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JÁN JARKOVSKÝ*

THE SUM OF Co + Ni + Cu + Mn CONTENTS IN PYRITE — INDICATOR OF PETROMETALLOGENETIC PARTICULARITIES OF ORE MINERALIZATION

(Figs. 4, Tabs. 4)

Abstract: In the work is discussed the problem of relation of pyrite mineralization to the rock environment on the basis of the sum of contents of systematically present microelements in pyrite, Co, Ni, Cu, Mn. It is proved that the sum of the mentioned elements, but mainly of Co + Ni is dependent on the sum of these elements in the maternal and surrounding rocks, in which the ore deposits and occurrences containing pyrite are formed.

Резюме: Автор статьи разбирает проблему соотношения пиритовой минерализации и породовой среды на основе расчета содержаний систематически присутствующих микроэлементов в пирите Co, Ni, Cu, Mn. Доказывается что расчет этих элементов, а найболее Co + Ni зависит от расчета этих элементов в материнских и окружающих породах, в которых возникают рудные месторождения и местонахождения, которые содержают пирит.

In the monographic work about the geochemistry of pyrite the authors B. Cambel and J. Jarkovský (1967) have presented a geochemical characterization of pyrite coming from various genetic and deposit types of sulphide mineralization, mainly from the West Carpathian region. The obtained results they compared with the data from foreign literature and have come to the conclusion, that on the basis of contents of indicator microelements of Co and Ni can be solved the genetic and metallogenetic questions of ore deposits and indications. They were directed to a numerous association of element (Ni, Co, Cu, Mn, Ti, V, Sn, Mo, As, Sb, Bi, Zn, Pb, Ag, Au, Tl).

From the mentioned elements only Ni, Co, Cu and Mn occur in pyrites systematically or relatively often in contents spectrochemically determinable. Therefore we paid attention to these elements in the last time from the viewpoint of their mathematical-statistical treatment on the computer. We obtained so further interesting data about relations of these elements in pyrite from individual genetic types of ore mineralization in the West Carpathians (J. Jarkovský, 1979).

In the presented contribution the subject of our study are the summary contents of Co+Ni+Cu+Mn in pyrite from different rock environments. They are elements, the differences in values of the summary contents of which in pyrite are a suitable criterion indicating the differences in the petrometallogenetic position of deposits and pointing to the differences in individual types of sulphide mineralization in the frame of the same genetic group.

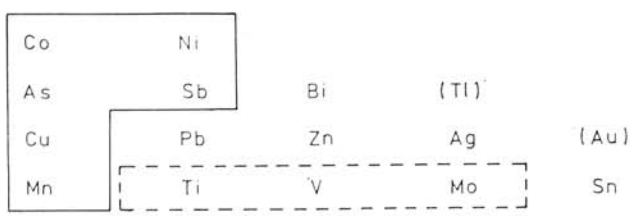
Pyrite as the main and more stable modification of iron disulphide is binding in its crystal structure geochemically related elements with iron,

* Doc. RNDr. J. Jarkovský, DrSc., Department of Geochemistry of the Faculty of Natural Sciences, Comenius University, Paulínyho 1, 881 00 Bratislava.

mainly Co and Ni but also Cu and Mn. We were dealing with the geochemical and crystallochemical aspect of Cu and Mn distribution in pyrites and pyrrhotite in a particular contribution (J. J a r k o v s k ý, 1980).

Cobalt, nickel, copper and manganese are thus elements, which are bound in crystals of pyrite to more or less homogeneous, but Cu, Ni, and Mn with higher contents always occur as heterogeneous. To a certain extent it concerns also cobalt. The mentioned four elements are typical in having common crystallochemical features from the viewpoint of the isostructural character of their sulphides with pyrite — FeS_2 (CoS_2 — cattierite. NiS_2 — vaesite. MnS_2 — hauerite, CuS_2 — fukuchilite). This is reflected chiefly from the geochemical viewpoint in the fact that Co, Ni, Cu and Mn are in pyrite the most frequent elements.

When we range association of elements in pyrite traced by B. Cambel and J. J a r k o v s k ý (1967) according to the criterii of the forms of their occurrence in this sulphide, we receive such a scheme:



The elements framed with full line have a direct crystallochemical relation to the crystal structure of pyrite, taking up (replacing) the positions of Fe atoms in low (Co, Ni) and very low contents (Cu, Mn) on the one hand, the positions of S atoms in low (As) and very low contents (Sb) on the other hand. Elements framed with interrupted line have a certain, also when experimentally not proved crystallochemical relation. This is testified by the data from pyrites occurring immediately in the rock environment containing these elements. There is a syngenetic (e.g. Smolník) but also specific epigenetic ore mineralization, e.g. pyrite from hydrothermally altered volcanic rocks of central Slovakia (Vtáčnik Mts.). It results at last also from the position of these elements, mainly of Ti and V in the periodical system of elements. On geochemistry of Ti in pyrite from hydrothermally altered volcanic rocks of the Vtáčnik Mts. we prepared for publication a particular information (J. J a r k o v s k ý — J. F o r g á č — D. J a n č u l a).

Finally, also the other in the scheme not framed elements display a certain relation to pyrite, because this disulphide accumulates them in certain contents, the value of which depends mostly from the surrounding environment of mineral association of the maternal rocks. There are essentially elements with heterogeneous position in pyrite in form of fine inclusions or present in form of colloids more or less individualized, the mineralogical identification of which is practically impossible at the contemporaneous level of technical equiment of geochemical laboratories.

Table 1

Represented are the average vaules of the sum of element contents in g/t from the number of analyses mentioned in the last but one column of the table, in cases with one analysis this value was mentioned

Ore district-locality	Genetic type — type of ore mineralization— surrounding rocks	Co+Ni+Cu+ +Mn	Co+Ni	Cu+Mn	Number of analyses	Designation in Fig. 1
Low Carpathians — Pezinok, Cajla, Pernek	syngenetic pyrite— graphite schists, graphite phyllites	2231	1659	572	172	1
Low Carpathians — Pezinok, Cajla, Pernek	graphite— quartz— sulphidic	1763	1272	491	30	a
Low Carpathians — Pezinok, Cajla, Pernek	amphibole-sulphidic	2066	1715	352	30	b
Low Carpathians — Pezinok, Cajla, Pernek	quartz-sulphidic	3036	2111	926	32	c
Low Carpathians — Pezinok, Cajla, Pernek	mineralized amphibolites	2868	2441	427	11	d
Low Carpathians — Pezinok, Cajla, Pernek	mineralized graphite schists	1671	1011	660	16	e
Low Carpathians — Pezinok, Cajla, Pernek	impregnation mineralization	1248	979	329	18	f
Low Carpathians — Pezinok, Cajla, Pernek	combination of older syngenetic with younger Sb-mineralization	2292	1611	681	11	g
Low Carpathians — Pezinok, Cajla, Pernek	re-migrated older mineralization	2312	1703	609	24	h
Low Carpathians-various localities	epigenetic-hydrothermal	1979	1142	851	31	2
Častá	polymetallic-phyllites and schists of the Harmónia group	2311	1027	1284	7	a
Cajla	Sb-ores, quartz-graphite schists	797	384	413	12	b

Continuation of Tab. 1

Ore district-locality	Genetic type — type of ore mineralization — surrounding rocks	Co + Ni + Cu + + Mn	Co + Ni	Cu + Mn	Number of analyses	Designation in Fig. 1
Pernek	Sb-ores, quartz, carbonates in proximity amphibolites	3307	2108	1200	5	c
Marianka	pyrite from phyllites	587	257	330	3	d
Hrubá dolina valley	pyrite from granites	2640	1890	750	2	e
Lošonc	pyrite from melaphyre	2450	1320	1130	1	f
Hrubá dolina valley	pyrite from Mesozoic limestones	248	8	240	1	g

In connection with these relations the question of the petrometallogenetic character comes to the foreground, thus the question of material influence of the surrounding rocks on pyrite mineralization and ore mineralization at all. Several deposits from the region of the West Carpathians can be mentioned, from which geochemical data on microelements in pyrite are available (B. Cambel — J. Jarkovský, 1967). Relative most data were gathered from pyrite deposits of the West Carpathians (Pezinok, Pernek — Little Carpathians, Heľpa — Low Tatra, Smolník, Mníšek — Spišsko-gemerské rudohorie Mts.), but also from hydrothermal plutonic and subvolcanic ore mineralizations. Recently we investigated pyrite in 39 samples from a deep borehole (1480 m) located in hydrothermally altered volcanic rocks of central Slovakia (J. Forgáč — J. Jarkovský, 1981).

The data about the sum of contents of traced elements in pyrite we document numerically and graphically. For simplification and clear treatment of the obtained data we present them in form of the sum of the average (arithmetic) contents. Individual samples of pyrites or their analytical data locally reflect the material composition of the given rock environment, which changes from place to place more or less. On an average, howecer, they trustworthy characterize the geochemical picture of pyrite from certain deposit or occurrence, situated in the given rock environment.

In tables we mention the data in 3 columns. The first of them contains the sum of average contents Co + Ni + Cu + Mn (g/t). The other columns contain a couple of average contents Co + Ni and Cu + Mn. From these data is to be seen, with

Table 2

Represented are the average vaules of the sum of element contents in g/t from the number of analyses mentioned in the last but one column of the table, in cases with one analysis this value was mentioned

Ore district-locality	Genetic type — type of ore mineralization— surrounding rocks	Co + Ni + Cu + + Mn	Co + Ni	Cu + Mn	Number of analyses	Designation in Fig. 2
Low Tatra — Heľpa	syngenetic-pyrite-rocks of basic character	2426	1550	910	36	3
Low Tatra — Heľpa	graphite-quartz-sulphidic	2840	1240	1210	12	a
Low Tatra — Heľpa	mineralized amphibolites	1410	970	2590	9	b
Low Tatra — Heľpa	mineralized gneisses	3359	2800	559	4	c
Low Tatra — Heľpa	quartz-sulphidic	2520	1420	1100	11	d
Low Tatra — various local. together	epigenetic-hydrothermal	2431	1432	1048	22	4
Dúbrava, Magurka, Medzibrod	Sb-mineralization in crystalline schists and granites	413	69	344	7	a
Staré Hory	quartz, concretionary marcasite — Permian	1370	60	1310	1	b
Polkanová	siderite, chalcopyrite, quartz — Permian	8020	6600	1420	1	c
Jasenie	polymetallic ore mineralization in gneisses to migmatites	1492	436	1056	3	d
Trangoška	polymetallic ore mineralization in crystalline rocks- granitoids, migmatites	3742	2575	1167	2	e
Kumštová dolina valley	barite with siderite and specularite— migmatites with layers of amphibolites	7840	6600	1240	1	f
Malužiná	pyrite in barite from melaphyres	7530	6600	930	1	g

Table 3

Represented are the average vaules of the sum of element contents in g/t from the number of analyses mentioned in the last but one column of the table, in cases with one analysis this value was mentioned

Ore district-locality	Genetic type — type of ore mineralization— surrounding rocks	Co+Ni+Cu+ +Mn	Co+Ni	Cu+Mn	Number of analyses	Designation in Fig. 3
Spiško-gemerské rudohorie Mts. — various localities	syngenetic—pyrite	1535	292	1243	60	5
Smolník	pyrite mineralization in chlorite schists and phyllites	1216	255	961	35	a
Mníšek— Jalovičí vrch hill	ditto, less pyrite	798	191	607	6	b
Mníšek— Hutná dolina valley	pyrite mineralization + chalcopyrite in chlorite schists	2363	332	2031	7	c
Mníšek— Prakovce	pyrite mineralization in chlorite schists	2591	537	2054	5	d
Mníšek— Bystrý Potok	polymetallic mineralization in quartz porphyries, porphyroids and their tuffs	1607	995	612	7	e
Spiško-gemerské rudohorie Mts. — various localities	epigenetic-hydrothermal-Palaeozoic rock-complex	2185	1382	803	55	6
Rudňany generally	predominating chlorite and chlorite-sericite phyllites alternating with volcanic members of basic chemical characteristics	2976	1974	1002	35	a
Rudňany— Droždiak, generally	ditto	3407	2446	961	24	b
Rudňany—Droždiak, 10. horizon	ditto	2067	1375	692	7	c
Rudňany—Dorždiak, 16. horizon	ditto	4156	3033	1123	6	d

Continuation of Tab. 3

Ore district-locality	Genetic type — type of ore mineralization — surrounding rocks	Co + Ni + Cu + + Mn	Co + Ni	Cu + Mn	Number of analyses	Designation in Fig. 3
Rudňany—Zlatník	ditto	2002	798	1204	9	e
Rožňava	predominating rocks of the Gelnica group, mainly graphite schitst	1794	1441	353	7	f
Nižná Slaná	ditto	2288	1631	657	3	g
Novoveská Huta	predominating Permian rocks	2715	1340	1375	2	h
Perlová dolina valley (Grellenseifen)	rocks of the Gelnica group	1561	392	1169	2	i

which part in pyrite the mentioned couples of elements are sharing. They point to the particularity of pyrite mineralization in various environments, which formed under various conditions in dependence on several factors of geological and physical--chemical character.

The individual tables (Tabs. 1—4) are compiled so that first the total group of pyrites from pyrite deposits of syngenetic origin from one ore district are mentioned. This group is divided into competent partial groups of pyrite representing the individual types of pyrite mineralization. In the same table further the total group of epigenetic (hydrothermal) pyrite mineralization from the same ore district and the competent partial groups representing the individual localities of the given area with hydrothermal mineralization follow. For clearness the numerical data from the tables are represented also graphically (Figs. 1—4).

Discussions to the tables and graphs

In Tab. 1 are mentioned and in Fig. 1 graphically represented the competent data of summary average content of the observed elements in pyrite from syngenetic (pyrite) and epigenetic (hydrothermal) mineralizations of the Low Carpathians (Malé Karpaty Mts.). From the graphical data distinct differences between the syngenetic and epigenetic pyrite mineralization result. Whilst in the frame of syngenetic ore mineralization smaller oscillations in chemical composition of pyrites caused by variability of the material composition of rocks of basic ophiolite volcanism and influenced by metamorphism of ores as a consequence of intrusion of granite magma, in the frame of hydrothermal mineralizations greater

Table 4

Represented are the average values of the sum of element contents in g/t from the number of analyses mentioned in the last but one column of the table, in cases with one analysis this value was mentioned

Ore district-locality	Genetic type — type of ore mineralization — surrounding rocks	Co+Ni+Cu++Mn	Co+Ni	Cu+Mn	Number of analyses	Designation in Fig. 4
Other ore districts or their parts generally	syngenetic	3606	2552	1058	16	7
Western Tatra—Žiarska dolina—valley	syngenetic-mineralized amphibolites	3010	2725	285	5	a
Polhora near Tisovec—(Nogová dolina—valley)	syngenetic-mineralized amphibolites and gneisses	3523	1637	1850	8	b
South-western part of the SGF —Šankovce near Jelšava borehole VS—1	syngenetic- Meliata group —pyrite in anhydrite, underlain by haematite deposit, in proximity serpentinite	4877	4610	267	3	c
Veporide zone near Tisovec	epigenetic-hydrothermal, various types of crystalline rocks	1593	1034	559	17	8
Veporide zone near Tisovec	pyrite from quartz veins in various types of crystalline rocks	1130	546	584	9	a
Veporide zone near Tisovec	pyrite from talcs	2160	1630	530	8	b
Veporide zone near Tisovec	pyrite from Palaeozoic limestones	490	180	310	1	c
Ľubietová	gersdorffite, chalcopyrite in silicified gneisses to migmatites	6322	5170	1152	2	d
Osrblie	ankerite veinstuff with sulphides in granitoids	1388	8	1380	1	e
Poniky—Drienok	pyrite in Triassic limestones with galena, sphalerite, chalcopyrite, rhodochrosite	2506	407	2099	3	f

Continuation of Tab. 4

Ore district-locality	Genetic type — type of ore mineralization — surrounding rocks	Co+Ni+Cu+ +Mn	Co+Ni	Cu+Mn	Number of analyses	Desig-nation in Fig. 4
Vtáčnik mountains, Prochoť, borehole MEB-1 depth 1480 m	epigenetic-pyritization in hydro-thermally altered volcanic rocks	350	196	154	39	9
Upper part of borehole to 700 m	predominating hypergenic alterations	254	111	143	18	a
Lower part of borehole fom 700 m to 1480 m	predominating hydrothermal alterations	433	269	163	21	b
Vtáčnik mountains — Prochoť, borehole MEB—1 depth 1400 m	hydrothermally altered volcanic rocks	935	18	917	Mn 30 120	10
Upper part of borehole from 170 m to 700 m	predominating hypergenic alterations	723	15	708	Mn 17 53	a
Lower part of the borehole from 700 m to 1400 m	predominating hydrothermal alterations	1220	23	1197	Mn 13 67	b

The data in the last column designated with 9 a, b indicate the sums of element contents in pyrite; the data indicated 10 a, b concern the sums of element contents in maternal volcanic rocks.
The data on the number of analyses in Mn are mentionel particularly. They were adopted from silicate analyses, of which MnO was converted to Mn.

oscillations in composition of pyrite in consequence of considerable heterogeneity of mineral composition of the surrounding rocks, in which pyrite formed, occur. From the mentioned results, that the syngenetic pyrite mineralization of the Low Carpathians divided into sub-groups according to geological position and mineralogical criterii (1 a—h in Fig. 1) is characterized by a relatively monolithic block also in spite of certain variation caused mainly by

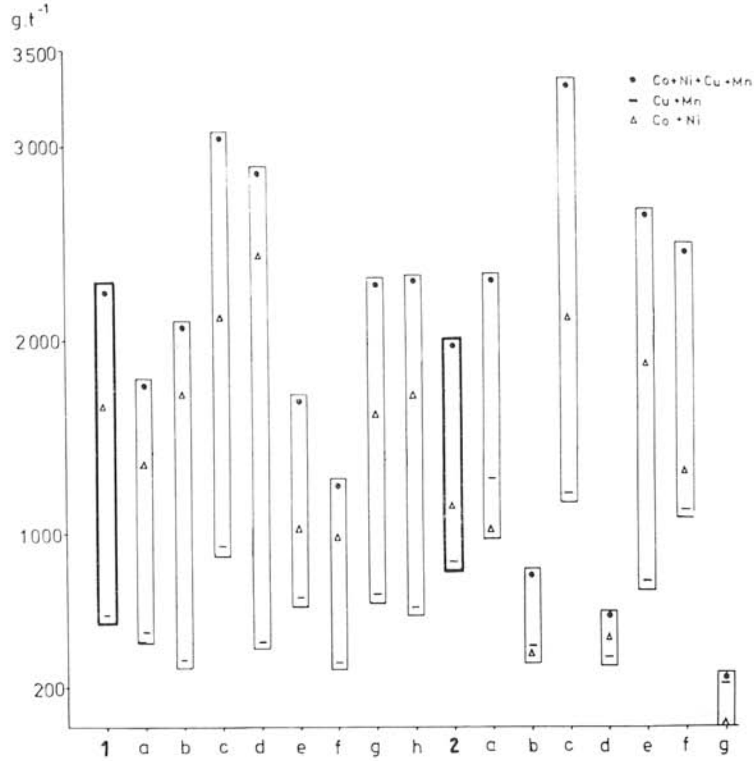


Fig. 1. Column diagram of the sum of contents of the traced elements in pyrite of syngenetic and epigenetic origin from the deposit region of the Low Carpathians.

Explanations: On the horizontal axis for clearness the sums of element contents in the individual groups and subgroups are framed in form of columns. The main groups are drawn with thicker line and designated with Arabic numerals; the sub-groups are drawn with thinner lines and designated with small letters.

metamorphism of ores. Due to the process of metamorphism the petrometallogenetic factor was weakened or obscurred to a certain extent, which distinctly is shown in case of epigenetic pyrite originated in hydrothermal way (graphs 2 a—g in Fig.1). Here also the difference in pyrite from Sb-mineralizations of Cajla and Pernek is to be seen.

Whilst pyrite from Sb-mineralization of Cajla is characterized by relatively low values of summary contents of the traced elements, pyrite from Sb-mineralization of Pernek shows considerably higher values (Fig. 1, columns 2 b, c). It may be explained by the fact, as mentioned by B. Cambel (1959), that the hydrothermal solutions in case of pyrite from Pernek were enriched in iron subsequently when passing through rocks with the content of earlier pyrite mineralization. In other cases, as it is evident from the columns in Fig. 1, in origin of hydrothermal pyrite mineralization mainly the petrome-

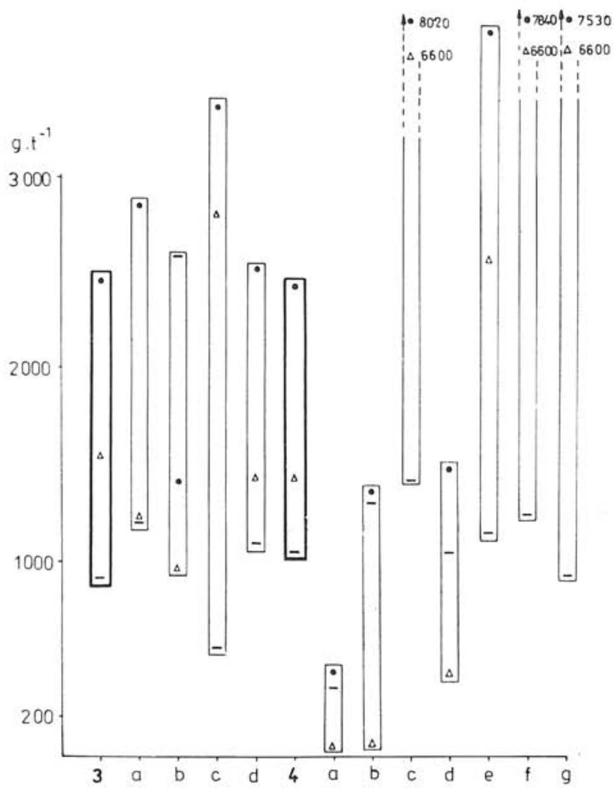


Fig. 2. Column diagram of the sum of contents of the traced elements in pyrite of syngenetic and epigenetic origin from the deposit area of the Low Tatra.

Explanations: ditto as in Fig. 1.

tallogenetic factor had an influence, by which the character of solutions was conditioned (sericite-graphite phyllites of the Harmónia group, granitoids, limestones and further ones).

In Tab. 2, Fig. 2 is presented the numerical and graphical documentation of the syngenetic and epigenetic pyrite mineralization from the ore district of the Low Tatra. Similarly as the syngenetic pyritization of the Low Carpathians in this case also (Heľpa) pyrite forms different types of syngenetic ores (Fig. 2, columns 3 a—d). These are analogously as those from, the Low Carpathians characterized by a relative uniform block, but are metamorphosed into a higher grade. The epigenetic pyrite mineralization of the Low Tatra has a very different picture, depending on the character of hydrothermal solutions ascending through various rock types (granitoids, gneisses, migmatites, Permian complexes and others). Interesting are in contrast to the Low Carpathian hydrothermal ore mineralization, pyrites with a relatively high content mainly of Co + Ni (Fig. 2, columns 4 c,f,g).

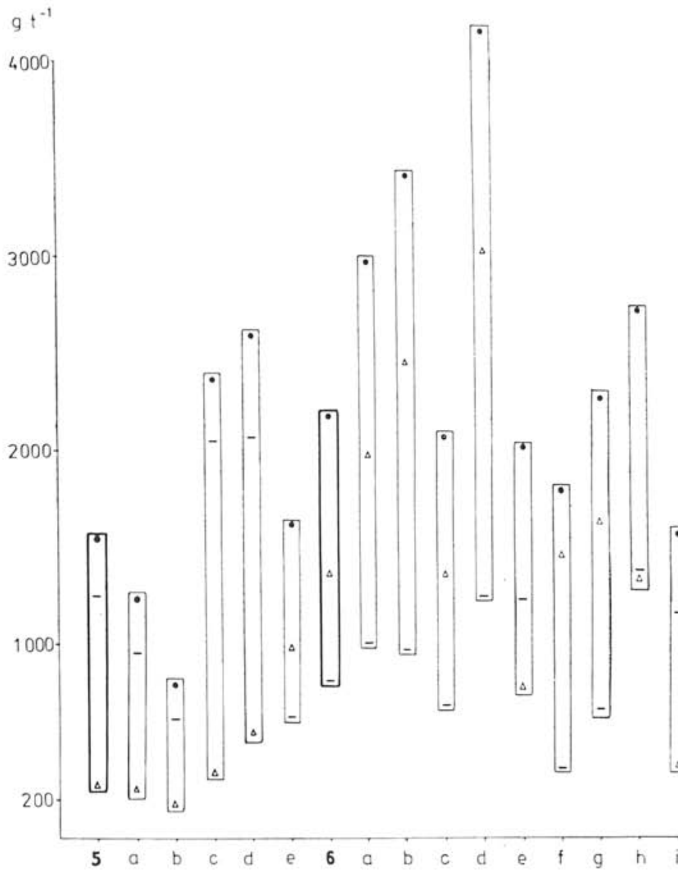


Fig. 3. Column diagram of the sum of contents of the traced elements in pyrite of syngenetic and epigenetic origin from the deposit area of the Spišsko-gemerské rudohorie Mts.

Explanations: ditto as in Fig. 1.

The further traced group are pyrites of syngenetic and hydrothermal origin of the Spišsko-gemerské rudohorie Mts. (Tab. 3, Fig. 3). Fig. 3 (columns 5 a—e) shows that syngenetic pyrites from the deposit area of Smolník have relatively low values of the average contents of the studied elements. The deposit area of Smolník is situated in the upper part of the southernmost strip of Silurian dark schists of the Gemerides alternating with volcanogenic basic rocks. The bearer of pyrite- chalcopyrite mineralization are chlorite schists (J. Ilavský — S. Polák, in Slávik et al., 1967). The relation of pyrite mineralization and alternating surrounding rocks thus determine together with manifestations of a relatively low-grade metamorphism the sum of contents of elements in pyrite. In the subgroups of syngenetic pyrite

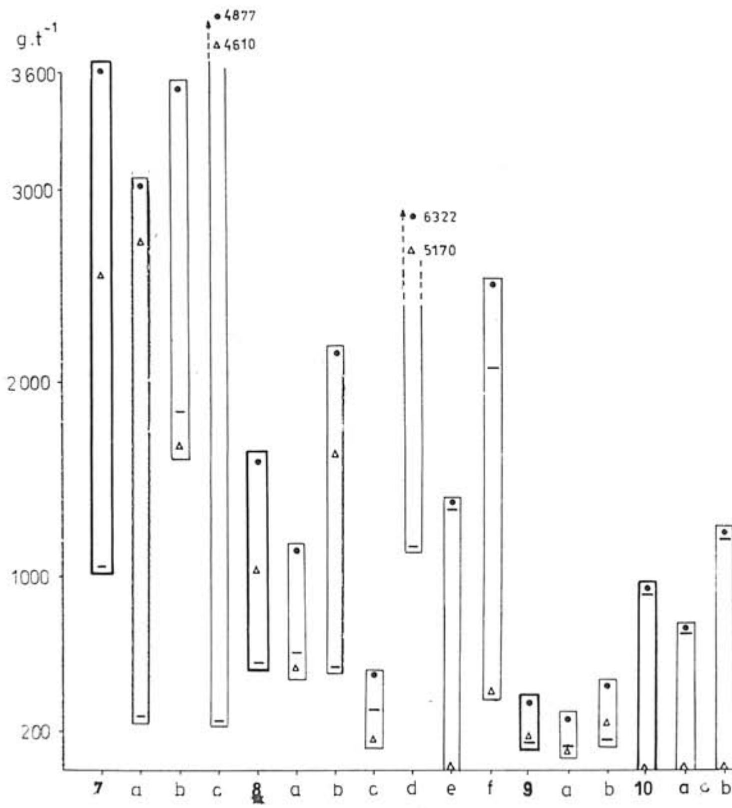


Fig. 4. Column diagram of the sum of contents of the traced elements in pyrite of syngenetic and epigenetic origin from the areas of the Western Tatra, Veporské pohorie Mts. and Vtáčnik Mts.

Explanations: ditto as in Fig. 1. Designation 9 a, b concerns pyrite, 10 a, b — maternal volcanic rocks.

of the Spišsko-gemerské rudohorie Mts. compared with the syngenetic pyrites from the Low Carpathians and Low Tatra, a greater variation of the traced values is evident. From the petrometallogenetic viewpoint it can be cleared up in a way, that whilst e.g. the pyrite mineralization at the Jalovičí vrch hill near Mníšek is located prevailingly in rocks of acid volcanism (tuffogenic rocks, tuffites, quartz porphyries), the ore mineralization in Prakovce and the Hutná dolina valley near Mníšek is accompanied by more basic members.

In the Tab. 4, Fig. 4 we show the competent data of syngenetic pyrite from mineralized amphibolites of the Žiarska dolina valley in the Western Tatra (column 7 a) and from the Nogova dolina valley near Tisovec (column 7 b), further data of syngenetic pyrite from Šankovce near Jelšava (column 7 c). Table 4 and Fig. 4 include then data of pyrite of epigenetic origin from various crystalline rocks of the Vepor zone near Tisovec, as well as from other localities of the Veporské pohorie mountains (Ľubietová, Osrblie, Poniky—Drienok).

Finally, in Tab. 4 and Fig. 4 we present data of the sum of contents of the traced elements in pyrite (column 9 a,b) as well as in their maternal rocks — hydrothermally altered volcanics of the Vtáčnik mountains (column 10 a,b). In all the mentioned cases are to be seen considerable differences in the sum of contents of the traced elements, but mainly of Co + Ni.

A particularly interesting case are pyrites and maternal volcanic rocks from the Vtáčnik mountains. It has been shown, that the competent data completed by the data of the ratio of Co/Ni contents in pyrite and mother rocks testify to that the source of the elements traced in pyrite are their maternal volcanic rocks. The mentioned rocks as a consequence of decomposition of femic minerals by hydrothermal solutions provided for formation of pyrite not only the fundamental element — iron, but also trace elements, mainly Co and Ni. Co and Ni in pyrite, on the contrary to mother rocks, were enriched almost 11 times, only confirming their role and crystallochemical properties in formation of iron disulphides under conditions of hydrothermal activity. When we valuate relation between pyrite and the mentioned mother rocks on the basis of sum Co+Ni+Cu, then the sum of these elements in pyrite is by 5.2 times higher in contrast to the competent rocks. As a consequence of its chalcophyllic properties a part of Cu passed from rocks into pyrite. As to Mn, this element, as known, displays lithophyllic properties also under conditions of hydrothermal activity and consequently passes in the essential part into secondary silicates or carbonates and only an insignificant part of Mn comes from rocks into pyrite.

Conclusions

The data obtained about the sum of contents of systematically present elements in pyrite, Co, Ni, Cu, Mn, testify that the microchemical characteristics of pyrite mineralization reflect the material composition of surrounding rocks. The summary contents of the mentioned elements in pyrite inform in which rock environment pyrite formed and what is the degree of the petrometallogenetic effect under the given geologic and thermodynamic conditions.

Finally the summary content of the traced elements in pyrite provides not only information for theoretic metallogenetic study, but on the basis of these data can be valuated the given ore mineralization containing pyrite from the viewpoint of possibilities of its potential utilization.

It would be possible to decipher more profoundly and more in detail the mentioned relations only then, when we knew the macro-and micro-chemical characteristics of rocks, however, mainly in Co, Ni, Cu, Mn. It would be ideal to know the contents of these elements in individual rock-forming minerals of the given rocks.

Translated by J. Pevný

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