BOHUSLAV CAMBEL, JÁN JARKOVSKÝ*

THE POSSIBILITY OF UTILISING OF THE NICKEL AND COBALT IN PYRITES AS INDICATORS OF ORE GENESIS

(Textfigs. 1-13)

Abstract: Submitted work presents information of results following from geochemical investigation of pyrites confirming possible clearing of deposit genesis problems on basis of Ni and Co contents (genetic classification of deposits and genetic conditions of pyrite rise, respectively conditions of metamorphosis, which the deposit had undergone).

In this report principal conclusions on the geochemistry of pyrites from West Carpathian deposits and from other regions of Czechoslovakia are submitted. On the whole about 800 quantitative spectrochemical analyses on the following elements have been carried out: Ni. Co. Mn. Mo. V, Ti. Ag. Cu, Pb, Zn, Sb. Bi, Sn, Tl. As and Au. The most detailed investigations have been carried out in Little Carpathians. From this region we have carried out numerous analyses. About 250 analyses enabled a comparison of pyrite analyses from various parts of deposits, from various types of ores and from differently metamorphosed ores. We compare the results with genetically analogous ore deposits of pyrite formation, especially with pyrites from Helpa, Smolník, Chvaletice, Zlaté Hory and other deposits. There are older metamorphosed deposits derived at least from Paleozoic, the genesis of which is connected with geosynclinal, for the most part submarine magmatism. For the purpose of comparison also fundamental data and diagrams of quantitative representation of nickel and cobalt on some occurences of unmetamorphosed, sedimentary pyrite and of pyrites from various hydrothermal deposits, mainly from West Carpathians are presented.

The authors put the task to examine the up to date conclusions of F. Hegemann (1943) according to which cobalt and nickel in pyrite may be applicated for determining of genesis of pyrite as well as of the stage ore metamorphosis.

In Little Carpathians the pyrite mineralization appears in coherent zones along the extension of amphibolic rocks having syngenetic, geosynchinal, submarine volcanogene character. The orebearing zones are intersected by protrusions or dikes of granitoid rocks derived from variscian orogene. The granitic intrusion had a dominant influence on the metamorphosis of rocks and ores of pyrite formation. By its influence arose amphibolites from epizonal metamorphosed products of diabase magmatism. The alteration of ore manifested under intesive influence of metamorphosis by the rise of pyrrhotite and silicate minerals as amphibole, biotite, muscovite, less of feldspar and other minerals. Since the main cause of metamorphosis in Little Carpathians had been periplutonic contact metamorphism sudden changes of the intensity of metamorphism influence on ores took place depending on the distance from the direct contact between ore-bearing zones and granitoid magma.

Therefore different stages of ore metamorphosis are found in one ore zone. There is the opportunity to investigate the recrystalisation and the geochemical influence of metamorphosis on ores. On the whole are distinguished there:

Firstly: graphite — quartz — sulphidic ores with abundant substance of graphite, resp. carbon. Characteristic of these ores ist that pyrite doesn't alterate to

^{*} Prof. Dr. B. Cambel, DrSc., Geological Institute of the Slovak Academy of Sciences, Bratislava, Obrancov mieru 41. Dr. J. Jarkovský, CSc. Scientific Research Institute for Geology and Geography, Faculty of Natural Sciences, Komenský University, Bratislava, Gottwaldovo nám. 2.

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pyrrhotite also under conditions of higher-grade metamorphosis because carbonaceous component had negative influence on recrystalisation. Therefore this type of ore is with regard to its common association of microelements close to original composition of ore. The other minerals being present are \pm quartz, \pm amphibole, \pm biotite, \pm muscovite, \pm feldspar, \pm carbonates and further secondary products arisen from above mentioned minerals (sericite, chlorite).

Secondly: amphibole — sulphidic ores, tending easier to metamorphic recrystalisation; why under higher-grade thermodynamic conditions a part of pyrite alters to pyrrhotine.

Thirdly: quartz — sulphidic ores with the fundamental minerals quartz, pyrrhotite and pyrite. Relatively abundant are biotite and muscovite. By these ores with the metamorphosis also easily recrystalisation takes place and pyrite alters to pyrrhotite.

Fourthly: As a particular type are mentioned accessoric pyrites in magmatogene amphibolites resp. dissipated ores in pyroclastic-sedimentogene actinolite and amphibole schists.

Hifthly: this type of ore is represented by pyrite mineralization in gneiss- with variable contents of actinolite and graphite. There is a typical sedimentary and partly biogeochemical type of ore.

Sixthly: the geochemical investigations have shown that a part of so called disseminated ores — in hydrothermal — altered amphibolites and actinoliteschists were a product of old propylitization simultaneous with geosynclinal, ophiolite volcanism (6, type).

The seventh type of ore includes secondary mobilised pyrites in veins or their accumulations.

To the eight type of ore belong younger hydrothermal postgranitic pyrites with Sb or Pb-Zn mineralization.

The ores from Helpa are similar to the ores from Little Carpathians but catazonal metamorphosed and have many pyrrhotites. The deposit is confined to amphibolites located in the region of Nizke Tatry mountains (Low Tatra) in biotite-garnet-sillimanite paragneiss and migmatitic gneiss.

The pyrites from Smolník in Spišsko-gemerské rudohorie mountains are of dissipated character lying in chlorite schists with monocrystals of pyrite of various size (2-3 mm); besides that there are also dense pyrite ores in banks and conformable lense-shaped layers. The deposit in its whole extension was uniformly epizonal metamorphosed.

Concerning Bohemian massive we have analysed the pyrites from Chvaletice. This deposit is situated in Algonkian schists in Zelezné hory mountains. There are quartzose schists with intercalations of green rocks and amphibolites as metamorphic products of submarine, ophiolite magmatites.

The pyrite and chalkopyrite deposits of Zlaté hory are situated in Jeseník mountains in East Sudetian metallogenetic district in Devonian phyllites, quartzites and metamorphic products of quartz porphyries and keratophyries. Since 3—4 years this mineralization has been ascribed to pyrite formation. Severe authors (Havelka. Palas, Scharm, Fojt) take them for geosyclinal-submarine-syngenetic and also our investigations confirm this opinion.

From our geochemical investigations follows that trace elements in pyrites —
especially the quantities of Ni and Co — may be very significant for the solving of
genetical questions. According to Ni and Co contents in pyrites of unmetamorphosed or

only little metamorphosed ores can be determined the intensity of metamorphosis. It is possible even to establish whether the pyrite mineralization originated before or after the metamorphosis. It has been proved that syngenetic pyrites have a relatively stabilized representation of microelements — mainly of Ni and Co and statistical data confirm that with progressive metamorphosis the contents of cobalt in pyrites increases more or less successively but the contents of nickel remains constant for the beginning. As soon as a certain stage of metamorphosis has been attained decreases the contents of nickel quickly and with recrystalisation of pyrites the nickel level falls under the cobalt level.

2. It follows that the regularity in representation of microelements contents, especially of Ni and Co, in pyrites appears as decisive factor in the determination of sedimentogene origine of ores. It has been proved that this regularity of Co- and Ni- contents in pyrites could be different in different paragenetic types of ore on one pyrite deposit. Irregular metamorphosis on the deposit may cause irregular distribution of these elements and their dispersion resulting in incorrect inclusions about deposit relations. Therefore the relations of geochemical distribution of elements can be established only by geochemical investigation, by means of numerous analyses having accurate knowledge of the geology of deposit but by no means only on basis of incomplete occasional sampling.

By each type of metamorphosed sedimentary syngenetic ore is decisive the primary level of Co and Ni in pyrite depending on the character of magmatism and different on different deposits; it is mostly specific for each separate deposit. Therefore the prevailing of cobalt in contradistinction to nickel in metamorphosed ores is not only a result of metamorphosis but also depends on primary Ni contents in pyrite. By the majority of deposits and occurences but can be taken for right the oppinion of H e g emann supposing a certain limit of Co- and Ni-contents characteristic of sedimentary pyrites (0.002~0/0~Co~and~0.02~0/0~Ni). An exception of this rule are the pyrites of Little Carpathians, which had before metamorphosis also higher Ni contents, although they are of syngenetic-sedimentary origine.

- 4. The particular deposits may have besides Co and Ni also further elements. They can characterize the mineralization of particular deposits. A characteristic element of the pyrites on pyrite deposits of the region of Little Carpathians is e. g. Mo but younger hydrothermal pyrites of antimonite mineralization of Little Carpathians have no Mo or only contents under the limit of analytical determinability. The younger hydrothermal pyrites are characterized by higher As contents. The polymetallic elements are characteristic of the pyrites of Smolník (Pb, Zn, Sb, Bi, As, Au). The Chvaletice deposit is characterized by higher Mn contents. It follows there that the association of microelements in pyrite is specific for specific deposits. In similar way other microelements may be applicated for the drawing of geochemical-genetic conclusions. The association of microelements in pyrite of one metallogenetic district can serve as distinctive mark for pyrites belonging to one or another metallogenetic phase. The presence of further elements in pyrites irrespective of being isomorphous or heterogeneous admixture also enables to characterize distinct types of deposits, mineralizations or periods of mineralization.
- 5. On basis of hitherto carried out geochemical investigations and detailed exploration of deposits of Little Carpathians has been proved that on one ore deposit or one ore district with geosynclinal, syngenetic pyrite meneralization appeared genetically different types of ore. It depends on more or less complicated influence of geosynclinal initial magmatism altering with time and space and manifesting in various manners. The

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genetic changeableness has been also heightened by differently intensive metamorphic processes. Therefore changes the primary geochemical association of microelements also on one deposit. We have to take in account also a combination of older and younger mineralization in ore-bearing regions since older, syngenetic ores and ore zones due to their tectonics and lithology frequently were not accessible to ore accumulation by younger ore forming processes.

6. Secondary (mobilised) pyrites or concretionary accumulations show different distribution of elements in contrary to unmobilised pyrites. This difference in the association of microelements depends on the character of ore mineralization and on PT conditions of ore transportation. Unmigrated pyrites can be weakly enriched or

impoverished on microelements.

A geochemical peculiarity signify the concretions in sediments (clays, coal, limestones) or also in metamorphites. They arose also by mobilisation of sulphides in rocks with diagenesis or metamorphosis. Geochemically the concretions represent therefore not always typical sedimentogene pyrites. Normal syngenetic pyrites have namely in contradistinction to concretions a monotonous, relatively stable contents of microelements as it was already established by F. Hegemann (1943).

It appears also that not only syngenetic-volcanogene, geosynclinal pyrite mineralization but also some Neogene subvolcanic ore mineralizations (e. g. in West Carpathian volcanites—Štiavnica) have pyrites with relatively uniform, characteristic contents of microelements.

Opposite to that are hydrothermal pyrites of plutogene origine very variable and the contents of microelements are influenced by rock wall, relations of temperature of solutions, periodicity of ore mineralization. Plutogene hydrothermal pyrites have Ni and Co contents irregularly distributed. Moreover follows that distinct layers or distinct regions have pyrites with certain specific geochemical contents of microelements having diagnostic signification for the characteristic of the whole metallogenesis or only of some mineralization periods.

Closing it is emphasized that the investigation of microelements in pyrites provides very interesting data on the metallogenesis only with well known geology and mineralogy of the deposit and applicating numerous carried out analyses.

The preparation of the pyrites samples and the analytical results were made by the following methods:

Separation Method

For separation of pyrite from accompanying minerals in ore or in rocks combined method has been applicated, consisting of hand choice by weezers under binocular microscope, of mechanical separation by water stream, of magnetic division, chemical division by admixture of diluted HCl and concentrated HF and at last by means of heavy liquids (bromoforme, methylenjodide). With present fine intergrowing quartz, silicate minerals and soluble sulphides another detailed homogenization in agate dish has been carried out and mentioned combined separation method has been repeated. Pyrite sample containing finely intergrown chalcopyrite and other minerals insoluble in admixture of mentioned acids has not been analysed. Pyrite has been distinguished from marcasite chemically or roentgenographically.

Spectrochemical Quantitative Method

For ascertaining of trace elements in pyrite spectrochemical quantitative method in three different variants has been applicated. In first phase of geochemical investi-

gation the first variant of the method has been elaborated, consisting of Co, Ni, Mn, Mo, V, and Ti ascertaining. Separated pyrites by this method have been roasted in muffle roaster on Fe₂O₃ and competent standards have been prepared also on basis of Fe₂O₃. Excitation has been carried out in d. c. arc of 220 V at 6 A, supporting electrode has been put in to positive pole of source, preexposition 60 sec., exposition 40 sec. These analytical lines were applicated: Co 3044.0 Å, Ni 3414.7 Å, Mn 2801.0 Å Mo 3170.3Å V 3183.9 Å and Ti 3361.2 Å.

As internal standard choiced Fe lines were applicated. Calibration curves have been constructed on basis of Δ Y values against log c. The reproducibility at particular ascertainments did not exceed \pm 15 0 /₀. The correctness control of ascertaining of some elements has been carried out by polarographic and colorimetric method.

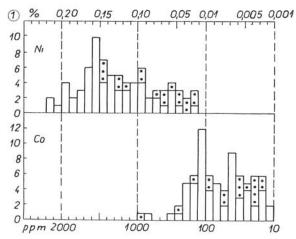


Fig. 1. Histogram of Ni and Co contents in pyrites of graphit-quartz-sulphidic ores of Little Carpathians weak metamorphic recristalisation.

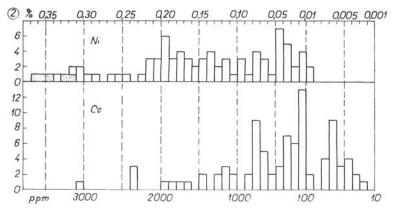


Fig. 2. Histogram of Ni and Co contents in pyrites of amphibole-sulphidic, quartz-sulphidic ores and amphibolites with pyrite contents strong metamorphic recrystalisation.

Fig. 3. Graphic illustration of Ni and Co contens by pyrite analyses of graphite-quartz-sulpidic ores of Little Carpathian

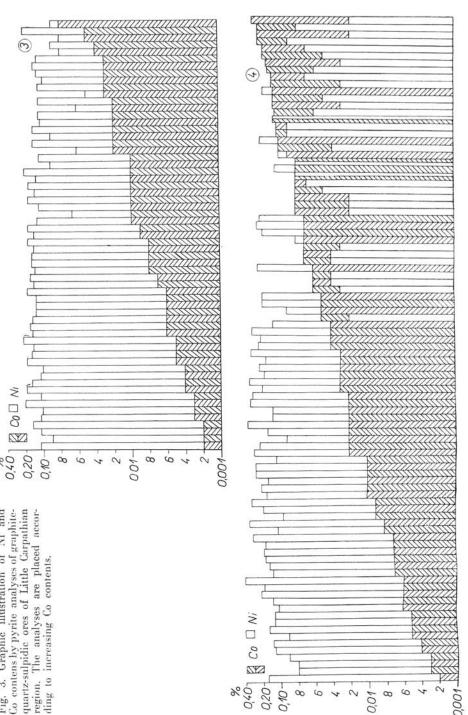


Fig. 6. Like fig. 3, however analyses of pyrite are from amphibole-sulphidic, quartz-sulphidic ores and amphibolites with pyrite contents.

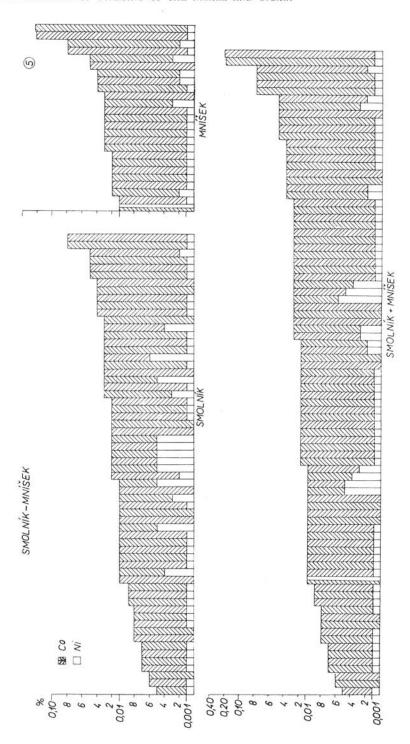


Fig. 5. Graphic illustration of Ni and Co contents by pyrite analyses of pyrite ores in Smolnifk and Mníšek region. The analyses are placed according to increasing Co contents.

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After acquiring of PGS 2 gride spectrograph the method has been partly overworked for this apparatus. Standards used in first variant of method have been applicated. The conditions of spectra exciting were not changed essentially. These analytical lines were applicated: Co 3453,5 Å, Ni 3414,7 Å, Mn 2801,0 Å, Mo 3170.3 Å,

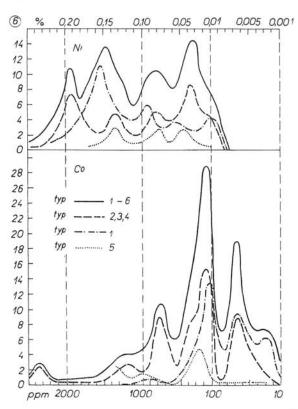


Fig. 6. Histogram curves of Ni and Co contents of pyrites in various ores of Little Carpathians. The curves are constructed drawing contours of Ni and Co values histograms.

V 3183,9 Å and Ti 3361.2 Å. By internal standard Fe lines were choiced. The reproducibility has been similar as at first variant of the method.

In next phase of geochemical investigation the necessity of investigation of also other microelements contents probably occuring in pyrite has been shown. Therefore the method on these 16 microelements has been elaborated: Co. Ni. Mn, Mo. V. Ti, As, Sb, Bi, Pb, Sn, Zn, Cu, Ag, Tl and Au. The ascertaining of mentioned elements has been carried out on original (unroasted) pyrites and the standards have been prepared on basis of FeS₂. It has been worked under following conditions: d. c. are of 220 V at 5 Å, supporting electrode put in anodically, first exposition 30 sec. for ascertaining of easily volatile elements, further 30 sec. preexposition for hardly volatile elements (by closed split), second exposition 40 sec. for ascertaining of hardly volatile elements. Following analytical lines have been applicated: Co 3453.5 Å Ni 3414.7 Å, Mn 2798.2 Å, Mo 3170.3 Å, V 3183.9 Å, Ti 3372.8 Å, As 2860.4 and 2349.8 Å. Sb

2877,9 Å, Bi 3067,7 Å, Pb 2833,0 Å, Sn 3175.0 Å, Zn 3345..0 Å. Cu 3273,9 Å, Ag 3382,8 Å, Tl 2767,8Å, Au 2675,9Å. As internal standard Fe for hardly and medium volatile elements, In and Cd for easily volatile elements have been applicated. Calibration curves have been constructed on basis for Δ Y values against competent

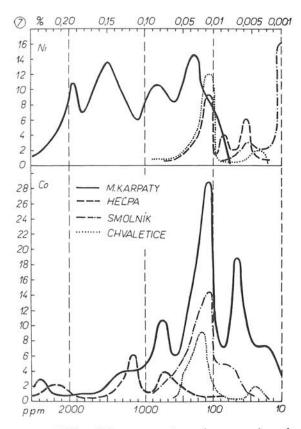


Fig. 7. Histogram curves of Ni and Co contents in pyrites at various deposits of the CSSR.

log c values. The reproducibility of particular ascertainments is in average \pm 9%. Least deviation is \pm 2,6% (Ag), greatest deviation \pm 22,4 (Tl).

Discussion to Graphs

The first thing in evaluation of a great number of geochemical analytical data is the application of appropriate graphic methods because the illustration by plates does not give sufficiant rewiews of results.

It is impossible to submit in this work all graphically treated spectrochemical data. Therefore only some data are mentioned significant with regard to the submitted text and to main conclusions drawn from geochemical investigation of pyrite. The graphs

Table 1

	Ni		Co		V		Мо	
Type 1 GQS	66 66 —	0,131	66 66 —	0,0137	66 44 22	0,0044 0,0063	66 60 6	0,0039 0,0043
Type 2 AS	32 32 —	0,175	32 32 —	0,0351	32 26 6	0,0050 0,0060	32 28 4	0,0040
Type 3 QS	43 43 —	0,133	43 43 —	0,0642	43 19 24	$0,0025 \\ 0,0051$	43 36 7	0,0050 0,0060
Typen 1+2+3 Summe	141 141 —	0,146	141 141	0,0376	141 89 52	0,0038 0,0058	141 124 17	0,0042 0.0048
Type 4 Am	17 17 —	190,0	17 17 —	0,0850	17 9 8	0,0049 0,0088	17 13 4	0,0036
Typen 2+3+4 Summe	92 92 —	0,133	92 92 —	0,0614	92 54 38	0,0041 0,0066	92 77 15	0,0038 0,0045
Type 5 QSch-GGn	24 24 —	0,078	24 24 —	0,0527	24 19 5	0,0053	24 17 7	0,0017 0,0023
Type 6a Imp.	28 28 —	0,0631	28 28 —	0,0199	28 13 15	0.002 0.004	28 9 19	0,0009 0,0026
Type 7 Premigr. Py	36 35 1	0,1205	36 35 1	0,0415	36 22 14	0,0036 0,0055	36 27 9	0,0034 0,0045
Type 8 Hydrotherm, Py	25 25 —	0,076	25 22 3	0.016	25 13 12	0,0049 0,0090	25 7 18	0,0004 0,0010
Summe der Typen 1+2+3+4+5+6a	210 210 —	0,112	210 210 —	0,0451	210 130 80	0,0059	210 163 47	0.0038

Table 1. Plate of average contents values of elements in pyrites of various ore types of Little Carpathians. Upper numbers designe the number of all analysed samples and the accompanying numbers are average values resulting from dividing of addition value by total number of analyses. The mean number indicates average of measured contents values of particular elements. Lower number indicates in how many analysed samples appeared belonging element in traces or values under the limit of spectral determinability in zero values.

	Ti		Mn		Zn		Cu	
Type 1 GQS	66 61 5	0,0148 0,0160	66 48 18	0,0098 0,0134	27 25 2	0,0409	27 27 —	0.0506
Type 2 AS	32 26 6	0,0085 0,0105	32 23 9	0,0107 0,0149	19 16 3	0,1050	19 19 —	0,0398
Type 3 QS	43 32 11	0,0089 0.0119	43 16 27	0,0037 0,0098	33 31 2	0,1064	33 33 —	0,0878
Typen 1+2+3 Summe	141 119 22	0,0108 0,0128	141 87 54	0,0079 0,0127	79 72 7	0,0767 0,0841	79 79 —	0,0594
Type 4 Am	17 16 1	0.0205	17 15	0,0143	6 6	0,1250	6 6 -	0,0330
Typen 2+3+4 Summe	92 74 18	0.0115 0.0143	92 54 38	0,0077 0,0130	58 53 5	0,1121	58 58 —	0,0535
Type 5 QSch-GGn	24 19 5	0.0664	24 19 5	0,0105	16 16 —	0,0455	16 15 1	0,0454
Type 6a Imp.	$ \begin{array}{c c} 28 \\ 25 \\ 3 \end{array} $	0,0242	28 23 5	0,0063	18 14 4	0.0320	18 18 —	0,0293
Type 7 Premigr, Py	36 31 5	0,0183	36 25 11	0.0119 0.0171	24 22 2	0,0356	24 22 2	0,0532
Type 8 Hydrotherm, Py	25 15 10	0,0066 0,011	25 22 3	0,029	16 12 4	0,047	17 16 1	0,055
Summe der Typen 1+2+3+4+5+6a	210 179 31	0,0249	210 144 66	0,0118	119 108 11	0,0741	119 111 8	0,0477

Type 1 GQS . Graphite-quartz-sulphide ores. Type 2 AS Type 3 QS Amphibole-sulphidic ores. Quartz-sulphidic ores.

Accesoric pyrites in magmatogene amphibolites.

Pyrite mineralisation in gneiss.

Type 4 Am . . . Type 5 QSch-GGn Type 6a Imp . . Disseminated ores in hydrothermal altered amphibolites and

actinolite schists.

Type 7 Premigr. Py Type 8 Hydrotherm. Py . . . Secondary mobilised pyrites. Hydrothermal pyrites.

Table 2

Lokality	Ni		Co		V		Mo	
Malé Karpaty	235 235 —	0,108	235 235 —	0,045	235 141 94	0,0036 0,0056	235 175 60	0,0028 0,0037
НеГра	36 36 —	0,0164	36 36 —	0,139	36 30 6	0,0071 0,0084	36 20 16	0,0078 0,0013
Smolník	63 50 13	0,0013 0,0016	63 63 —	0,0222	63 29 34	0,0018 0,0033	63 23 40	0,0007 0,0019
Chvaletice	29 29 —	0,0174	29 28 1	0,0258	29 9 20	0,0038 0,0113	29 2 27	0,0002 0,0010
Zlaté Hory	16 13 3	0,0062 0,0076	16 16 —	0,0458	16 2 14	0,0005 0,0050	16 3 13	0,0012 0,0061
Sedimentary pyrites	35 35 —	0,0249	35 35 —	0,0037	35 24 11	0,0026 0,0036	35 23 12	0,0041 0,0062

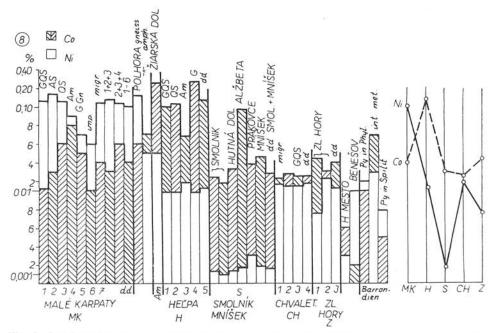


Fig. 8. Graphic illustration of average Ni and Co values by pyrites analyses of ore types at main pyrite deposits in CSSR.

Ti		Mn		Zn		Cu		Pb	
235 201 34	0,0223 0,0261	235 165 70	0,0079 0,0112	135 124 11	0,0631 0,0686	134 133 1	0,0458		
36 26 10	0,0073 0,0101	36 36 —	0,0508	16 3 13	0,0028 0,0107	16 16	0,0399		
$\frac{63}{62}$	0,0362	63 58 5	0,0058 0,0063	35 29 6	0,0565 0,0680	35 35 —	0,0840	35 32 3	0,1021
29 21 8	0,0222 0,0307	29 25 4	0,0790 0,0916	24 3 21	0,0068 0,0478	24 24 —	0,0057	24 7 17	0,0166 0,0546
16 10 6	0,0160 0,0255	16 12 4	$0,0041 \\ 0,0054$	15 9 6	0,4195 0,6985	15 15 —	0.1257	15 8 7	0,0440 0,0816
35 28 7	0,0121 0,0151	35 24 11	0,0124 0,0181	21 14 7	0,0056 0,0079	19 19	0.0068		

Table 2. Like table 1, however average values refering to pyrites of Little Carpathian deposits, Helpa, Smolník, Chvaletice, Zlaté hory and sedimentary pyrites in coal, clay and limestones.

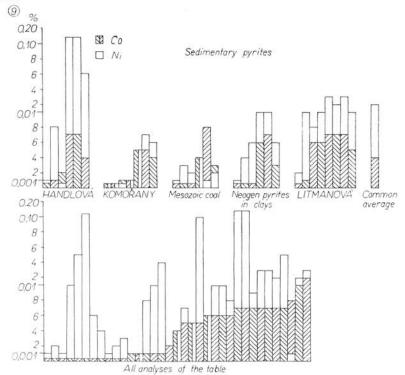


Fig. 9. Graphic illustration of Ni and Co values by analyses of sedimentary pyrites in coal Handlová, Komořany, clays Piešťany, carbonates Litmanová.

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are to explain the contents as also the methods of the works. Following graphic textfigs have been applicated: histograms of particular elements; histogram curves constructed drawing histogram contours of elements; graph of Ni and Co contents of particular analyses placed according to increasing Co contents. Average values of

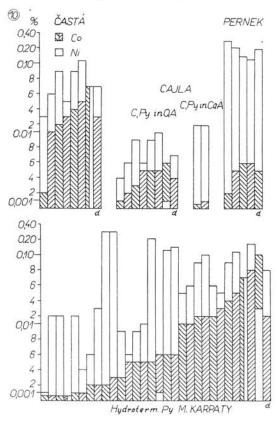


Fig. 10. Graphic illustration of Ni and Co values by analyses of hydrothermal pyrites in Little Carpathians. Lower part of graphs show all analyses placed according to increasing Co contents, in upper part of graph analyses are divided according to particular deposits or periods of mineralization.

element contents on separate deposits or ore types given on plates 1 and 2 are also graphically illustrated. On vertical axis per cent of represented elements are plotted.

The fig. 1 and 2 are histograms of Co and Ni contents of Little Carpathian pyrites belonging to graphite-quartz-sulphide ores, i. e. ores with least metamorphosis and to quartz-sulphide as also to amphibole-sulphide ores with high metamorphosis. Where — as on the one hand in first case (Fig. 1) geochemistry of pyrite is close to unaltered primary microelement contents in original pyrite, on the other hand in second case alteration of Ni and Co contents with progressive metamorphosis is seen. Considerable dispersion of Co as also of Ni values opposite to pyrites of graphite-quartz sulphide ores is shown there (Co contents is increasing, Ni contents is decreasing).

The figs 3, 4, 5 show that by placing of analyses according to increasing Co contents Ni contents remain on the same level and only with higher grade metamorphosis conditions of pyrite recrystalisation decrease of Ni contents under Co contents level proceeds. Graphs 3 to 6 show Co and Ni contents of typical syngenetic pyrite mine-

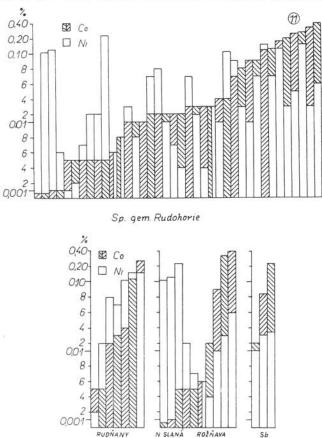


Fig. 11. Graphic illustration of Ni and Co values analyses of Spišsko-gemerské rudohorie mountains. Other text like in fig. 10.

ralization of West Carpathian region characteristic by considerably uniform and stable Co and Ni contents. The regularity of Ni and Co distribution in syngenetic mineralization has been caused by relatively small changes of genetic, thermodynamic and other conditions at the time of rise of sedimentary pyrites being characteristic of pyrites of that origine.

Comparison graphs on figs 6 and 7 show histogram curves of Ni and Co distribution of particular types of Little Carpathian pyrite ores and of sedimentary pyrites of various deposits in the ČSSR (Fig. 7).

Fig. 8 shows a graph of average values of Ni and Co analyses of particular pyrite

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ores of Little Carpathian region and of other deposits of metamorphic genesis in the ČSSR. From the graph follows that Ni and Co in syngenetic pyrites may have various ratio and values not only within a limit supposed by H e g e m a n n $(0.002 \, ^0/_0$ Co and $0.02 \, ^0/_0$ Ni). For sedimentary pyrites only primary relative regularity of Ni and Co

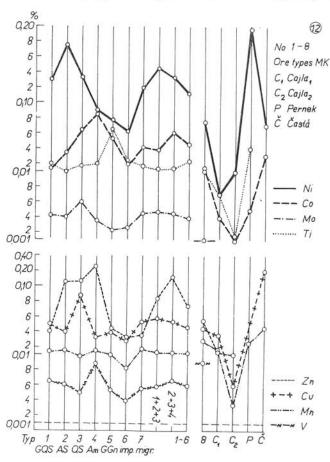


Fig. 12. Graphic illustration of elements contents of pyrites belonging to older syngenetic ore mineralization left part of graph and epigenetic hydrothermal Sb-mineralisation (right part of graph) of Little Carpathians. Nrs. 1—7 are particular pyrite ore types of Little Carpathians.

contents of particular syngenetic ore types is characteristic. Small number of pyrite analyses of different types of ore on one deposit may result in irregular high Ni and Co contents.

For the purpose of comparison a graph illustrating analytical values of Ni and Co according to increasing Co contents of sedimentary concretionary pyrites in coal, limestones and clays is presented (Graph nr. 9). From the graph follows that in contradistinction to pyrite deposits (fig. 3, 4, 5) concretionary sedimentary pyrites have irregular Ni and Co contents caused by iron bisulphide migration during diagenesis and compaction and by environment influence on their recrystalisation. Similar ir-

regularity has been observed also at hydrothermal pyrites of Little Carpathians and Spišsko-gemerské rudohorie monutains (Graph no 10 and 11). This fact agrees with the opinions of H e g e m a n n (1943) proving variable trace elements contents in plutogene hydrothermal pyrites. The microelements contents depends more sensible on thermo-

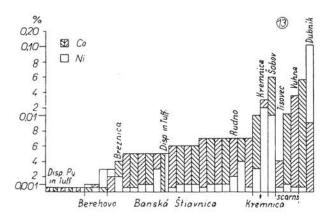


Fig. 13. Graph illustration Ni and Co contents in pyrites of subvolcanic ore mineralization in volcanites region of West Carpathians.

dynamic conditions at the rise of sulphides, on changes of solutions character and on geochemical influence of surrounding rocks. This fact is seen on fig. 12 having illustrated average microelements contents of particular genetic pyrite ore types of Little Carpathian region. From the graph follows that geochemical picture of hydrothermal postgranitic pyrites (symbols c1. c2. s, č) differs fully from the picture of microelements of older syngenetic pyrites (1 to 7) and may become diagnostic in determining metallogenesis or period of mineralization.

Hydrothermal pyrites of Spišsko-gemerské rudohorie mountains (Fig. 11) have also different microelements contents including Ni and Co within regions as also within deposits. An exception are hydrothermal deposits in the region of volcanites, especially Pb and Zn mineralization, having according to fig. 13 considerable regular Ni and Co distribution in pyrite. This fact should be proved by additional analyses.

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