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MATHEMATIC-STATISTICAL VALUATION OF Ni AND Co CONTENTS IN PYRRHOTITES

(Figs. 1—5)

Abstract: The presented work brings fundamental statistical characterizations (arithmetic average, dispersion, standard, deviation, variation coefficient, correlation coefficient, test of lognormal distribution) of the contents of Co and Ni in pyrrhotites of various genetic groups. It was found out that by aid of the mentioned data individual genetic groups of pyrrhotites may be characterized, differences registered and mutully compared. Certain values of these characterizations (variation coefficient, coefficient of correlation) are shown to be typical of certain genetic groups of pyrrhotites.

Резюме: Продлагаемая статья приносит основные статические данные (арифметрическое среднее, дисперсию, стандартное отключение, коэффициент вариации, коэффициент кореляции, испытание логнормального разделения) содержания Co и Ni в пиротинах различных генетических групп. Было определено, что благодаря использованию приведенных данных можно характеризовать отдельные генетические группы пиротинов, замечать отличия и сравнивать их между собой. Как видно, некоторые фактические данные этих характеристик (коэффициент вариации, коэффициент кореляции) типичны для определенных генетических групп пиротинов.

The presented work is continuation of the foregoing study by the authors on geochemistry of pyrrhotites from various genetic types of ore mineralization. The total results of this investigation are summarized in the monograph „Geochemistry of Pyrrhotite of Various Genetic Types" 1969, Publishing House of the Comenius University, Bratislava. In the quoted work are mentioned in tables all analytical data of (529) contents of several microelements in pyrrhotites especially of Co and Ni.

In this work contents of Ni and Co are statistically valuated, these elements have the greatest importance from the standpoin of study of pyrrhotite genesis. We performed mathematic-statistical treating according to groups, mentioned in the individual tables of the quoted work from 1969.

The following groups of pyrrhotites are concerned:[1]

1. Pyrrhotites form highly metamorphosed syngetic pyrite deposits in aktinolitic and graphitic schists of the Malé Karpaty Mts. (Czechoslovakia).

2. Pyrrhotites from syngenetic highly metamorphosed ore mineralization in amphibolites and gneisses near the community of Heľpa (Nízke Tatry, Czechoslovakia).

3. Pyrrhotites with high contents of Ni and Co from Peklo near Habry (Czechoslovakia). The pyrrhotites are of unclear genesis, foud in amphibolites (inclusion of Ni mineral in pyrrhotite was found).

4a. Metamorphogenic pyrrhotites in graphitic schists of the katacrystalline of the Passauer Wald (Federal Republic of Germany, analyses of F. Rost 1940).

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[1] Numbering of groups is identical with the numbers of tables of analyses in the quoted work from 1969. There are spectrochemical quantitative analyses carried out on grating graph Zeiss PGS-2. The method is mentioned in detail in the work by the authors Geochemie der Pyrite einiger Lagerstätten der ČSSR, Published House of the Slovak Academy of Science, Bratislava, 1967.

4b. Pyrrhotites from Outokumpu (Finland) of undetermined primary genesis in gneisses and mica schists. (The pyrrhotites are probably remobilized — analytical data taken over from the work by F. H e g e m a n n 1943.).

5a. Pyrrhotites from the syngenetic pyrite deposit of Smolník (Spišsko-gemerské rudohorie Mts. — Czechoslovakia). The deposit is situated in chloritic and graphitic phyllites (pyrrhotite is probably remobilized).

5b. Pyrrhotites from Zlaté Hory (East Sudetic ore region, Czechoslovakia) in epizonally to mesozonally metamorphosed crystalline schists (genetically dependent on Devonian geosynclinal volcanism).

6a. Syngenetic pyrrhotites from Bohemia and Moravia from more or less metamorphosed schists (Petříkov and others).

6b. Pyrrhotites from Bodenmais (Federal Republic of Germany) in syngenetic metamorphosed pyrite deposits with content of pyrrhotite (analyses of the authors).

7a. Pyrrhotites from Bodenmais (analyses by F. R o s t 1940 and F. H e g e m a n n 1943).

7b. Sedimentogene pyrrhotites from various localities of Europe (analysed by F. R o s t 1940).

8. Pyrrhotites from various European metamorphosed sedimentogene pyrite deposits (analysed by F. H e g e m a n n 1943).

9. Pyrrhotites form deposits of the Skellefte area (Sweden) of uncleared and unequal genesis in the leptite formation (analyses taken over from S. G a v e l i n and O. G a b r i e l s o n 1947).

10. Pyrrhotites of liquation mineralization or with the character of sulphidic accessories in magmatites of various home and foreign deposits (analysed by the authors).

11. Pyrrhotites of the same genetic type as No. 10 (analysed by F. H e g e m a n n 1943, H. B j ö r l y k k e and S. J a r p 1950).

12. Hydrothermal plutonogene pyrrhotites, especially of the siderite mineralization of the Spišsko-gemerské rudohorie Mts. (West Carpathians, Czechoslovakia).

13. Pyrrhotites of hydrothermal pyrite-pyrrhotite mineralization from Slavošovce (area at the boundary of the Veporides and Gemerides, Czechoslovakia) probably belonging to the pre-siderite metallogenesis.

14. Pyrrhotites from hydrothermal-plutonogene deposits of Bohemia and Moravia.

15. Pyrrhotites from foreign hydrothermal-plutonogene deposits (analyses of the authors).

16. Pyrrhotites from the hydrothermal-plutonogene deposit of Coeur d'Alene, USA. (Analyses taken over from R. C. A r n o l d, R. G. C o l e m a n n and V. C. F r y k l u n d 1962 and V. C. F r y k l u n d and R. S. H a r n e r 1955).

17. Hydrothermal plutonoge pyrrhotites from various deposits of Europe (analyses by F. H e g e m a n n 1943).

18. Pyrrhotites from hydrothermal subvolcanic ore mineralization from various foreign deposits (analyses of the authors).

19. Pyrrhotites from skarn deposits.

It is to remark that not from all above mentioned groups of pyrrhotites fundamental statistical characterizations of the contents of Ni and Co as well as correlation coefficients were calculated and testing on lognormal distribution of the contents of these elements performed. It is because from some groups of pyrrhotites we have only a small number of analyses, not sufficient for statistics. These data therefore were only included into sets of groups.[2]

The sets of groups are ordered with regard to the genetic and also regional standpoint, even with regard to the authors of the analyses working with various methods. The main sets may be characterized as follows:

I. Set of the groups 1 + 2, characterizing highly metamorphosed pyrrhotites originated from sedimentogene pyrites as a consequence of metamorphosis. (Deposits of the Malé Karpaty Mts. and Heľpa.)

II. Set of the groups 5a+5b+6a+6b characterizing originally syngenetic ore mineralization of sedimentogene character affected together with source sediments by subsequent metamorphic effects. Although also primary genesis of these deposits corresponds to the genesis of deposits of the so called „Pyrite formation" and consequently it is already primarily different in details, also metamorphic effects could have caused remigration of sulphides and in this way also changes in Ni and Co contents. The deposits are considerably distant from each other regionally (Zlaté Hory, Smolník, Petříkov etc.) and originated in different lithological environment. Therefore a relatively heterogeneous set of deposits is present there though all these ore mineralizations are of sedimentogene origin.

III. Set of 1+2+4a+6a+6b+7a represents pyrrhotites from syngenetic-sedimentary, relatively highly metamorphosed deposits, at which pyrrhotite could have mostly originated by alteration from pyrite.

IV. Set of 3+4b represents pyrrhotites from highly thermal deposits of unclear genesis, but also primary syngenetic origin may be admitted.

V. Set of 5a+5b+6a+6b+7a+7b+8 represents pyrrhotites from syngenetic deposits without those groups that were extremely highly metamorphosed (katazonal or peri-plutonic contact metamorphism).

VI. Set of 1+2+4a+5a+5b+6a+6b+7a+7b+8 represents a heterogeneous set of analyses of pyrrhotites from syngenetic deposits of various regions, from various lithological environments and variously contaminated by metamorphosis.

VII. Set of 1+2+3+4a+4b+5a+5b+6a+6b+7a+7b+8+9 includes pyrrhotites from syngenetic deposits mentioned in the foregoing set and pyrrhotites from deposits of problematic genesis are added (Skellefte, Outokumpu), at which original genesis is completely wiped out by subsequent ore mineralization processes.

VIII. Set of 10+11 represents liquation and scattered pyrrhotites appearing as accessories in magmatic rocks.

IX. Set of 12+13+14 represents pyrrhotites from plutonogene hydrothermal deposits of Czechoslovakia.

X. Set of 12+13+14+19 represents pyrrhotites from hydrothermal-plutonogene and skarn deposits of Czechoslovakia.

XI. Set of 15+16+17+18 represents pyrrhotites from hydrothermal plutonogene and hydrothermal subvolcanic, deposits outside Czechoslovakia (mainly analyses of foreign authors).

XII. Set of 12+13+14+15+16+17+18+19 includes analyses of pyrrhotites from all hydrothermal (plutonogene and subvolcanic) deposits from Czechoslovakia and abroad, analysed by the authors of this work and foreign authors.

XIII. Set of analyses of pyrrhotites of all genetic groups, i. e. groups 1—19, representing average values of Co and Ni contents and values of fundamental statistic characterizations.

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[2] The sets of groups are designated with Roman numerals while the individual groups with Arabic numerals.

Table 1

Tab.	Element	Number of elements	Arithmetical average ($\bar{x}$) in ppm	Dispersion (s^2)	Standard deviation (s)	Variation coefficient (V %)	Correlation coefficient (r)
1	Ni Co	24 24	1859 99	842 703 57 048	918 239	49 242	0,37063
2	Ni Co	14 14	724 35	27 268 778	165 28	23 81	0,75667
5a	Ni Co	6 6	688 334	463 888 21 081	681 145	99 43	0,24221
5b	Ni Co	9 8	134 299	21 132 22 700	145 151	108 50	−0,67287
6a	Ni Co	10 10	458 140	98 136 23 071	313 152	68 109	0,85161
6b	Ni Co	5 5	57 44	122 383	11 19	19 45	−0,23422
9	Ni Co	100 100	175 203	128 094 140 550	358 375	204 185	0,13951
10	Ni Co	41 41	6697 862	209 726 466 579	4480 683	67 79	0,39660
12	Ni Co	17 18	566 753	188 611 508 616	434 713	77 95	0,21572
14	Ni Co	64 67	240 279	100 359 90 817	317 301	132 108	0,31104
15	Ni Co	32 32	115 176	47 226 47 106	217 217	188 123	0,23351
17	Ni Co	17 17	728 892	109 257 135 694	1045 1165	143 131	0,75412
18	Ni Co	9 9	2 10	4 593	2 24	92 217	−0,37844
19	Ni Co	30 29	235 143	246 108 49 915	496 223	210 156	0,50988

Fundamental statistical characterizations of the individual groups are meat:oned in tab. 1 and statistical data of sets of groups in tab. 2. Numbering of the individual groups we explained in the foregoing text. Nummerical values were calculated b,

J. Klučárová form the Institute of Technical Kybernetic of the Slovak Academy od Science on GIER calculator according the following formulas:

$$\text{arithmetic average} - \bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i$$

$$\text{dispersion} - s^2 = \frac{1}{n} \sum_{i=1}^{n} (x_i - \bar{x})^2$$

$$\text{standard deviation} - s = \sqrt{s^2}$$

$$\text{variation coefficient} - V(\%) = \frac{s}{\bar{x}} \cdot 100$$

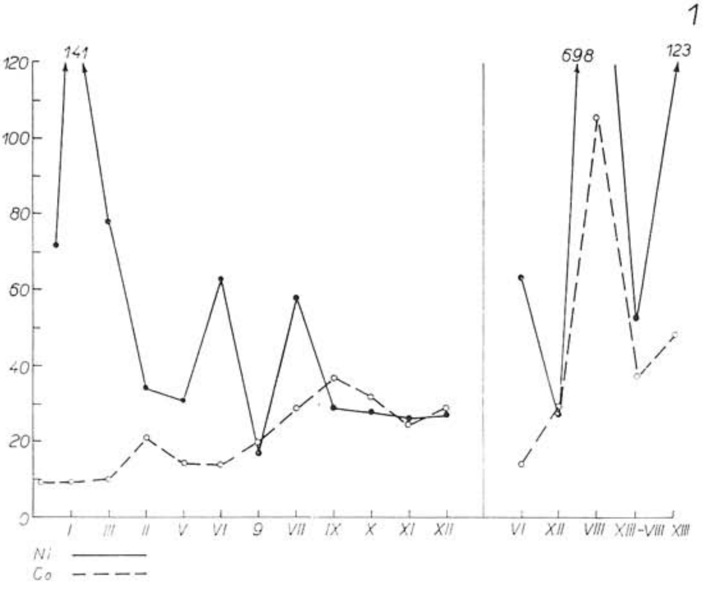

Fig. 1. Graphic presentation of the arithmetic average ($\bar{x}$) of Ni and Co of the sets of groups of pyrrhotites (the original values are divided by ten).

Explanations: I — pyrrhotites syngenetic-sedimentary, highly metamorphosed from the Malé Karpaty Mts. and Hefpa; II — pyrrhotites from deposits of the „pyrite formation", less metamorphosed; III — syngenetic-sedimentary pyrrhotites, relativelly highly metamorphosed; V — syngenetic-sedimentary pyrrhotites without pyrrhotites from deposits extremely metamorphosed; VI — all pyrrhotites of syngenetic-sedimentary origin variously metamorphosed; 9 — pyrrhotites from deposits of the area of Skellefte (Sweden); VII — the same as set VI — plus pyrrhotites of unclear genesis from the area of Skellefte; VIII — liquation pyrrhotites and pyrrhotites present as accessory in magmatic rocks; IX — hydrothermal-plutonogene pyrrhotites from Czechoslovakia; X — hydrothermal-plutonogene pyrrhotites and pyrrhotites from skarns in Czechoslovakia; XI — hydrothermal-plutonogene and hydrothermal-subvolcanic pyrrhotites outside Czechoslovakia; XII — all hydrothermal-plutonogene and subvolcanic pyrrhotites from Czechoslovakia and abroad; XIII — pyrrhotites of all genetic types; XIII—VIII — pyrrhotites of all genetic types without liquation and accessory pyrrhotites in magmatic rocks.

$$\text{correlation coefficient} - r_{xy} = \frac{1}{n} \sum \left(\frac{x - \bar{x}}{s_x} \right) \left(\frac{y - \bar{y}}{s_y} \right)$$

In he first four fundamental statistical characterizations some extremely hig values of Co and Ni contents were omitted in the calculation, their number, however, does not exceed 10 % of the values in the individual groups.

In the calculation of correlation coefficients those data about Co and Ni contents were not taken into consideration, of which one was left out from the calculation. Where analytical data were designated with the sign of approximation (≈) and the sign „more than" (>), i. e. over the limit of accurate determinability, the value quoted behind the signs was included into the calculation.

At values under the limit designated with the sign „less than" (<) the concrete number was included at Co and Ni (50 or 10 ppm at Co according to the applied method, 20 ppm at Ni). The values designated with a line in the tables (—), i. e. values under the limit of quanlitative determinability of Co and Ni, were included into the calculation of correlation with the value of 1 ppm for both the elements.

In the tables also the values of testing of lognormal distribution of corresponding Co an Ni contents are presented. The values Y and Z mentioned in the table were calculated according to the following formulas: $Y - \left|\frac{\bar{\gamma}_1}{\delta_{\bar{\gamma}_1}}\right|$, $Z - \left|\frac{\bar{\gamma}_2}{\delta_{\bar{\gamma}_2}}\right|$ where $\bar{\gamma}_1$ = asymmetry, γ_2 = excess, δ_{γ_1} = standard deviation of asymmetry, $\delta_{\bar{\gamma}_2}$ = standar deviation of excess.

Distribution is lognormal, when the values are less than or equal 3.

The values of arithmetic averages, standard deviations, variation coefficients and correlation coefficients, considered as the most important statistical data, were used for compilation of graphs making us possible to compare the above mentioned values in the individual groups or sets of groups of pyrrhotites.

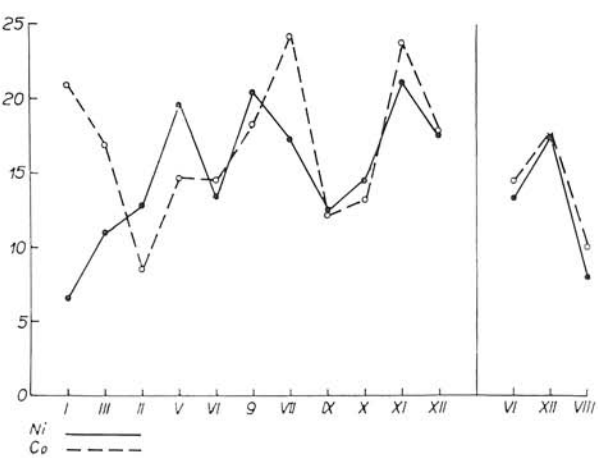

Fig. 2. Graphic presentation of variation coefficient (V %) of Ni and Co of sets of groups of pyrrhotites (the original values are divided by ten). The explanations are with fig. 1.

Discussion to Tables and Graphs

To some statistical characterization certain explanation is necessary. As it is apparent, the arithmetic average of Ni contents to be very high at set XIII (1229 ppm of Ni), which represents all the studied pyrrhotites. This high value of the arithmetic average of Ni is caused by set VIII, i. e. a part of 60 analyses of liquation pyrrhotites, as well

Table 2

Tab.	Element	Number of elements	Arithmetical average in ppm ($\bar{x}$)	Dispersion (s^2)	Standard deviation (s)	Variation coefficient (V %)	Correlation coefficient (r)	Test of lognormal distribution	
								Y	Z
I	Ni	38	1413	895 497	946	67	0,35699	5,59378	11,22817
	Co	38	92	36 663	191	208		3,77282	0,80547
II	Ni	30	340	18 678	432	127	0,31856	0,44976	1,2609
	Co	29	207	30 469	174	84		2,53828	1,44845
III	Ni	93	778	763 237	874	112	0,20982	0,56543	2,41907
	Co	93	102	29 254	171	168		2,06351	2,80377
IV	Ni	11	3525	286 981	1694	48	0,70298	1,3652	0,1465
	Co	11	3101	187 250	1368	44		1,0262	0,6656
V	Ni	99	308	362 657	602	195	0,11215	4,69244	5,70379
	Co	99	139	42 102	205	147		1,30304	2,88170
VI	Ni	149	634	725 355	852	134	0,24358	1,15766	1,23187
	Co	148	144	43 305	208	145		2,96315	2,82408
VII	Ni	260	580	101 810	1009	174	0,64050	0,32984	1,64146
	Co	259	292	509 275	714	244		1,57758	4,85442
VIII	Ni	60	6977	316 945	5630	81	0,36245	2,92297	0,53230
	Co	63	1060	113 423	1065	100		0,34163	1,35737
IX	Ni	87	290	132 196	363	125	0,37578	1,8895	0,3039
	Co	91	373	203 484	451	121		2,6173	0,2316
X	Ni	117	276	161 970	402	146	0,27219	1,8635	0,8060
	Co	121	316	175 254	419	132		2,8453	1,2785
XI	Ni	91	256	290 656	539	211	0,75323	1,59550	1,63444
	Co	91	254	368 180	607	239		1,74894	2,33080
XII	Ni	208	267	218 373	467	175	0,56568	2,44295	1,90667
	Co	212	289	259 028	509	176		2,85336	2,72289
XIII	Ni	529	1229	956 793	3093	252	0,45331	1,57609	3,03967
	Co	534	382	545 178	738	193		3,41296	5,09655

as by set IV, which includes 11 analyses only, but represents pyrrhotites with observed unmixing of Ni minerals being unseparable (Peklo near Habry).

Characteristic contents of Ni and Co in pyrrhotites are therefore more evidently indicated by set VII (Ni = 580 ppm, Co = 292 ppm, there are all syngenetic pyrrhotites including those from Skellefte) and by set XII (Ni = 267 ppm and Co = 289 ppm) representing all hydrothermal pyrrhotites. Variation of average contents of Co and Ni can be traced in graph 1 (Fig. 1).

The mentioned example show, how a relatively small number of analyses with extraordinarily high values of microelements contents may misrepresent the average content of the element in a relatively nomerous of data (529).

Among the fundamental statistical characterizations interesting data are supplied by the values of variation coefficient (V %). From the variation coefficient in the individual groups or set of groups the degree of unequability of the contents of these elements as well as the difference in variation of the contents of one element in contrast to the other in one group or set of groups may be read out well. Such a great differrence is to be seen, for instance, in group 1 (Malé Karpaty), group 6a (Petřikov), group 18 (pyrrhotites from subvolcanic deposits). In these groups Co has higher value of variation coefficient than Nn. It is the contrary at a lesser number of groups of pyrrhotites only, e. g. in group 15 (hydrothermal-plutonogene pyrrhotites) and group 19 (pyrrhotites from skarns) also when the difference between the variation coefficients of Co and Ni is not as great, in some groups variation coefficient of both the elements is even slightly different only (group) 9, 14, 17). As it is to be seen, they are just hydrothermal plutonogene pyrrhotites that are characterized by greater dispersion of Ni in contrast to Co or only by a small difference in variation coefficients at both the elements.

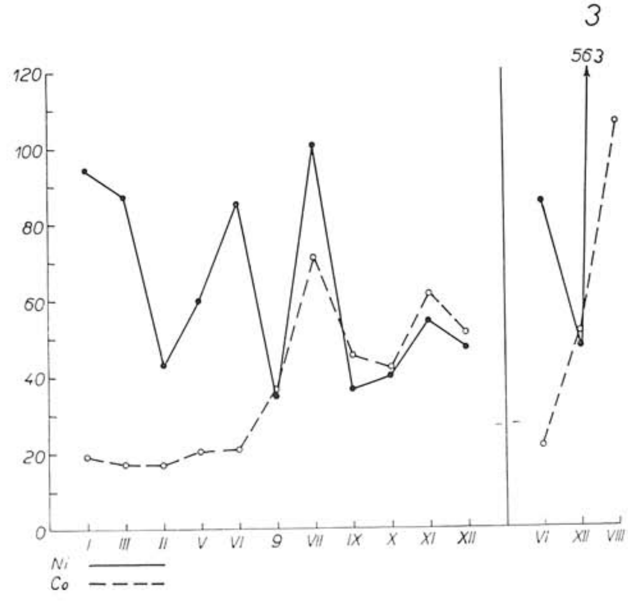

Fig. 3. Graphic presentation of standard deviation (s) of Ni and Co of sets of groups of pyrrhotites (the original values are divided by ten). The explanations are with fig. 1.

As it may be seen from the mentioned before and as it was found out by us in the foregoing works, equability of Ni contents is a characteristic feature of syngenetic-sedimentary pyrrhotites. This need not be only as a consequence of primary equability of Ni contents but a consequence of the influence of metamorphosis that sometimes evoked lowering of extreme contents of some elements.

On the other hand pyrrhotites of hydrothermal-plutonogene ore mineralization have variation coefficient of Ni greater than of Co, what we can take as feature characteristic of the groups of hydrothermal-plutonogene pyrrhotites. From this standpoint subvolcanic pyrrhotites are approaching syngenetic ones.

Tab. 2 and fig. 2 show that where syngenetic sets of pyrrhotite type are clearly present, mainly in metamorphosed ore mineralization, variation coefficient is greater at Co than at Ni. This rule is not valid in large sets of pyrrhotites of less metamorphosed syngenetic ore mineralization (set II, V), but it is valid for set VI representing all syngenetic pyrrhotites as one whole.

The set of all hydrothermal pyrrhotites including subvolcanic pyrrhoties and those from skarns (VII) has Co and Ni with almost equal variation coefficients. Similar is the situation in all sets with hydrothermal pyrrhotites (IX, X, XI). Greater difference in correlation coefficient of Co and Ni is to be seen in set XI, caused by the presence of subvolcanic pyrrhotites in the set, with dispersion of Co greater than of Ni.

Tab. 2 shows that variation coefficients are higher the larger is the number of deposits of various genesis comprising the set, as it is quite natural.

The individual statistical characterizations of the main sets of groups are also indicated in graphs (Figs. 1—4) so that the mentioned values may be mutually compared also from the standpoint of the individual groups and mutual variation of he values of Co and Ni in the individual sets of groups. It is to be seen there that mainly at hydrothermal pyrrhotites arithmetic averages (Fig. 1), standard deviations (Fig. 3) and variation coefficients (Fig. 2) have values sligthly different at Co and Ni but at pyrrhotites from syngenetic deposits it is the contrary with correspoding values at Co and Ni showing great difference. The figures also show fundamental statistical characte-

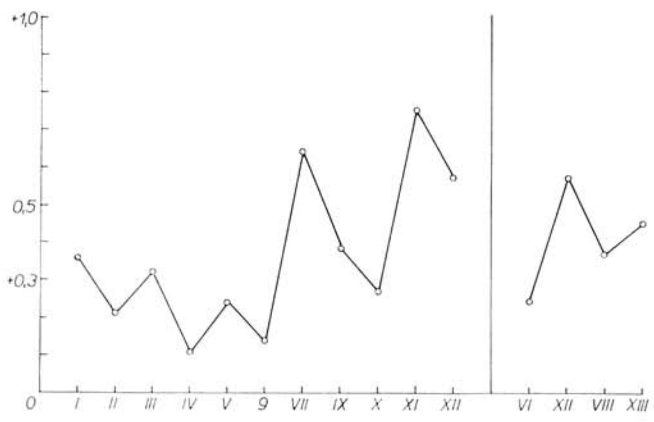

Fig. 4. Graphic presentation of correlation coefficient (r) of Ni/Co of sets of groups of pyrrhotites.

Explanations: XIII — pyrrhotites of all genetic groups generally. Other explanations are with fig. 1.

rizations at Ni, evaluated in graph, to have mostly higher and more variable values than at Co.

The graph of correlation coefficient of the sets of groups (Fig. 4) makes evident that syngenetic pyrrhotites as well as pyrrhotites from the area of Skellefte (Sweden) have lower positive correlation than the larger part of sets of groups of hydrothermal pyrrhotites. Only the set including pyrrhotites from skarns (X) has lowered correlation under the value 0,3. This is also to be seen on the right side of the graph, where there are correlation coefficients of Co and Ni from all syngenetic (VI), hydrothermal (VII) and liquation pyrrhotites (VIII) side by side.

In order to compare quite considerable variation of correlation coefficients in the individual groups of pyrrhotites we mention graph 5, which shows some groups, e. g. 5b (Zlaté Hory), 18 (subvolcanic pyrrhotites) to have relativelly high negative correla-

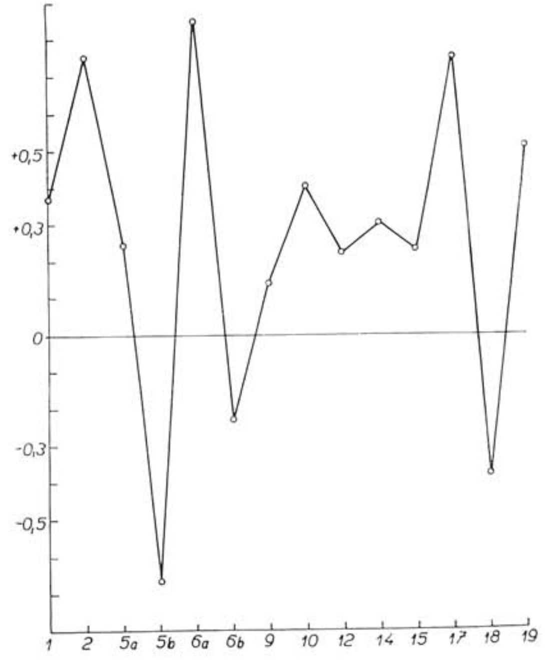

Fig. 5. Graphic presentation of correlation coefficient (r) of Ni/Co of groups of pyrrhotites. Explanations: 1 — syngenetic highly metamorphosed pyrrhotites from the Malé Karpaty Mts.; 2 — syngenetic highly metamorphosed pyrrhotites from Heľpa; 5a — pyrrhotites from the syngenetic pyrite deposit of Smolník; 5b — epi- to mesozonal metamorphosed pyrrhotites from the area of Zlaté Hory; 6a — syngenetic pyrrhotites from schists more or less metamorphosed (Petříkov and others); 6b — pyrrhotites from the syngenetic metamorphosed pyrite deposits of Bodenmais (Federal Republic of Germany); 9 — pyrrhotites of unclear genesis from deposits of the area of Skellefte (Sweden); 10 — liquation pyrrhotites including accessory pyrrhotites in magmatic rocks; 12 — hydrothermal-plutonogene pyrrhotites from the Mountains of Spišsko-Gemerské rudohorie; 14 — hydrothermal-plutonogene pyrrhotites from Bohemia and Moravia; 15 — hydrothermal-plutonogene pyrrhotites from abroad; 17 — hydrothermal-plutonogene pyrrhotites from deposits of Europe according to F. Hegemann 1943; 18 — hydrothermal subvolcanic pyrrhotites from abroad; 19 — pyrrhotites from skarns.

tion while at the set of groups of pyrrhotites (graph 4) negative correlation has not been found out.

The tests of lognormal distribution show contents of Co and Ni to have lognormal distribution in the individual sets of groups in most cases or distribution near to such a division. The most evident deviation from lognormal distribution is mainly manifested at Ni in set I (metamorphogene pyrrhotites) or also at those sets which include such metamorphogene pyrrhotites too. This permits us to deduce that disturbing of original lognormal distribution was mainly appearing in the course of metamorphic redistribution of the elements Ni and Co, similarly as it was also established at pyrites (B. Cambel, J. Jarkovský 1967).

The above mentioned data make possible to establish that the fundamental statistical characterizations of Ni and Co distinctly manifest dependences on genetic and metamorphic factors and therefore can be successfully used for solution of significant genetical-deposital and mineralogical-problems.

Translated by J. Pevný.

REFFERENCES

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