹⁾	Pb	Sb ¹⁾	Se ²⁾	Sn ²⁾	Zn	Ga	Ni	U	Th
U - 31	0.08	14.5	17	0.03	3	1.7	0.05	4	22	22	233	12	10
U - 32	0.02	29.3	59	0.03	2	0.7	0.05	4	106	18	40	5	3
U - 37	0.08	1.1	58	0.01	1	0.4	0.05	6	97	22	55	1	4
U - 38	0.08	11.7	36	0.01	4	0.5	0.05	5	127	21	53	1	3
U - 41	0.15	1.7	89	0.01	6	0.8	0.05	7	73	20	52	2	3
U - 43	0.19	2.2	43	0.14	515	0.3	0.05	5	251	20	24	1	4
U - 44	0.05	56.3	41	0.01	1	0.3	0.05	4	37	19	78	0.5	4
U - 45	0.2	27.4	55	0.01	4	0.4	0.40	5	83	21	34	2	4
U - 54	0.02	34	56	0.01	4	0.6	0.05	4	64	20	38	2	6
U - 55	0.02	24.4	46	0.01	5	0.5	0.05	5	82	19	30	1	3
Standard	0.08	104	74	0.15	32	4	0.3	5	76	20	128	56	10
U - 31	1	0.1	0.23	0.2	0.09	0.4	0.17	0.8	0.29	1.1	1.82	0.21	1
U - 32	0.25	0.3	0.8	0.2	0.06	0.18	0.17	0.8	1.39	0.9	0.31	0.09	0.3
U - 37	1	0.01	0.78	0.07	0.03	0.1	0.17	1.2	1.28	1.1	0.43	0.02	0.4
U - 38	1	0.1	0.49	0.07	0.13	0.13	0.17	1	1.67	1.05	0.41	0.02	0.3
U - 41	1.88	0.02	1.20	0.07	0.19	0.2	0.17	1.4	0.96	1	0.41	0.04	0.3
U - 43	2.38	0.02	0.58	0.93	16.09	0.08	0.17	1	3.3	1	0.19	0.02	0.4
U - 44	0.63	0.5	0.55	0.07	0.03	0.08	0.17	0.8	0.49	0.95	0.61	0.01	0.4
U - 45	2.5	0.3	0.74	0.07	0.13	0.1	1.33	1	1.09	1.05	0.27	0.04	0.4
U - 54	0.25	0.3	0.76	0.07	0.13	0.15	0.17	0.8	0.84	1	0.3	0.04	0.6
U - 55	0.25	0.2	0.62	0.07	0.16	0.13	0.17	1	1.08	0.95	0.23	0.02	0.3

0.XX < 1/3 of standard; X.XX > double and multiple of the standard value; ¹⁾ – according to Belinda Arbogast, 29. 1. 1989;

²⁾ according to Geochemical atlas of Finland, column 6. schists

K₂O:Na₂O varies from 1:3 through 1:1 up to 4:1. From the trace elements (Tab. 2a) in majority of samples As (7.8–37.53) more than five times overreaches the clark content, in some samples three to five-times this content is overreached by B, Cr, Ag, Cu, Sb, Se and Ni, scarce elements are Sr and Hg of less than 1/3 of clarks. All other elements vary between 1/3 and double clark values. The increase of Ag, Pb and Zn values in sample 43 shows the influence of hydrothermal processes. The higher value of B, As, Sb, Ni and U in the sample 31 is interesting and relates the schist intercalation in sandstone, tectonically

wedged in granitic rocks, in area with occurrences of Fe and polymetallic mineralization in the range of influence of Rochovce granite.

Mineralization

The rocks of Slatviná Formation contain low elements concentrations, which do not overreach the double values of SDO-1+FNB standard and triple value of clarks. The higher contents of As, Sb and Zn are caused by ingress of epigenetic solutions bringing these elements and forming

Table 2a. Veporicum, Slovenské rudohorie Mts., Slatviná Formation, Upper Carboniferous
Recalculation of the elements content in ppm for clark content in the Earth crust (content : clark)

Sample	La	Ce	Co	Rb	B	Ba	Be	Cr	Sr	V	Y	Zr	Li
U - 31	27	48	5	107	495	439	3.2	85	40	97	27	211	36
U - 32	19	38	15	51	22	447	1,1	94	161	121	17	179	34
U - 37	18	35	19	121	57	560	1,9	99	73	140	16	152	54
U - 38	28	54	16	62	23	419	1,2	102	148	147	26	138	41
U - 41	17	37	21	113	35	837	1,8	75	71	107	19	177	38
U - 43	32	60	10	93	42	831	1,5	105	70	144	26	162	41
U - 44	29	57	21	96	40	479	1,8	112	67	141	30	156	40
U - 45	30	61	15	98	62	513	1,3	106	62	147	28	171	42
U - 54	33	70	14	89	37	721	1,3	99	83	132	33	233	47
U - 55	20	37	8	64	20	538	1,4	96	76	135	21	147	38
Clark	30	64	10	112	15	550	3	35	350	60	22	190	20
U - 31	0,9	0,75	0,5	0,96	33	0,8	1,07	2,43	0,11	1,62	1,23	1,11	1,8
U - 32	0,63	0,59	1,5	0,46	1,47	0,81	0,37	2,69	0,46	2,02	0,77	0,94	1,7
U - 37	0,6	0,55	1,9	1,08	3,8	1,02	0,63	2,83	0,21	2,33	0,73	0,8	2,7
U - 38	0,93	0,84	1,6	0,55	1,53	0,76	0,4	2,91	0,42	2,45	1,18	0,73	2,05
U - 41	0,57	0,58	2,1	1,01	2,33	1,52	0,6	2,14	0,20	1,78	0,86	0,93	1,9
U - 43	1,07	0,94	1	0,83	2,8	1,51	0,5	3	0,20	2,40	1,18	0,85	2,05
U - 44	0,97	0,89	2,1	0,86	2,67	0,87	0,6	3,2	0,19	2,35	1,36	0,82	2
U - 45	1	0,95	1,5	0,88	4,13	0,93	0,43	3,03	0,18	2,45	1,27	0,9	2,1
U - 54	1,1	1,09	1,4	0,79	2,47	1,31	0,43	2,83	0,24	2,2	1,5	1,23	2,35
U - 55	0,67	0,58	0,8	0,57	1,33	0,98	0,47	2,74	0,22	2,25	0,95	0,77	1,9

Sample	Ag	As	Cu	Hg	Pb	Sb	Se	Sn	Zn	Ga	Ni	U	Th
U - 31	0,08	14,5	17	0,03	3	1,7	0,05	4	22	22	233	12	10
U - 32	0,02	29,3	59	0,03	2	0,7	0,05	4	106	18	40	5	3
U - 37	0,08	1,1	58	0,01	1	0,4	0,05	6	97	22	55	1	4
U - 38	0,08	11,7	36	0,01	4	0,5	0,05	5	127	21	53	1	3
U - 41	0,15	1,7	89	0,01	6	0,8	0,05	7	73	20	52	2	3
U - 43	0,19	2,2	43	0,14	515	0,3	0,05	5	251	20	24	1	4
U - 44	0,05	56,3	41	0,01	1	0,3	0,05	4	37	19	78	0,5	4
U - 45	0,2	27,4	55	0,01	4	0,4	0,40	5	83	21	34	2	4
U - 54	0,02	34	56	0,01	4	0,6	0,05	4	64	20	38	2	6
U - 55	0,02	24,4	46	0,01	5	0,5	0,05	5	82	19	30	1	3
Clark	0,05	1,5	25	0,09	20	0,2	0,05	5,5	71	17	20	2,3	8,1
U - 31	1,6	9,67	0,68	0,33	0,15	8,5	1	0,73	0,31	1,29	11,65	5,22	1,23
U - 32	0,4	19,53	2,36	0,33	0,1	3,5	1	0,73	1,49	1,06	2	2,17	0,37
U - 37	1,6	0,73	2,32	0,11	0,05	2	1	1,09	1,37	1,29	2,75	0,43	0,49
U - 38	1,6	7,80	1,44	0,11	0,2	2,5	1	0,91	1,79	1,24	2,65	0,43	0,37
U - 41	3	1,13	3,56	0,11	0,3	4	1	1,27	1,03	1,18	2,60	0,87	0,37
U - 43	3,8	1,47	1,72	1,56	25,75	1,5	1	0,91	3,54	1,18	1,20	0,43	0,49
U - 44	1	37,53	1,64	0,11	0,05	1,5	1	0,73	0,52	1,12	3,9	0,22	0,49
U - 45	4	18,27	2,2	0,11	0,2	2	8	0,91	1,17	1,24	1,7	0,87	0,49
U - 54	0,4	22,67	2,24	0,11	0,2	3	1	0,73	0,9	1,18	1,9	0,87	0,74
U - 55	0,4	16,27	1,84	0,11	0,25	2,5	1	0,91	1,15	1,12	1,5	0,43	0,37

0.XX content beneath 1/3 of clark value; **X.XX** – content above triple of clark value; **X.XX** – content above quintuple of clark value.

also bigger accumulations, e.g. Fe and Cu ore occurrence Cinobaňa - Jarčanisko (quartz, siderite, pyrite, tetrahedrite, accessoric jamesonite); occurrence of Sb and Au ore Ozdín-Cerina (antimonite, pyrrhotite, pyrite, arsenopyrite, gold, less tetrahedrite, chalcopryite, magnetite, galenite, sphalerite, accessoric berthierite, jamesonite, ullmannite a.o.); occurrence of Sb ore Chyžné - Kubej (quartz, berthierite, antimonite, less carbonates, pyrite, arsenopyrite, pyrrhotite, sphalerite, marcasite, chalcopryite, secondary antimonite ochres and limonite). The isotopic composition of sulphur from pyrrhotite

is close to meteoric standard $\delta^{34}\text{S} = -1.3\text{‰}$, it was enriched with isotope ^{32}S (Kantor and Ďurkovičová, 1977), which confirms its hydrothermal origin; occurrence of Cu ore Kopráš-Slnná (chalcopryite, pyrrhotite, pyrite, arsenopyrite, marcasite, sphalerite, actinolite, secondary covellite, limonite and malachite. In Slatviná Formation we do not suppose the possibility of finding the larger bodies of syngenetic sedimentary ore, but they are suitable environment for bigger accumulation of epigenetic ore (compare Slavkay et al., 1995, 1997, 2004).

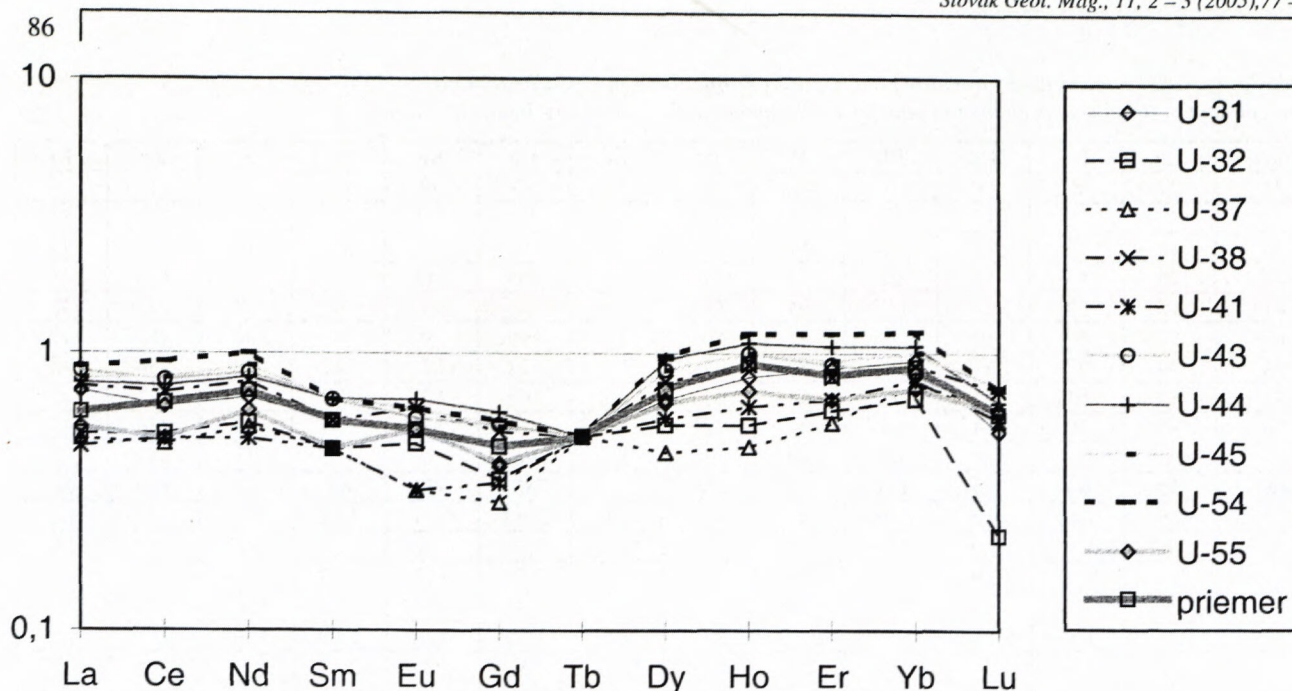


Fig. 3. Normalized REE values according to standard SDO-1. Veporicum, Slatviná Formation, Carboniferous.

Table 3. Results of organic matter analyses

Sample	rock	Lokalita	C _{org}	C _{resid}	C _{bit}
U - 8	graphitic metaquartzite	Mútnik	2,90	98,8	0,5
U - 9	graphitic metaquartzite	Mútnik	3,76	98,8	0,5

C _{hum}	C _{anorg}	karb	koef. bit.10 ⁻³	bit.ppm	oil	pitch
0,7	0,19	1,6	15	273,7	40,4	9,6
0,7	0,19	1,4	19	338,2	12,7	8,2

asphaltenes	A1460-1735	A720-1610	CP1	prist-fyt	prist-C17	fyt-NC18
50	0,48	4,0	1,15	1,54	0,97	1,24
79,1	0,63	6,0	1,22	1,19	0,80	1,42

Tatricum

Nízke Tatry Mts.

Proterozoic? – Lower Paleozoic

On the southern slopes of the Nízke Tatry Mts. the volcanosedimentary complex is developed with southern (Medzibrod to Suchá dolina valley) strip of graphitic schists as well as the northern one (Husárka and Mlynárova dolina valley) along the contact of nebulites and ophthalmites (Vybírál and Molák, 1989). In the boundary zone of nebulites with ophthalmites the disseminated sulphidic mineralization is developed and in the contact zone of nebulites with granitoids of Prašivá type the occurrence of Sb ore Husárka (Slavkay, 1971). The graphite from nebulites has a high degree of crystallinity. The isotopic ratio $\delta^{13}\text{C}$ (PDB) = -24.10‰ shows its organic origin (Molák in Molák et al., 1993).

The bed of graphitic schists with Sb (Au) mineralization between Vážna and Suchá dolina valley has a character of micaschists to phyllites. Chlorite-sericite phyllites with intercalations of dark schists are supposed to be a product of regressive alteration of migmatites. The low

grade metasediments with volcanites in these phyllites are interpreted as tectonically wedged (Michálek, 1988). The zone is supposed as metalliferous horizon with ore bodies formed by antimonite, quartz, Fe-dolomite, barite and arsenopyrite, rarely tetrahedrite, jamesonite, berthierite, chalcopyrite, marcasite, gold and gold tellurides.

The rocks have low content of organic matter. The normalized values are towards standard SDO-1 + FNB enriched by SiO_2 , Al_2O_3 , Na_2O , Au, Sn, W, Zr and distinctly by Sb. They are moderately depleted by Ag, Co, Cu, Nb, Ni and distinctly low is Mo. The mineralized samples are strongly enriched by Zn and Pb, and moderately by Ag. The organic matter was recrystallized for semigraphite to graphite. The graphite is of organic origin and probable is derived from Precambrian source, because the high ratio of light carbon isotope, typical for Precambrian organic matter, was lowered by metamorphism to recent level $\delta^{13}\text{C}$ around -30‰ .

On the southern slopes of Ráztocká hoľa (Suchá dolina valley, Bukovská dolina valley, Pod Matúšovou a. o.), were found the low-grade metamorphic dark schists with Lower Paleozoic spores (Molák et al., 1989). They

are in the vicinity, or continuation of W-Au mineralization Jasenie, Kyslá. The standard SDO-1 + FNB is double overreached by As, Au, Bi, W, to this standard converge the Ag content, highly anomalous is Sb (50-x). Following correlations of elements were found: Ag with Pb, V and W; Au with As; W with Pb and B; Cu with Ni; Sn with Sm and negative correlation W with Bi. The depleted Ni, Co and Cr show the low ratio of basic to ultrabasic component in former rocks and probable they had the recycled crustal origin. About crustal origin of these rocks prove also increased contents of La and Rb. Molák (in Molák et al., 1993) the increase of Au, Sb, W and Bi contents assigns to shear and shear-deformation zones and fluids with epigenetic mineralization. As protolith he supposes the schists and arkoses with admixture of acid, rarely basic volcanoclastics. The hydrothermal origin is indicated by increased contents of $\delta^{13}\text{C}$.

The micaschists of Klinisko type (Lower Paleozoic, Čorná and Kamenický, 1976) are locally metamorphosed to chlorite-sericite to quartz schists with subgraphite and crystalline graphite. The average schist (Koljonen, 1992) shows comparing to standard the relative increased contents of Bi, Hf, Sb.

The rocks from geothermal drill FGL-1 (in the depth interval 1800–2108.5 m) - the phyllites of Pavčina Lehota type are compared by Biely (in Biely et al., 1988) with the micaschist of Klinisko type a supposed to be pre-Upper Carboniferous. They contain metaanthracite, semi-graphite and graphite. The protolith of these rocks was represented with pelites, resp. sandstone with low content of organic matter. The samples after normalization to SDO-1 + FNB show moderate increase of contents SiO_2 , MgO, Ba, La, W, Zr and multiple increase of Na_2O , Ag and Sb. In contact with Mesozoic sequences the Hg content is 36-fold overreaching the standard (1.09 ppm) and the ratio $\text{U} \times \text{K}/\text{Th} = 2.1$ is also very high, which indicates the Alpine hydrothermal alteration and the possibility of mineralization in underlier of the Mesozoic cover.

Malé Karpaty Mts.

Sedimentary rocks of the Malé Karpaty Mts. in volcanosedimentary series of Pezinok-Pernek crystalline basement and in Harmónia Formation contain the disseminated sulphidic minerals and organic matter. According to Khun (in Molák et al., 1993) with increasing degree of metamorphism in black schists the contents of SiO_2 and Al_2O_3 are increasing and according to ratio $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ they have varying degree of maturity. In productive zones of Pezinok-Pernek crystalline and Harmónia formation the Cu, Ni, Au, As and Sb contents are increased, and especially V (6000 ppm = 37.5x SDO-1), but B neither 50 ppm (0.38x SDO-1), which is characteristic for Malé Karpaty Mts. The Au contents up to 1.45 ppm (725x SDO-1) represent very promising concentration for economic prognoses. Khun (l. c.) states, that the concentration of Au is indirectly influenced by organic matter, because underlies the course of the forming sulphides in reduction conditions and such produce the suitable en-

vironment. The Th/U ratio is characteristic for identification of black schists of Harmónia Formation (differing from Pezinok-Pernek crystalline) and similarly also the V/Cr ratio (in productive zones the value 4.35; in Harmónia Formation 3.65). The increased contents of uranium in black schists (so-called productive zones according to Cambel, 1959) reach up to 48 ppm.

According to the stable ratio La/Ce the calmer sedimentary conditions of Harmónia Formation are assumed, contrasting with the sedimentation of schists of productive zones, being influenced by basic volcanism. The content C_{org} is higher in fine-grained varieties (2.8 %) as it was in the case of medium-grained (1.1 %) and it represents the highly kerogened organic matter poor in bitumens. The sedimentation occurred in coastal marine zone and organic matter originated from marine fauna, flora and from plant detritus brought from the continent.

There were geochemically studied the graphitic schists with intercalations of quartzstone of Pezinok-Pernek Formation (Lower Paleozoic ?) being outcropped in the open pit left at the road Pezinok – Baba (Pulec & Širáňová, in Molák et al., 1993). Regarding the standard SDO-1 they have increased contents Pb, Zn, Cu, V, Sn, Ni and lowered contents of Mo and Co. The standard is highly overreached by V (1.75x–6.79x), in average 5.24x (838.25 ppm). The Malé Karpaty black schists, as a part of Harmónia Formation and the Pezinok-Pernek crystalline basement, are supposed as metalliferous. Their elements V, Cu, Ba, Sr, Au, As, Sb, Ag and Zn overreach and elements Ni and Cr are close to values of SDO-1 standard.

Mineralization

The syngenetic deposits are represented with the pyrite deposit Pezinok - Karolína and Ferdinand. The ore bodies are developed in actinolite and black schists together with amphibolites and amphibolitic schists in biotite gneisses and migmatites (Lower Paleozoic). Pyrite originated partly as a product of organisms decomposition, but its essential part originated from post-magmatic exhalations of basic volcanism (Silurian – Devonian?). The mineralization underwent the regional Hercynian metamorphism and contact metamorphism by granite (Polák, 1986). The deposit Jablonové - Turecký vrch (Rudolf) with pyrite mineralization is developed in beds of quartz-graphite schists at the contact with actinolite schists as well as in these schists (Lower Paleozoic). It is supposed that the deposit represents the sedimentary exhalative-volcanogenic type with Hercynian and Alpine metamorphic overprint (Rak a Polák, 1983). The same is demonstrated by the pyrite-pyrrhotite deposit Augustín in actinolite schists above graphite schists and amphibolites (Lower Paleozoic) and its continuation - Sb-pyrite mineralization of deposit Pernek - mining district Pavol štôlne developed in actinolite schists. Here belongs also the pyrite deposit Pezinok-Čertov kopec and deposit Pezinok-Rybníček with pyrite and Sb mineralization.

The stratiform hydrothermal Sb vein-stockwork deposit Pezinok-Kolársky vrch (Hercynian type) in my-

lonitic gneisses, graphitic, actinolitic, sericite-clayey schists, amphibolites and granitoids could originate by mobilization by metamorphic solutions before or during granitoid intrusions. There was found the important role of biogene sulphur and Alpine migration of sulphides (Polák, 1986; Chovan et al., 1994; Slavkay et al., 1994). In deposit of Sb-Au-As ore Pezinok-Vinohrady the mineralization is developed in gneisses, amphibolites and black schists in so-called black fault with parallel gold vein (see Molák et al., 1995; Molák and Slavkay, 1995).

Považský Inovec

Kálnica Group, Permian

The Permian rocks were divided by Novotný and Mihál (in Štimmel et al., 1984) into four formations of Kálnica Group: Chalmov, Klenkov vrch, Selec and Kričovsúd Fms. The variegated clastic rocks consist from polymict conglomerate, quartz-, greywacke- and arkose sandstone, variegated schists, acid volcanoclastics, rhyolites and their ignimbrites with U mineralization, silicites and quartzites. The schists and sandstone beds are bearing the intercalations of carbonate, gypsum and anhydrite.

The uranium mineralization was investigated by Rojkovič (1980a, 1980b). It is formed by uraninite, less Ti oxides, in oxidation zone torbernite and numerous accompanying minerals: arsenopyrite, bornite, digenite, dolomite, galenite, goethite, hematite, chalcopyrite, ilmenite, covellite, quartz, magnetite, molybdenite, pyrite, rutile, sphalerite, tennantite and tetrahedrite. The sediments have very low content of C_{org} . The positive U correlations with Pb, Cu, Mo and S were found. The contents of trace elements (which form also the ore bodies) vary in the range U = 5–5000 ppm; Mo = 10–2010 ppm; Cu = 20–890 ppm; V = 30–2000 ppm, at the same time the highest contents are in the ashy tuff. The content of Th in mineralized rocks is about 6 ppm. The distinct difference of coefficient of radioactive balance in bed with rhyolite tuff (0.87) regarding to bed in conglomerate (1.00) proves the distinct migration of U and Ra in the first bed (Rojkovič and Novotný, 1993). The age of stratiform mineralization is 270 ± 30 Ma and Alpine remobilized richest mineralization (geochronology by U-Pb method was performed on 82 samples) showed the youngest age with maxima in Middle Cretaceous 100 ± 30 Ma (Štimmel et al., l. c.). Rojkovič and Novotný (l. c.) state the origin of oldest pour ore from U deliberated during devitrification and diagenesis of acid tuff and tuffite after its coagulation in horizons with reduction environment (pyrite) and suitable adsorbents (Ti oxides and clay minerals).

Conclusion

Veporicum

The Paleozoic (to Proterozoic?) rocks of Veporicum with higher content of C_{org} are bearing the conformable bodies of magnetite and pyrite-pyrrhotite ore as a product of regional metamorphism of former sedimentary ore. The

iron ore originated during sedimentation in a part of the basin with oxidation conditions, the pyrite ore in parts with reducing environment. The distribution of hydrocarbons testifies their source of marine origin and in formation of Jánov grúň in Veporicum of the Nízke Tatry Mts. also of mixed origin. There is possible to suppose also the presence of further ore bodies of similar mineralization. Comparing with the standard SDO-1 + FNB, despite some anomalous contents, the investigated rocks can be supposed only as weakly metalliferous and not metalliferous and these ore types in this area are economically non-perspective. The former bodies of carbonates, ultrabasics and organic matter, changed to magnesite, talc and graphite by later metamorphic and hydrothermal processes, we suppose from the economic viewpoint as perspective for exploration of further deposits.

The Carboniferous rocks of the Slatviná Formation contain low contents of C_{org} . The values above double of SDO-1+FNB standard of the elements Ag, Pb and Zn in the sample 43 are caused by the influence of hydrothermal processes. The increased clark contents of As and in sporadic samples also of some next elements can be caused by tuffitic admixture, which is indicated by the high variability of $K_2O : Na_2O$ ratios. The formation is not metalliferous and no more important accumulations of syngenetic sedimentary mineralization can be expected.

Tatricum

The Paleozoic to Proterozoic? volcanosedimentary complex of Tatricum in the Nízke Tatry Mts. with beds of graphite schists shows the low content of organic matter comparing the standard metalliferous schists. The distinct enrichment of graphite beds by Sb, as well as increased content of As, Au, W and Bi would indicate the increased metal contents, but with uncertainty whether it is its primary accumulation and Sb was remobilized into younger Alpine structures, or whether Sb was brought by hydrothermal solutions into the suitable environment.

For Pezinok-Pernek crystalline basement and Harmónia Formation of the Malé Karpaty Mts. the increased contents of Cu, Ni, Au, As, Ba, Sb, Zn and V are characteristic, locally also U and contain the highly kerogenized organic matter poor to bitumens. According to until obtained results and the presence of exploited and explored bodies of pyrite, pyrite-pyrrhotite and pyrite-antimonite ores, we suppose this so-called productive zone as metalliferous and perspective formation.

The productive formation in the Považský Inovec Mts. is represented by Permian sediments of the Kálnica Group with very low content of C_{org} , but high contents of U, Mo, Cu and V, bearing the known and explored stratiform uranium mineralization.

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