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J. FORGÁČ — J. JARKOVSKÝ*

GEOCHEMICAL CHARACTERIZATION OF PYRITE FROM THE NEOGENE VOLCANIC COMPLEX OF THE VTÁČNIK MOUNTAINS

(Figs. 1—5, Tabs. 1—4)

A b s t r a c t : In the paper the question of trace elements distribution in pyrite from the volcanic complex in vertical profile encountered in borehole to depth of 1400 metres is being solved. In pyrite the elements Ni, Co, Cu, Ag, Pb, Zn, Mn, Ti, As, Sb, Bi, Mo, Sn, V, Tl were determined by spectrochemical method. A part of the elements in pyrite is concentrated in contents below the lower detection limit of the applied analytical method. The authors further investigated the changes of element contents in pyrite toward depth of the volcanic complex as well as mutual relations of the trace elements.

Р е з ю м е : Авторы исследовали проблему дистрибуции микроэлементов в пирите из вулканического комплекса в вертикальном профиле в соответствии с скважиной в глубину 1400 м. В пирите спектральнохимическим методом были исследованые эти элементы: Ni, Co, Cu, Ag, Pb, Zn, Mn, Ti, As, Sb, Bi, Mo, Sn, V, Tl. Часть элементов в пирите сосредоточена в содержаниях под нижним пределом возможности определения использованного аналитического метода. Авторы дальше исследовали изменения содержаний элементов в пирите в направлении в глубину вулканического комплекса и тоже взаимные отношения исследованных элементов.

We studied pyrite geochemistry on the example of structural borehole MEB-1, located west of the village Prochoť in the Vtáčnik Mts. (Fig. 1). The borehole penetrated rocks of the Neogene volcanic complex to depth of 1400 metres, not encountering its substratum. In the whole profile of the volcanic complex pyrite is found in form of impregnations, coatings on joints and in thin veins. With the performed borehole we received a continuous vertical profile of 1400 metres with occurrence of pyrite in intermediate rocks, which correspond to andesites in material composition. In this profile it was possible to pursue changes in trace element contents in pyrite from the surface to considerable depth.

From the view-point of the form of rocks occurrence it is predominantly formed by products of surficial volcanic activity represented by lava bodies of pyroxenic andesite and volcanoclastic material. From volcanoclastic material are present volcanic breccias, epiclastic volcanic breccias, tuffs and tuffites with distinct sorting of material. In the major part of the profile of borehole it is difficult to determine original texture elements of volcanic bodies and volcanoclastic material as a consequence of intensive alterations in rocks. On the basis of petrographic analyses also diorite porphyries were distinguished in the borehole profile by A. M i h a l i k o v á (1980). The geological profile of the volcanic complex is represented graphically in Fig. 2.

* RNDr. J. F o r g á č, CSc., Doc. RNDr. J. J a r k o v s k ý, DrSc. Department of Geochemistry of the Faculty of Natural Science, Comenius University, Paulínyho 1, 801 00 Bratislava.

Petrographic characterization of rocks

In the whole borehole profile the volcanic complex is intensively altered. In rocks a wide scale of alterations up to partial alteration of rocks to their complete decomposition and formation of clay minerals was taking place. The alterations were taking place in almost equal intensity in volcanoclastics (including tuffs and tuffites) as well as in lava bodies. In processes of alterations in the volcanic complex hydrothermal and hypergenic alterations were evident (J. F o r g á č, 1980).

Hydrothermal alterations

When penetrating the rock environment the hydrothermal solutions react with rocks and evoke in them alteration of primary minerals and formation of secondary minerals. Hydrothermal alterations are of distinctly selective character. Most intensively are altered dark minerals, pyroxenes in the borehole profile. Pyroxenes are completely altered to chlorite while plagioclases were subjected to alteration, sericitization and only partly to carbonatization. It may be said that plagioclases are almost fresh, corresponding to andesine — labradorite in basicity. The most abundant secondary mineral is chlorite. Further secondary minerals, originated in the process of hydrothermal rock alteration, are epidote, sericite, quartz, pyrite, carbonates (calcite, less dolomite) and in some places adular formed. The mentioned secondary minerals are found in rock, in pseudomorphs after pyroxenes, in plagioclases as well as in groundmass of rock, where they form various clusters of aggregates and joint fillings. The most conspicuous visible secondary mineral, which formed in the process of hydrothermal alterations, is pyrite. It is developed in forms of small clusters and cubes, in places forms coatings on joints or their fillings in form of veinlets. Impregnations of pyrite are present in variable amount in the whole borehole profile.

In the volcanic complex ore minerals, represented by galena, sphalerite, chalcopyrite, pyrite and pyrrhotite, formed in the course of the hydrothermal process. The mentioned ore minerals are found in the volcanic complex, in form of sporadic clusters or form filling of thin veins together with quartz and carbonates (A. B r l a y — J. F o r g á č, 1980). Distribution of Pb, Zn, Cu mineralization in the vertical profile or the volcanic complex is shown in Fig. 2.

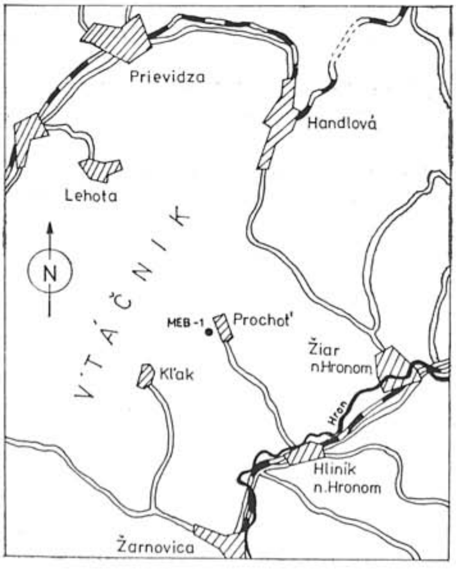

Fig. 1. Scheme of location of borehole MEB-1.

Hypergenic alterations

The process of hypergenic alterations followed in time after hydrothermal alteration. Hypergenic alterations were most intensive in the upper parts of the volcanic complex where rocks are completely altered even to bentonite. More deeper the rocks are more solid to solid, however, bleached

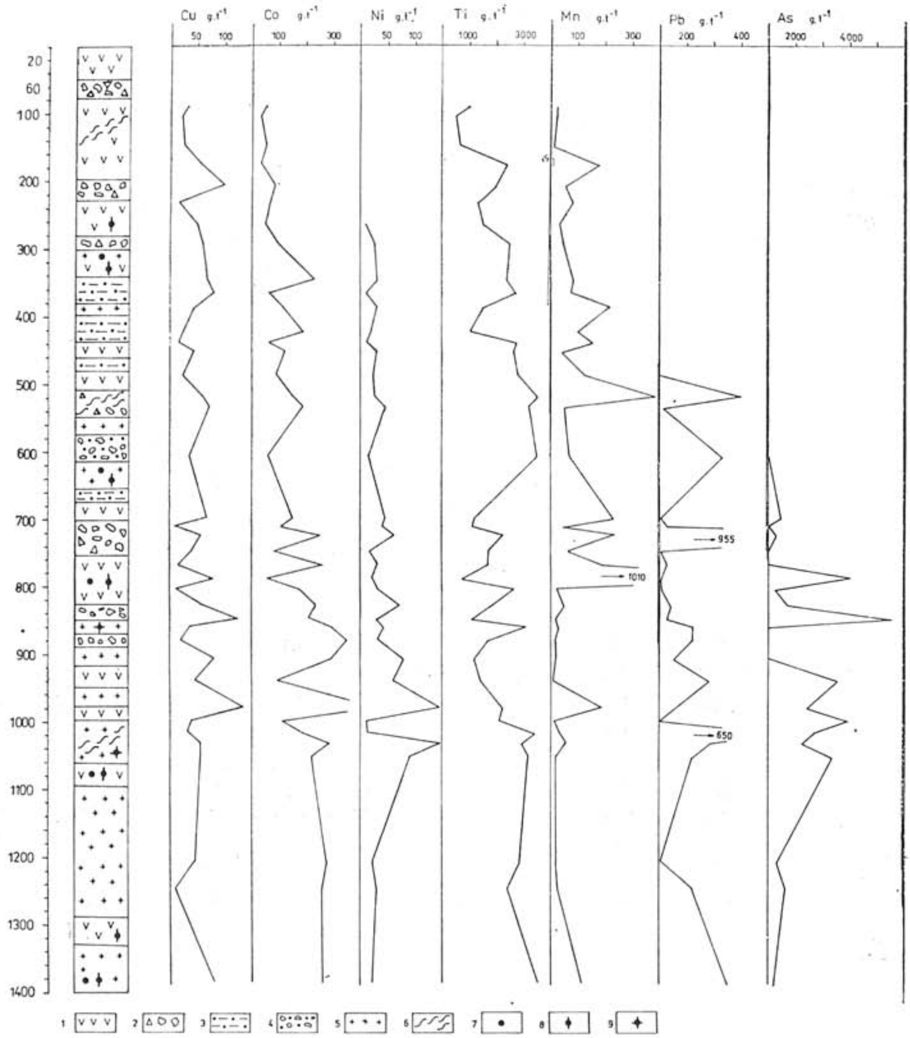

Fig. 2. Graph of distribution of Cu, Co, Ni, Ti, Mn, Pb, As in the profile of borehole MEB-1. (Geological profile of the borehole from the work by J. F o r g á č — A. B r l a y, 1980).
Explanations: 1 — pyroxenic andesite, 2 — andesitic breccia, 3 — pyroclastic tuff, tuffite, 3 — pumice tuff, 5 — dioritic porphyr, 6 — tectonic breccias, 7 — mineralization of galena, 8 — mineralization of sfalerite, 9 — mineralization of chalcopyrite.

and often differences in the intensity of alterations are observed. Distinct manifestations of hypergenic alterations are dominant to depth of about 500 metres, Toward depth intensity of bleaching of rocks is less. From 750 m to 1400 m bleaching of rocks and argillization is mainly i crushed zones and on joints.

With action of hypergenic solutions on rocks hydrothermally altered their bleaching is evident in the first stages. Chlorites and epidotes lose iron, acquire lighter colour and disintegrate with higher alteration. Plagioclases, which behaved as relatively stable minerals in the process of hydrothermal alterations, are desintegrating into a light—coloured isotropic mass in hypergenic processes, from which gradually clay minerals crystallize. Similar alterations, as mentioned on the example of chlorite and plagioclase, are also acting in the groundmass of rocks. Besides clay minerals clusters of secondary quartz form in rocks, carbonates, partly pyrite and also other minerals decompose. With intensive alterations argillitization of rocks occurs. In argillitized bleached rocks in the upper parts of the volcanic complex mainly montmorillonite formed in other parts to montmorillonite, illite joint and from 270 m deeper illite was found (J. Forgáč, 1980).

Trace elements in pyrite

Pyrite as the mostly wide-spread sulphide mineral in earth crust forms under various genetic conditions. It occurs from accessory amounts in rocks to deposit accumulations. Pyrite as the main and more stable modifikation of iron disulphide can bind elements geochemically related to iron in its crystal structure, mainly Co and Ni. Pyrite reacts sensitively to various rock environments as well as to thermodynamic conditions evoked by geological factors.

Geochemistry of pyrite in regional extent was studied by B. Cambel and J. Jarkovský (1967) in the latest years by us. The mentioned authors directed their investigations to pyrite from various genetic and deposit types, mainly from the region of the West Carpathians. This way a huge factural material about the contents of 16 microelements was obtained (Co, Ni, Mn, Ti, V, Mo, Cu, Sb, As, Bi, Pb, Zn, Ag, Sn, Au and Tl). From the, mainly Co and Ni are of greatest importance for genetic interpretation. This was proved in the study of geochemical characterization, mainly of volcano—exhalatory sedimentogenic deposits of the West Carpathians (Little Carpathians, Low Tatra—Heľpa, Spišsko-gemerské rudohorie Mts., Smolník). The cited authors also investigated a larger group of pyrites from hydrothermal plutonic and subvolcanic deposits of the West Carpathians.

By means of geochemical study it is possible to distinguish well pyrites coming from hydrothermal plutonic deposits from pyrites occurring in subvolcanic ore mineralizations. When comparing total geochemical data on average contents (g/t) of traced trace elements, but mainly Co, Ni, Mn, Pb, As, Cu, Zn, Ti, Ag, V, Mo in pyrites from both types of hydrothermal mineralizations of the West Carpathians mentioned by B. Cambel and J. Jarkovský (1967) (Tab. 1) we state these differences:

The contents of Co and Ni are distinctly different. In hydrothermal pluto-

Table 1

Average contents of trace elements in pyrite from hydrothermal deposits of the West Carpathian (in g/t) according to B. Cambel and J. Jarkovský, 1967

Type of hydrothermal mineralization	Co	Ni	Mn	Pb	As	Cu	Zn	Ti	Ag	Mo	V	Co/Ni
Plutonic	750	500	140	780	5620	450	90	100	20	20	30	1,5
Subvolcanic	50	20	220	200	<1000	230	620	700	<10	20	70	2,5

nic pyrites Co content is 15 times higher and Ni content even 25 times higher than the contents of these elements in subvolcanic pyrites. The value of Co/Ni ratio is, however, distinctly higher in pyrites of subvolcanic origin (2,5) than in hydrothermal pyrites (1,5). Essential differences in average contents are further in As, Zn, Ti, Pb and Cu.

When we mutually compare pyrites from hydrothermal plutonic deposits from individual deposit types of the West Carpathians (Fig. 3), we see that

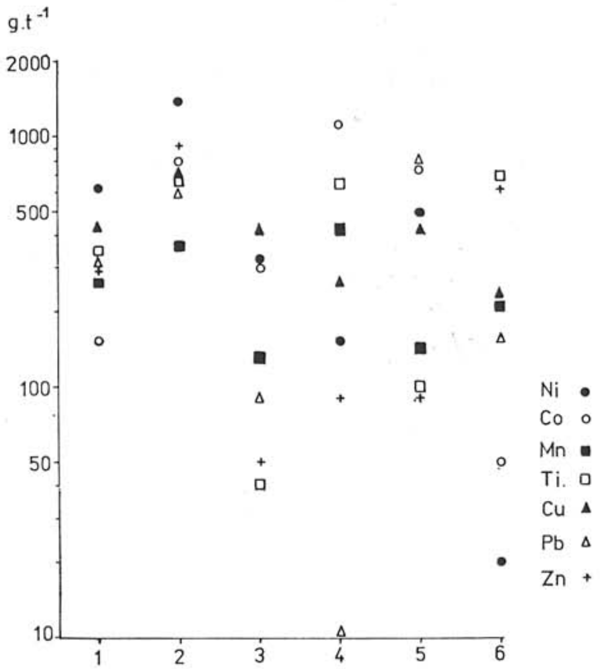

Fig. 3. Graphical representation of average contents of Co, Ni, Mn, Ti, Cu, Pb, Zn in pyrites from individual types of deposits of hydrothermal mineralization of the West Carpathians.
Explanations: 1 — Little Carpathians, 2 — Low Tatra, 3 — Veporské pohorie Mts., 4 — pyrites from talc deposits, 5 — Spišsko—gemerské rudohorie Mts., 6 — pyrites from subvolcanic deposits.

there are differences in content representation of traced elements. It is caused by differences in material composition of the rock environment of individual types of deposits, thermodynamic conditions, particularly of hydrothermal process at each deposit type and resulting sulphidic mineralization following from this. In Fig. 3 is visible that the contents of Co and Ni differ from each other and the Co/Ni ratio also varies as follows: Little Carpathians 0,25; Low Tatra 0,63; Vepor mountains 1,0; Spišsko—gemerské rudohorie Mts. 1,5; pyrite from talc deposits 7,7. Considerable differences are also in contents of Pb, Zn and Ti. Relatively balanced are the contents in Mn and Cu, testifying to certain crystallochemical relation of these elements to pyrite.

Distribution of elements in pyrite in vertical profile of volcanic complex

In effort in contribute to clearing up the metallogenetic characterization of the studied volcanic complex occurring in the whole profile of borehole in rocks of andesite composition we were focused on geochemical study of pyrite from this complex. Pyrite originated here as product of hydrothermal alteration of rocks. After separating of pyrite from 39 rock samples, in which pyrite was scattered, it was analysed by the method of emission quantitative spectral analyses (SPA) in the Geological Institute of Natural Science Faculty of the Comenius University in Bratislava (analyst J. Chudý) on elements Ni, Co, Cu, Ag, Pb, Zn, Mn, Ti, As, Sb, Bi. Mo, Sn, V. Tl. The obtained data about contents of trace elements in pyrite we quote in Table 2.

Further we are going to compare distribution of the trace elements in pyrite from the volcanic complex in the Vtáčnik mountains with contents in pyrite according to A. Levinson (1976) in general conception and also with contents in pyrites from hydrothermal subvolcanic deposits of the West Carpathians, represented mainly by the Neogene volcanic complex of the Štiavnické pohorie mountains on the basis of the works by B. Cambel and J. Jarkovský (1967).

The Cu concentration in pyrites occurs according the data of A. Levinson (1976) often within the range from 10 g/t to 1 %, the maximum concentration is quoted with 6 % by the cited author. In pyrites from hydrothermal deposits of the West Carpathians Cu is from 80 to 1200 g/t and in Banská Štiavnica Cu 230 g/t on an average (from 8 samples) and within the range from 30 to 870 g/t (B. Cambel — J. Jarkovský, 1967). The concentration of Cu in pyrites from the volcanic complex of Vtáčnik is within the range from 10 to 132 g/t. In the vertical profile in direction to depth no essential changes occurred in Cu-contents in pyrites (Fig. 2). The content of Cu in pyrites from the volcanic complex of Vtáčnik in comparison with data from literature is relatively low.

The concentration of Zn in pyrites is most often varying from 1000 to 5000 g/t and can reach maximum up to around 4,5 % Zn (A. Levinson, 1976). In pyrites from hydrothermal deposits of the West Carpathians Zn is within the range from 50 to 2290 g/t, in Banská Štiavnica this element occurs from 140 to 1380 g/t most often from 140 to 260 g/t and the average

Table 2

Trace elements in pyrites in g/t

Depth of borehole in m	Pb	Zn	Cu	As	Ni	Co	Mn	Ti	Co/Ni
97	<100	<300	27	<1000	<10	53	20	995	13,25
105	<100	<300	24	<1000	<10	<30	17	500	3,0
150	<100	<300	26	<1000	<10	51	12	650	12,75
177	<100	<300	56	<1000	<10	32	182	2390	8,0
207	<100	2880	101	<1000	<10	87	54	1950	21,75
235	<100	<300	13	<1000	<10	69	79	1320	17,25
265	<100	<300	49	<1000	<10	51	29	1510	12,75
290	<100	<300	59	<1000	26	91	39	2570	3,5
353	<100	1660	68	<1000	30	229	83	2390	7,6
374	<100	<300	79	<1000	10	69	72	2750	6,9
390	<100	<300	47	<1000	27	115	214	1510	4,25
424	<100	<300	23	<1000	17	191	98	1020	11,2
443	<100	<300	14	<1000	<10	63	155	2690	15,75
450	166	<300	44	<1000	30	123	42	2630	4,1
485	<100	<300	23	<1000	22	89	123	2820	4,0
522	390	<300	63	<1000	22	151	410	3500	6,9
530	<100	<300	72	<1000	45	191	53	3200	4,2
604	234	330	34	<1000	15	58	71	355	3,9
702,5	<100	<300	71	1480	47	151	229	1260	3,2
708,5	126	<300	10	<1000	41	107	53	1120	2,6
722	955	<300	56	1170	59	251	234	1190	4,25
745	<100	<300	42	<1000	15	79	65	1740	5,3
770	123	<300	14	<1000	28	263	195	1780	9,4
790	<100	<300	78	4000	21	62	1010	690	2,95
805	101	<300	10	1170	29	174	15	2630	6,0
828	145	<300	56	1700	71	239	48	1910	3,4
845	129	300	126	5500	27	209	12	1070	7,7
862	219	<300	34	<1000	41	295	22	3020	7,2
882	219	<300	19	<1000	29	350	14	1660	12,1
910	148	<300	78	<1000	78	288	16	1200	3,7
943	275	<300	45	1350	59	91	10	1380	1,5
978	159	<300	132	2240	148	460	186	2240	3,1
1004	<100	<300	37	3900	10	112	10	2090	11,2
1017	650	<300	29	2750	14	182	26	3400	13,0
1031	288	<300	56	2240	145	282	54	2950	1,9
1050	214	890	56	3300	91	219	13	3160	2,4
1211	<100	<300	44	1200	21	275	10	2880	13,1
1244	244	<300	10	1660	27	269	16	2400	10,0
1385	355	<300	81	1170	18	269	110	3500	14,9

The contents of Ag are below the spectrochemical detection limit (10 ppm). Only two samples from depth 1031 and 1385 m contain 10 and 33 g/t of Ag.

concentration of Zn is 620 g/t (from 8 samples). In determination of zinc in pyrites from the studied borehole profile the lower detection limit of the analytic method was 300 g/t. In the majority of samples the concentration of Zn is lower than 300 g/t and only in three samples the content of Zn is higher (Tab. 2).

The contents of Pb in pyrites from hydrothermal deposits of the West Carpathians are varying from 10 to 760 g/t. In Banská Štiavnica the Pb content is from 10 to 340 g/t, in most samples the concentration of Pb is lower than 100 g/t. In the studied pyrites Pb was established with the lower analytical detection limit 100 g/t. In the upper parts of the profile (to 700 m) in the prevailing part of traced samples is the concentration of Pb less than 100 g/t. From 700 m to the depth of 1400 m concentration of Pb is prevailingly higher and reaches maximum the value of 955 g/t (Tab. 2, Fig. 2).

Distribution of Ni in pyrites occurs in wide range, from 10 to 500 g/t, maximum to about 2,5 % (A. Levinson, 1976). Within the range of 70 to 1970 g/t was recorded the content of Ni in pyrites from hydrothermal deposits of the West Carpathians. In pyrites from Banská Štiavnica Ni is found in concentrations 2 to 110 g/t and on an average 30 g/t (from 21 samples). In the studied volcanic complex concentration of Ni is within the range less than 10 to 149 g/t. The Ni content increases from the surface to depth. In the upper half of the borehole profile (to 700 m) the mean value of Ni is 15,33 g/t and the mean value in the lower half of the borehole profile (700 to 1400 m) increases up to 48,52 g/t.

Similarly as Ni also Co is a frequent element in pyrite. Most often its content varies from 200 to 5000 g/t (A. Levinson, 1976), maximum it may reach up to 2,5 % (data from 1094 samples). In pyrites from hydrothermal deposits of the West Carpathians Co is within the range 30 to 2140 g/t and from Banská Štiavnica the average value of Co is 40 g/t (from 21 samples), maximum concentration attains 600 g/t. In the studied volcanic complex Co is distributed in pyrite from 30 to 460 g/t, representing the minimum part of its concentration in pyrites mentioned by A. Levinson (1976) only. The concentration of Co in pyrites from the upper profile distinctly increases from surface to depth (Tab. 1, Fig. 2). These differences are well visible from data of medium values in the upper and lower half of the borehole. In the upper half of the borehole profile, i.e. from surface to 700 m the medium value of Co in pyrites is 95,83 g/t, whilst the medium value in the lower part of the borehole profile (from 700 to 1400 m) raises to 220,33 g/t, what is twice and half time more.

An element frequent in pyrite is As. Its usual concentration is within the range 500 to 1000 g/t and can maximum reach about 5 % (A. Levinson, 1976). High contents of As were found also in pyrites from hydrothermal deposits of the West Carpathians, where it varies within the range 1240 g/t to 1 %. In pyrites from the volcanic complex of Vtáčnik As was established with the spectrochemical detection limit 1000 g/t. In the upper half of the volcanic complex (to 700 m) concentration of As is less than 1000 g/t. In the lower part of the volcanic complex (from 700 to 1400 m) its concentration distinctly increases, within the range from less than 1000 to 5500 g/t.

Further observed elements are Mn and Ti. Manganese has usually the range of concentration in pyrites from 10 to 50 g/t with maximum content to 1 % Mn (A. Levinson, 1976). At hydrothermal deposits of the West Carpathians Mn is represented in pyrites from 30 to 1400 g/t and in Banská Štiavnica from less than 20 to 650 g/t and on an average 310 g/t. In the volcanic complex of Vtáčnik Mn in pyrites is concentrated within the range from 10 to 1010 g/t, however, in the majority of samples Mn concentrations are less than 100 g/t (Tab. 2). In the content of manganese no essential differences were shown in its average content in the upper and lower half of the borehole profile.

Usual concentrations of Ti in pyrites are from 200 to 500 g/t (A. Levinson, 1976). Pyrite from hydrothermal deposits of the West Carpathians contains Ti from 20 to 1630 g/t. In pyrites from the Vtáčnik volcanic complex Ti is distributed in the wide range from 355 to 3500 g/t. In the borehole profile are no more essential differences in Ti content in pyrite.

Further elements in pyrites are in concentrations less than the lower spectrochemical detection limit, which is for the individual elements as follows:

Sb — 30, Ag — 10, Bi — 10, Mo — 30, Sn — 30, V — 100, Tl — 100.

Mutual relations of elements

It is visible from the data mentioned in Tab. 2 and from the graph (Fig. 2) that in the studied pyrites there is a prevalence of Co over Ni content, what is not common generally. In pyrites, as a rule, Ni predominates over Co. Thus there is a particular geochemical picture typical not only of pyrite from hydrothermal subvolcanic deposits (B. Cambel — J. Jarkovský, 1967) but specifically also of Co and Ni in pyrites, which originated in the process of alteration of volcanic rocks themselves.

The source of Co and Ni in pyrites formed in volcanic as a consequence of hydrothermal activity is necessary to seek mainly in own rocks containing prevalence of Co over Ni. According to J. Forgáč and G. Kupčo (1974) the average content of Co and Ni is in andesites of Slovakia as follows: Co = 12,8 g/t (from 45 analyses) and Ni = 9 g/t (from 45 analyses). The ratio Co/Ni on an average in andesites of Slovakia is 1,42. whilst the ratio Co/Ni in pyrites from altered andesites of the Vtáčnik mountains is, 8,59. It is evident from the mentioned values of Co/Ni ratio that in pyrites, on the contrary to andesites, this ratio is considerably higher, pointing to the specific character of processes of andesite alteration, also to the genetic conditions of pyrite origin. Under the given conditions Co concentrated mainly in pyrite and a part of Ni probably re-migrated, besides pyrite, into secondary silicate minerals, mainly chlorites.

If we compare Co/Ni value in andesites of Slovakia, which is 1,42, with the value Co/Ni from analogous rocks, mentioned by A. Mookherjee — R. Philip (1979), which is 1,33, we may state, that this value is very close to our value and can be a good basis for the petrometallogenetic study. The ratio Co/Ni in pyrites from quartz- sulphide veins (pyrite — chalcopyrite mineralization) in metavolcanics from Ingladhal (Karnataka, India) varies from 1,02 to 26,84 according to the mentioned authors. Most often the value Co/Ni varies within the range from 5 to 10 and the average value is 7,4. It is visible that also this value is very close to the average value of Co/Ni in pyrites from the Vtáčnik mountains studied by us. A. Bralia — G. Sabatini — F. Troja (1979) traced Co/Ni ratio in volcanogenic pyrites from Southern Tuscany (Italy). They have found that Co/Ni value varies in values higher than 5, these values are, however, prevaillingly higher than 10. On the basis of Co/Ni ratio in pyrites from sulphide ores of southern Tuscany, the mentioned authors distinguished two metallogenetic models. The first (Paleozoic) characterized by volcanogenic sulphide deposits originated in submarine volcanogenic — exhalational environment and the second, later (Mio—Pliocene) characterized by smaller, predominantly hydrothermally remobilized deposits of original older ores. It is evident from the above mentioned data that the source of Co and Ni in pyrites as well as relative representation of the contents of both elements is a reflection of relative representation of the contents of these elements is in volcanic rocks, in which pyrite is found. This is one side of the problem, more or less understandable, also when not directly proved.

In our case there is an increase in the contents of both elements in pyrites from the surface toward depth of the volcanic complex. This question requires a more detailed study in the sense that it is necessary also the fundamental rock — forming minerals as to the contents of Co and Ni in fresh rocks as well as in hydrotermally altered rocks in the studied volcanic complex (in borehole profile). As we have no available data on the contents of Co and Ni in rocks — forming minerals of fresh and altered andesites, it is not possible to solve the question of quantification of supplay and transport of elements in this beginning stage of treatment of the problem given. It is necessary to know further important factors of physical character in hydrothermal alteration of andesites and with formation of pyrite in them. The study of these factors can significantly contribute to solving of the question of metallogenesis of the area under consideration. It is evident that Co and Ni contents in pyrite are on an average considerably higher on the contraty to analogous data from unaltered andesites of Slovakia, with Co by 12,7 x and Ni by 3,6 x. It is an important knowledge testifying to relatively high concentration of Co in pyrite on the contrary to mother rocks. This is also testified by the relatively high average Co/Ni ratio in pyrites attaining the value of 8,59 on the contrary to an analogous ratio in pyrites from fresh andesites of Slovakia.

The relations between contents of trace elements found in the studied pyrite in contents spectrochemically detectable, i.e. Cu, Ni, Co, Mn and Ti determine distinctly the statistical characteristics (arithmetic mean, deviation from geometric mean, standard deviation, variation coefficient and correlation coefficient) mentioned in Tables 3 and 4. The average contents of elements expressed by arithmetic and geometric average with corresponding deviations are the fundamental statistical characteristics determining the value of contents in relation to the statistical type of distribution of the group. The fundamental group representing the entire borehole profile for the elements Cu, Ni, Co and Ti can be valuated as homogeneous. The average arithmetics contents of Cu, Ni, Co are from the upper half of the borehole profile, distinctly lowe than from the lower half and the standard deviations of allmost all elements are less than the value of corresponding arithmetic means, e.g. in the group from the lower part of the borehole in case of Mn the standard deviation is considerably higher than the arithmetic mean, pointing to the competent group of Mn contents approaching asymmetric division. In this case the standard deviation should be consi-

Table 3

Main statistical charakteristics

For the group from the whole borehole profile (o — 1400 m, 39 analyses)

	Cu	Ni	Co	Mn	Ti
arithm. mean (A. P.)	48,87	33,20	162,87	105,15	2026,15
deviation from A. P.	$\pm$9,43	$\pm$10,73	$\pm$32,41	$\pm$54,02	$\pm$297,80
geom. average (G. P.)	39,62	20,66	128,25	51,34	1785,30
deviation from G. P.	$\pm$2,01	$\pm$2,84	$\pm$1,15	$\pm$3,23	$\pm$1,75
standard deviation	30,06	34,20	103,26	172,10	891,37
variation coefficient	61,52	103,01	63,40	163,66	43,99
min. concentration	10,00	4,00	12,00	10,00	355,00
max. concentration	132,00	148,00	460,00	1010,00	3500,00

For the group from the upper half of the borehole profile (0—700 m, 18 analyses)

	Cu	Ni	Co	Mn	Ti
arithm. mean (A. P.)	45,66	15,33	95,87	97,38	1930,55
deviation from A. P.	$\pm$7,76	$\pm$3,96	$\pm$18,86	$\pm$30,36	$\pm$304,85
geom. mean (G. P.)	39,09	10,47	78,05	65,93	1624,37
deviation from G. P.	$\pm$1,81	$\pm$2,55	$\pm$2,03	$\pm$2,52	$\pm$1,96
standard deviation	24,73	12,62	59,92	96,73	971,18
variation coefficient	54,17	82,31	62,53	99,33	50,30
min. concentration	13,00	4,00	12,00	12,00	355,00
max. concentration	101,00	45,00	229,00	410,00	3500,00

For the group from the lower half of the borehole profile (700—1400 m), 21 analyses

	Cu	Ni	Co	Mn	Ti
arithm. mean (A. P.)	51,61	48,52	220,33	111,80	2108,09
deviation from A. P.	$\pm$10,78	$\pm$12,37	$\pm$30,90	$\pm$68,92	$\pm$261,24
geom. mean (G. P.)	40,09	36,99	196,29	41,44	1935,88
deviation from G. P.	$\pm$2,20	$\pm$2,10	$\pm$1,69	$\pm$3,80	$\pm$1,55
standard deviation	34,35	39,41	98,47	219,59	832,26
variation coefficient	66,55	81,23	44,69	196,40	39,47
min. concentration	10,00	10,00	62,00	10,00	690,00
max. concentration	132,00	148,00	460,00	1010,00	3500,00

dered as a formal aid only. When we compare the values of arithmetic mean and geometric mean, it is to be seen that they relatively diverge mostly in Mn and Ni of the total group whilst approach mostly in Ti, Cu and Co, testifying to closeness to symmetric division of the group. In the total group and mainly in the group from the lower half of the borehole profile the values of arithmetic and geometric means are closest in Ti and Co but also in Cu and Ni.

Table 4

Correlation matrixes

For the group from the whole borehole profile

	Cu	Ni	Co	Mn	Ti
Cu	1,00				
Ni	0,38	1,00			
Co	0,28	0,66	1,00		
Mn	0,22	−0,02	−0,11	0,99	
Ti	0,10	0,19	0,35	−0,11	0,99

For the group of the upper half of the borehole profile (0—700 m)

	Cu	Ni	Co	Mn	Ti
Cu	0,99				
Ni	0,30	1,00			
Co	0,31	0,77	1,00		
Mn	0,10	0,16	0,24	0,99	
Ti	0,48	0,51	0,42	0,47	1,00

For the group from the lower half of the borehole profile (700—1400 m)

	Cu	Ni	Co	Mn	Ti
Cu	0,99				
Ni	0,42	1,00			
Co	0,27	0,51	1,00		
Mn	0,25	−0,07	−0,27	1,00	
Ti	−0,18	0,10	0,37	−0,40	0,99

That all attensts that the mentioned elements represented components of genetic importance in the course of action of hydrothermal alteration of the volcanic complex, by means of which it is possible to clear up closer their mutual relations in pyrite as well as in rock environment, which gave rise to the studied disulphide. We continue in the study of the problem given.

An important statistical characteristic are correlation coefficients. It has resultet from the performed correlations that the most important positive correlation is between Co and Ni (in the whole profile 0,66, in the upper half of the profile 0,77 and in the lower half of borehole 0,51). Essentially lower correlation relations in all three groups were shown between Cu — Ni and Co, also between Co and Ti. Further correlation relations between the observed elements may be considered as insignificant (Tab. 4). Whilst in the upper part of the studied profile Co and Ni contents increase, in the lower part of the profile Co nad Ni contents increase more, what could be in accordance with higher extraction of Co from mother rock with hydrothermal formation of pyrite in greater depths when compared with Ni. In this connection we refer to the work by B. C a m b e l and J. J a r k o v s k ý (1967), who proved that with higher temperature with pyrite formation the content of Co increases in it.

We represented correlation dependence of the average contents of Co and Ni in pyrites from several localities of the Neogene volcanic complex of central Slovakia in Fig. 4. The overwhelming majority of values fall to the field with value Co/Ni from 1 to 10. They are mainly pyrites observed by us from the vertical profile of the volcanic complex of the Vtáčnik

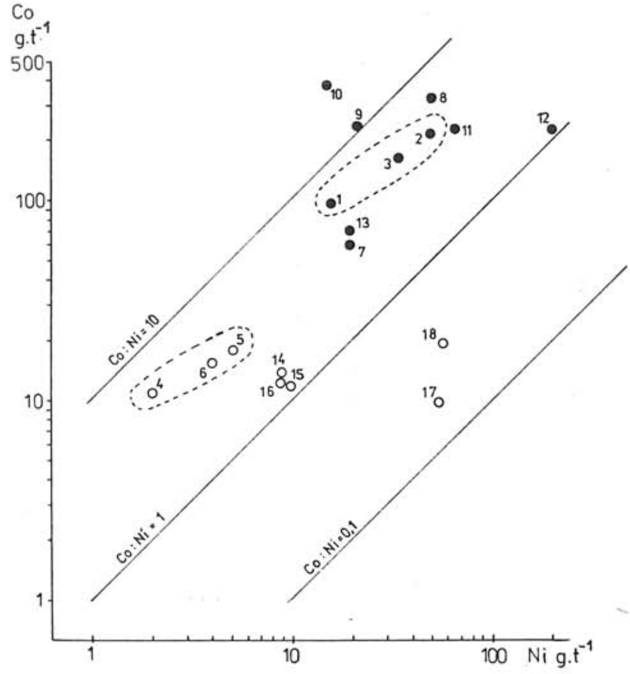

Fig. 4 Correlation diagram of Co and Ni average contents in pyrites and rocks of volcanogenic origin of the West Carpathians.

Explanations: 1 — pyrite from the upper part of the borehole profile (to 700 m); 2 — pyrite from the lower part of the borehole profile (700 — 1400 m); 3 — pyrite from the whole borehole profile (0 — 1400 m); 4 — andesite from the upper part of the borehole profile (to 700 m); 5 — andesite from the lower part of the borehole profile (700 — 1400 m); 6 — andesite from the whole borehole profile (0 — 1400 m); 7 — pyrite from ore veins in Banská Štiavnica; 8 — pyrite from the locality Pukanec (impregnations of pyrite in andesite); 9 — pyrite from the borehole R-23 at the locality Zlatno (impregnations of pyrite in andesite); 10 — pyrite from the borehole D-9 from altered andesites in the central part of Poľana; 11 — pyrite from tuffites at the locality Šobov near Banská Štiavnica; 12 — pyrite from andesites in Kremnica; 13 — pyrite from ore veins in Rudno n/Hronom; 14 — andesites from central Slovakia; 15 — andesites from eastern Slovakia; 16 — andesites from Slovakia on the whole (fresh); 17 — clarke contents of Ni and Co in intermediate rocks (andesite, diorite), according to A. P. V i n o g r a d o v (1962).

mountains, (points 1, 2, 3 in Fig. 4) and their altered mother andesites (points 4, 5, 6) from the same profile. Pyrites from ore veins of Banská Štiavnica and Rudno n/Hronom (points, 7, 13) are of particular position from the view-point of Co/Ni ratio. Of particular position is also pyrite from the Kremnické pohorie Mts. (point 12) where the value of Co/Ni ratio is only a little higher than that of pyrites from tuffs of Šobov near Banská

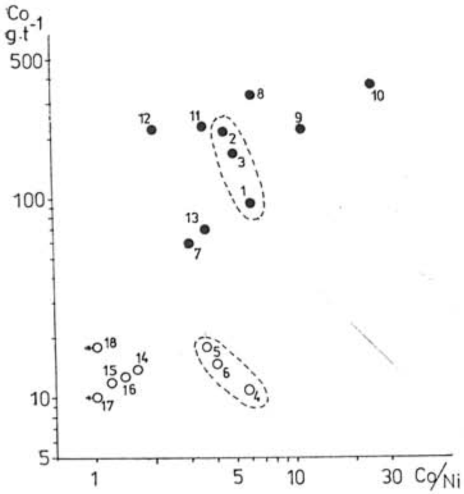

Fig. 5 Correlation diagram of average contents of Co and of ratio Co/Ni of average contents in pyrites and rocks of volcanogenic origin of the West Carpathians.

Explanations as in Fig. 4.

Štiavnica. Unaltered (fresh) andesites of Slovakia have also a relatively low value of Co/Ni (points 14, 15, 16). It may be seen from the graph that pyrite from altered andesites contains a prevalence of Co and Ni on the contrary to mother rocks and the most probable source of Co and Ni in pyrites are the contents of these metals in mother rocks and both elements, mainly Co, show considerable sulphophily in pyrites. Typical of the Neogene volcanism of the West Carpathians is that Co prevails over Ni in andesites and pyrites. The contents of Co and Ni of clarke values from rocks representing andesites and diorites on the whole are plotted in point 17 (according to A. P. V i n o g r a d o v, 1962), exceeding the contents of Ni over Co.

When we plot the content of Co in contrast to Co/Ni in the diagram, we are getting a still more distinct geochemical picture of the particularity of the geochemical — genetical and metallogenetical position of the investigated volcanogenic pyrites on the one hand and of neovolcanic rocks of Slovakia, altered and unaltered, represented by andesites, on the other hand (Fig. 5).

Conclusions

From the study of trace elements in pyrites from altered andesite rocks of the Neogene volcanic complex of Vtáčnik, encountered in borehole MEB - 1 to depth of 1400 m has resulted as follows:

1. From the surface toward depth concentration of Ni, Co, Pb and As increases in pyrites. In Cu only a weak tendency of increasing content in vertical direction appears. Most conspicuosly the tontent of Co, less of Ni increases. The increase in Co and Ni contents toward depth could point to rising temperature of hydrothermal solutions with depth. The higher contents of Pb and As in the lower half of the borehole profile could be in connection with the occurrence of galena, sphalerite and chalcopyrite at several places in the lower half of the borehole profile as well as with distinct primary aureoles of the elements Pb, Zn, Cu, and Ba. If we set out from these considerations, the higher contents of Pb and As in pyrites could represent a wide primary aureole of Pb — Zn — Cu, which would be of great practical importance. In distribution of Mn and Ti no more distinct changes in dependence on the occurrence of Pb — Zn — Cu mineralization have been shown.

2. It would be desirable for the study of distribution of the elements Zn, Ag, Sb, Bi, Mo, Sn, V, Tl, also Pb and As in pyrites to lower considerably the lower analytical detection limit in their analytical establishment. In up to present form the results are of orienting importance only.

3. Between the elements traced in pyrites positive correlation between the contents of Co and Ni is most distinct.

4. The most probable source of Co and Ni in pyrites are the contents of these elements in mother rocks, from which they were released in the process of hydrothermal alterations of these rocks when pyrite formed.

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