BOHUSLAV CAMBEL, JÁN JARKOVSKÝ*

ON THE CHARACTER OF Cu AND Zn DISTRIBUTION IN PYRITES

(Textfigs. 1—14)

Abstract. In this article the authors deal with the character of Cu and Zn distribution in separated pyrites. They base on almost 600 spectrochemical analyses carried out on the named elements. The discussion is based on histograms and frequency curves and on the comparison of the results of investigations of Ni and Co distribution in pyrites.

Introduction

The authors published already in the journal Geologický sborník (vol. XVII, 1966, no. 1) an article about pyrite geochemistry of some deposits of ČSSR and about the possibility of the application of particulary Ni and Co contents in the solution of genetic problems. It is recommended to the readers of this work to study the above mentioned article because some of the conclusions given in this article are applied in this work and we shall not repeat them. We remark that the relations of Ni and Co distribution are presented in a monographic work, which will come out as a book in 1967. In this work we present only conclusions deduced from the investigation of Co and Ni distribution in pyrites.

One of the fundamental problems of geochemistry is the knowledge of the distribution of chemical elements in earth's crust. So far several authors paid attention to this question. In 1922 already W. A. Richardson and G. Sneesby (in. A. B. Vistelius 1960) touched this problem and in 1923 they interpreted it theoretically. Afterwards an interruption in the investigation of this problem was evident till 1940, when N. K. Rasumovsky, published an extensive general work about the frequency of distribution of elements concentration and in 1948 he presented another work about lognormal distribution in gold prospection.

The systematic study of the frequency of distribution for the purpose of geochemistry was the subject of the work of A. B. Vistelius (1945, 1949). In his work from the year 1960, A. B. Vistelius formulated on basis of modern mathematical-statistical methods the law of geochemical processes when he stated that the frequency of elements reflected the geochemical environment. In the formulation of this law the author based on the investigation of deposits. He ascertained the possibility of distinguishing of 2 distribution groups of chemical elements in the earth's crust. The first distribution group- he characterized as stable stage of geochemical process. In this case the distribution has a character of normal division. The second type of distribution includes the combination of results of several distribution causing stages of the geochemical process. The sum of individual microelement distributions caused by natural chemical reactions produces wide-spread positive asymmetry. This asymmetry in the distribution of elements shows that low microelement concentrations form in the course of geochemical processes usually more frequently than higher concentrations of these elements by the same geochemical process. A. B. Vistelius dealt with this question also in his other works 1948—1952).

As considerable contribution to the solution of the problem of distribution relations analyses were obtained have greatest influence on the form of the frequency curve.

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

can be considered the works of L. H. Ahrens (1954—1966), who dealt with this question since 1954 when he formulated the fundamental geochemical law of elements distribution as follows: „The concentration of an element in specific igneous rock is lognormally divided." The division of the values „x" is lognormal there when the division of log x values is normal.

Since 1954 several works concerning the law of lognormality were published. Many of these works expressed at the beginning a critical point of view to the validity of the law of L. H. Ahrens (Chayes F., 1954; Miller R. L., Goldberg E. D. 1955; Aubrey K. V. 1956; S. Ďurovič 1957 and others). Till 1966 L. H. Ahrens wrote only in the journal Geochim. et Cosmochim. Acta 8 works concerning the problem of lognormality law (1954a, 1954b, 1957, 1963a, 1963b, 1963c, 1964a, 1966), which he completed according to great number of analyses.

In 1963 L. H. Ahrens published a paper, in which he pointed to possible distribution forms of elements in specific igneous rocks. He divided these forms into 4 categories: a) positive asymmetric lognormal division (most frequent), b) negative assymmetric lognormal division (one to two examples), c) normal or approximately normal division (one example) and d) uncertain division (five examples). In 1966 L. H. Ahrens published his last work, in which he summarized division data of 34 macro- and micro-elements in igneous rocks from 158 works of various authors. The majority of distributions displays positive asymmetric division, which he considered as lognormal distribution type. Two elements only, Si and K showed different tendency in favour of negative asymmetry of lognormal division.

Other authors also dealt with the problem of elements distribution. D. A. Rodionov (1961) gave a brief review about the question of lognormal division of elements in igneous rocks. He concluded that the lognormal and normal divisiou of elements in igneous rocks were extreme distribution types. The lognormal division arose according to him when the main quantity of the element in the rock was concentrated in one mineral and normal division arose in the case of regular division of the entire element quantity in several minerals. One can observe an innumerable quantity of mean division types between the mentioned two extreme distribution types, the character of which depends on the number of element bearing minerals and on their quantitative representation. The various division types represent a combination of lognormal and normal division in various ratio.

Our up to date investigations concerning the relations of the distribution of Ni, Co, and other elements in pyrite base on he fact that in nature we hardly can find ideal (extreme) division types of elements (with only lognormal and only normal division type). It is caused by the fact that natural processes take place under the influence of numerous factors which affect the distribution of elements. We can therefore rather speak only about a dominant factor which maximally affected terminal distribution of elements in the observed mineral. The majority of the present elements passed through more-act distribution process from the standpoint of distribution.

After evaluating analytic data and making histograms of analyses from various deposits of various regions and various genesis the summary histogram characterize distribution which can be considered as a combination of the effects of all distribution factors affecting the formation of all investigated samples.

These are the reasons why we consider as importat for the determination of distribution character also the proportions in which samples from individual localities were taken. It is evident that geochemical data from pyrites of deposit from which most The method of separation of mineral and the analytical method showing certain dispersion (certain analytic deviation) should also not be undervalued. In this way we would point also to the importance of the determination of distribution character.

We emphasize that in spite of above mentioned circumstance relations exist in the distribution of microelements which could be revealed and which express to more or less degree the common validity of natural distribution laws of certain elements in certain minerals (e. g. in pyrite) or in specific concrete rocks of certain genetic type. The distribution of elements in ores or rocks of polymineral composition is evidently more complicated with more complicated relations of distribution of individual elements in minerals represented in different and variable rate in ore or rock.

The complicateness of microelements distribution in monomineral fractions depends on the conditions of the formation of corresponding mineral-under various geological processes or there are few possible ways of origin. Pyrite belongs to the category of minerals arising under various conditions under the influence of manifold geological processes. Therefore such a mineral could show higher variability of the distribution of individual elements. The crystallochemical characters of the lattice of minerals and the ability to accept microelements in crystals in various way are particularly to be taken into consideration. The distribution depends also on individual microelements which can have various position in certain crystals and can be isomorphous or unisomorphous (heterogeneous). It is evident that the distribution of microelements in monomineral fraction shows a complex of relations which we can only partially determine but we are not able to attain to definite relatively universal conclusions.

The up to present lognormality investigations in the distribution of elements are mostly based on analyses of igneous rocks, mainly of granites. Till now no more extensive work exist which deals with the validity of the law of elements distribution in individual minerals. This question has been studied least at separated ore minerals. whereas on silicate minerals some studies were made. S. Ďurovič (1957) examined by us the distribution character of Mn, Ni, Cu, Zn in unseparated pyrrhotite ore from Heľpa and his considerations about distribution character were based on conversion to pure pyrrhotite.

The authors of this work intend therefore to apply the up to present knowledges about microelements distribution relations in separated pyrites namely to Zn and Cu contents, whereas Ni and Co contents were already investigated and will be published in the work by B. Cambel, J. Jarkovský (1967 in press). The distribution of other elements, Mn, Mo, V, Ti will be also gradually evaluated. The results of our investigations can be followed by means of graphs and one table. In table 1 the number of analytic values of Ni, Co, Zn and Cu divided into concentration intervals are given. The table is also illustrated graphically (fig. 1, 2). In the table not only analyses of the authors of this article are included but also analyses of F. Hegemann (1943), C. M. Wright (1965) and H. Lange (1957) are included.

In fig. 1 the specific course of Co frequency curves of syngenetic pyrites (more values with higher Co contents) compared with hydrothermal pyrites (left side of graph) is shown. Frequency curves of Ni contents of syngenetic (left side of graph) and of hydrothermally epigenetic pyrites (right side of graph) on the contrary do not show any differences in its course.

Fig. 2 shows the rapid rise of frequency curves of Zn contents at low to zero contents as well as in the interval of high contents. Besides that the regular increase of pyrite analyses with Zn contents at the value of 250 ppm perhaps can indicate that a part of Zn can be isomorphous as it supposed F. Hegemann. Cu frequency curves show more regular course. The frequency curves of Cu and Zn similarly as those of Co and

Table 1. Comparative table of values of contents frequencies divided into 13 concentration groups

Element		>4000	3999—3000	2999—2000	1999—1500	1499—1000	999—750	749—500	499—250	249—100	99—50	49—10	<10	not found	Total sum
Co	1	1	3	15	9	32	27	36	98	88	85	58	1	10	463
	2	23	5	11	5	16	16	35	59	47	11	70	—	19	317
	3	24	8	26	14	48	43	71	157	142	108	130	—	29	800
	4	—	—	—	—	—	—	—	—	7	22	29	—	34	92
	5	7	12	3	7	13	9	16	21	32	60	32	1	26	239
	6	37	7	3	16	17	6	24	25	38	21	47	153	42	436
	7	44	19	6	23	30	15	40	46	70	81	79	1	68	522
	8	68	27	32	37	78	58	111	203	219	211	238	154	131	1567
Ni	1	1	11	17	52	49	32	34	57	55	34	91	4	26	463
	2	—	—	1	2	—	4	7	24	54	33	161	2	29	317
	3	1	11	18	54	54	41	46	87	129	105	326	6	75	953
	4	—	—	—	1	9	1	2	15	11	9	26	—	18	92
	5	12	10	5	5	13	6	16	19	30	29	52	2	40	239
	6	14	2	4	4	16	5	18	25	46	26	89	3	31	283
	7	26	12	9	9	29	11	34	44	76	55	141	5	71	522
	8	27	23	27	64	92	53	82	146	216	169	493	11	164	1567
Zn	1	25	10	11	5	17	15	12	37	86	—	—	—	80	298
	2	98	5	17	20	15	—	11	6	17	—	—	—	128	317
	3	123	15	28	25	32	15	23	43	103	—	—	—	208	615
	4	—	—	—	—	—	—	—	1	14	2	—	—	57	74
	5	6	7	4	3	4	—	2	6	69	7	—	—	49	157
	6	9	2	—	4	2	—	15	—	8	—	—	—	243	283
	7	15	9	4	7	6	—	17	6	77	7	—	—	292	440
	8	138	24	32	32	38	15	40	50	194	9	—	—	557	1129
Cu	1	7	15	5	7	35	23	29	39	64	39	30	—	6	298
	2	108	13	26	13	9	2	31	20	16	25	13	19	22	317
	3	115	28	31	20	44	25	60	59	80	64	43	19	28	615
	4	—	—	—	—	—	—	2	—	3	12	21	8	28	74
	5	3	9	1	2	28	12	6	28	29	21	17	1	3	157
	6	21	1	3	8	7	2	37	17	15	34	31	53	54	283
	7	24	10	4	10	35	14	43	45	44	55	48	54	57	440
	8	139	38	35	30	79	39	105	104	127	131	112	81	113	1129

Explanations: 1 — syngenetic metamorphosed pyrites presented by B. Cambel, J. Jarkovský 1967; 2 — analyses of syngenetic pyrites presented by F. Hegemann; 3 — 1+2+ foreign pyrites presented by B. Cambel, J. Jarkovský 1967 + analyses of C. M. Wright 1965; 4 — concretionary pyrites in unmetamorphosed sediments and coal analyzed by the authors and

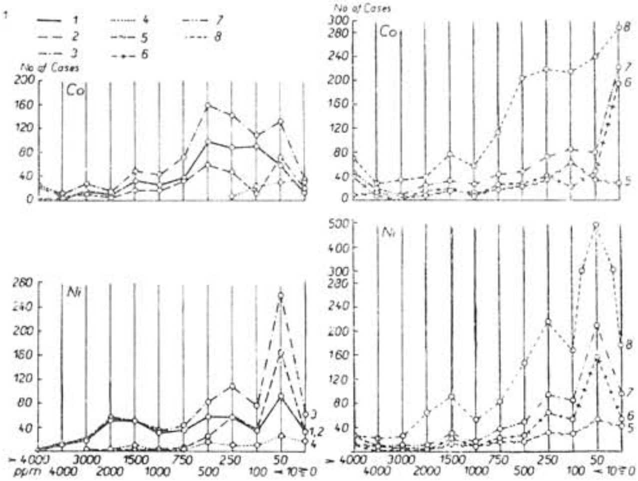


Fig. 1. Graph of Ni and Co contents (according to table 1) divided into concentration groups. Explanations: 1 — syngenetic metamorphosed pyrites of ČSSR; 2 — syngenetic metamorphosed pyrites analyzed by F. Hegemann (1943); 3 — addition 1+2+foreign pyrites analyzed by B. Cambel, J. Jarkovský (1967) + analyses of C. M. Wright (1965); 4 — sedimentary pyrites of concretionary character in limestones, clays and coal from occurrences in ČSSR and taken from the work by F. Hegemann; 5 — hydrothermal pyrites of ČSSR; 6 — hydrothermal pyrites analyzed by F. Hegemann (1943); 7 — addition of values 5+6+ analyses of H. Lange (1957); 8 — sum of all analyses. Similar explanations with table 1.

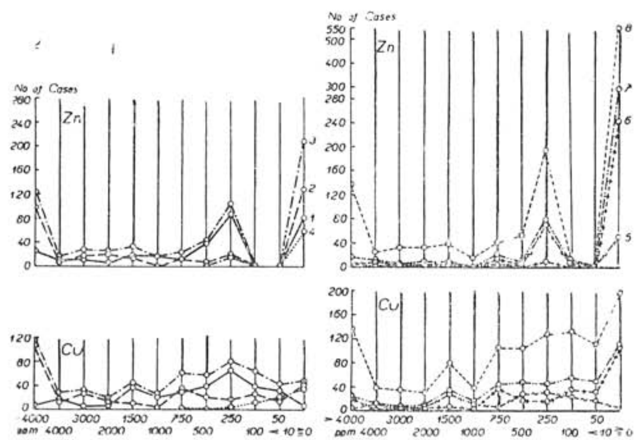


Fig. 2. Graph of Zn and Cu contents values divided into concentration groups. The values are taken from table 1. Explanations to figure 1, table 1.

Ni in contradiction to Co curves do not display different course at syngenetic pyrites (left side of graph) and at hydrothermally epigenetic pyrite (right side of graph).

Distribution of Cu and Zn in Pyrite

According to existing opinions which we confirm essentially, appear Zn and Cu in pyrite prevailingly as unisomorphous heterogeneous admixtures and a small part of these elements can form an isomorphous admixture in pyrite. The problem of crystallochemical position of microelements is treated by the authors in the work which is now in press (B. Cambel, J. Jarkovský 1967).

The complete evaluation of distribution of elements contents was carried out in the following way: we investigated Zn and Cu contents first of all in higher metamorphosed syngenetic pyrites from West Carpathian region (Malé Karpaty Mts., Heľpa, Polhora, Žiar Valley), afterwards particularly in Smolník pyrites (epimetamorphosis) as well as in Chvaletice and Zlaté Hory pyrites and at last we made Zn and Cu values histograms of all pyrites of main deposits in ČSSR analyzed by us being of syngenetic character and metamorphosed in various stage. We present particularly Zn and Cu contents histograms of hydrothermal pyrites from deposits in ČSSR analyzed by us. In histograms in other figures also analyses of F. Hegemann (1943), H. Lange (1957), C. M. Wright (1965) are included. These analyses were included into various graphs according to the genesis of the pyrites.

We remark that considerable difficulties in graphical illustration were caused by the analytic results of F. Hegemann which show raised frequency in certain regular intervals of values (e. g. 500, 1000, 1500, 2000 ppm — fig. 11). F. Hegemann has also considerable pyrite analyses with high Zn and Cu contents which we could not include into graphs for saving place but in two cases we made from analyses presented by F. Hegemann histograms with the interval of 250 ppm on another scale (fig. 11).

A brief rewiew of separation and spectrochemical method employed by us is given in the article by B. Cambel, J. Jarkovský (1966). We add that the width of the interval as it is applied in histograms is for Zn as well as for Cu equal (50 ppm on linear scale and 0,1 log. ppm on logarithmic scale). Therefore it is possible to compare frequencies of the both elements in pyrites from various deposits.

In this work we deal with the problem of differences in the distribution of isomorphous (Ni, Co) and unisomorphous elements (Zn, Cu) and therefore we present except histograms of Zn and Cu also comparative Ni and Co frequency curves.

We suppose that isomorphy of certain elements in minerals manifests with regard to the contents of these microelements by certain relatively fixed concentrations of microelements in minerals and the frequency of the microelements contents is delimited in some way. It could be supposed on the other hand that the way of representation of unisomorphous microelements in the mineral would be manifested by more variable contents without more determinable delimitation of concen.rations. The high number of low to zero contents of microelements on the one hand and a considerable number of cases with high contents on the other hand therefore can sometimes point to heterogeneous position of these elements in minerals. We present for the purpose of comparison frequencies of concentration values of Co Ni, Zn and Cu given in table 1.

It is evident from the table that whereas at Co and Ni there is a relatively small number of trace and zero values as well as of high values (above 4000 ppm) at Cu and Zn it is the contrary. It is evident further that from 1567 analyses on Co 131 data lie under the sensitivity limit of he method (10 ppm). After adding of still 153 analyses of H. Lange (1957) it will be together 284 analyses, e. i. 18.12 % of the total number of analytic data. Cases of above 4000 ppm Co are from 1567 only 68 (4.34 %). Ni has from 1567 analyses 175 cases of zero to trace values (under 10 ppm, 11.17 %) and 27 cases of values above 4000 ppm (1.72 %). Zn has 557 cases of zero to trace values (under the sensitivity limit of 100 ppm) i. e. 49.33 % and 138 (12 %) analyses above

4000 ppm from 1129 analyses. Among 1129 Cu analyses there are 194 zero values and values under the limit (17,18 %) and 139 cases are above 4000 ppm (12,31 %).

We call attention to the fact that the above mentioned assupmtions of the possibility of determination of microelements position in pyrite on basis of the investigation of their contents frequency can be only relatively correct and are not valid in every case for certain elements in certain minerals. It is evident that the crystallochemical position of individual microelements in the lattices of minerals is not clear and requires further discussion. Various transitions exist between homogenous mixture crystals (isomorphy) and proper heterogeneity. Heterogeneous mixture crystals (epitaxis — in V. A. Frank-Kameneckij 1964) and anomal mixture crystals (in M. Kyrš, M. Křivánek 1960) stand in the middle. We remark that we put to heterogeneous form also types of representation close to homogenous ones as it is the form of inner adsorption of elements arising with gradual crystal growth when crystalloid particles of colloidal dimensions adsorbing some microelements originate in crystal individuals.

This structure is observable under electron microscope as so called „defect structure" (S. Kipikašová, G. Kminiaková 1966).

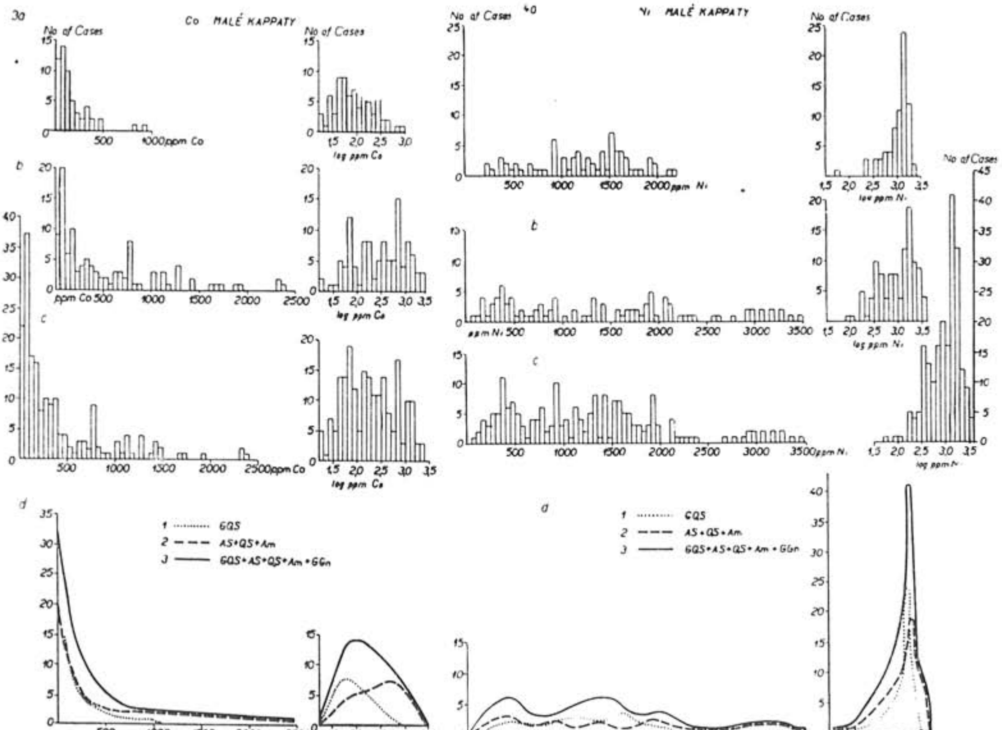


Fig. 3. Histograms and frequency curves of Co contents in pyrites from various Malé Karpaty ore types made on linear and logarithmic scale. Explanations: 1 — pyrites from graphite-quartz-sulphide ores least metamorphosis; 2 — pyrites from high metamorphosed ores amphibole-sulphide, quartz-sulphide ores and pyrites from amphibolites; 3 — sum of pyrites from all Malé Karpaty ore types 1+2+ mineralized graphitic gneisses.

Fig. 4. Histograms and frequency curves of Ni contents in pyrites from various ore types of Malé Karpaty mineralization made on linear and logarithmic scale. Explanations to figure 3.

The character of Ni and Co distribution in pyrites can be seen in following figures by means of comparative frequency distribution curves which were made by drawing histogram contours.

Fig. 3 shows Co contents frequency in various metamorphosed Malé Karpaty pyrite ore types. All these types show clear positive asymmetric lognormal division (in the sense of L. H. A h r e n s 1963).

In fig. 4 wide dispersion of Ni contents concentrations in Malé Karpaty is given expressed at low excess values by irregular shape of frequency curve. On logarithmic scale Ni distribution values show moderate negative asymmetry and considerable excess. Fig. 4 shows clearly that Ni in Malé Karpaty pyrites has no lognormal distribution, which fact we ascribe particularly at Ni to redistribution process caused by metamorphic recrystallization.

Fig. 5 presents frequency curves of pyrites from main pyrite deposits of ČSSR. The essentially lognormal division of Co contents in syngenetic pyrites from Malé Karpaty Mts., Smolník as well as in hydrothermal West Carpathian pyrites is evident from the histograms. The frequency curve at hydrothermal pyrites shows two tops on logaritmic scale. In this case there are pyrites from numerous hydrothermal West Carpathian deposits, the subvolcanites particularly have different Co and Ni contents. The frequency curve of Co contents in Hel'pa pyrites (high metamorphosed pyrites in catazone) which does not point to lognormal distribution character deserves particular attention. All Ni distribution curves on fig. 5 except those from Malé Karpáty Mts. show lognormal distribution character although they have relatively irregular course (hydrothermal pyrites and pyrites from Chvaletice and Zlaté Hory).

Fig. 6 shows Co and Ni distribution curves of pyrites from metamorphosed syngenetic deposits in ČSSR, to which existing analyses of F. H e g e m a n n, C. M. W r i g h t

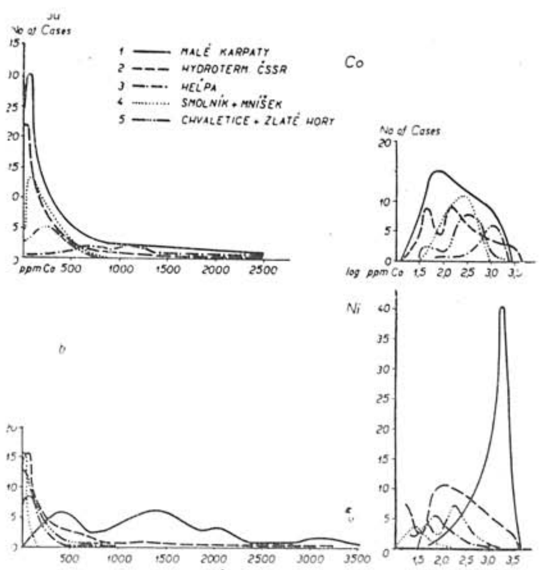


Fig. 5. Comparative frequency curves made by drawing histogram contours of Co and Ni contents in pyrites from main pyrite deposite in ČSSR. The curves were made by drawing histogram contours.

and H. L a n g e were added. The curves show clearly the lognormal division of Co in all cases given in the graph. Frequency curves of Co distribution in pyrites of metamorphosed deposits analyzed by F. H e g e m a n n and syngetic West Carpathian pyrites only show complicated course on logarithmic scale. In the case it is the result of genetic heterogeneity of pyrites derived from various world deposits and in the second case (in West Carpathian pyrites) it is caused by various grade of metamorphosis of pyrite deposits in ČSSR.

Ni on the contrary to Co has not so typical lognormal distribution. It is caused by the fact that Malé Karpaty pyrites being very numerous (around 250) have not lognormal distribution. The simultaneous combining of various distribution character in pyrite analyses from various genetic types of deposits is evident from fig. 6 from Ni

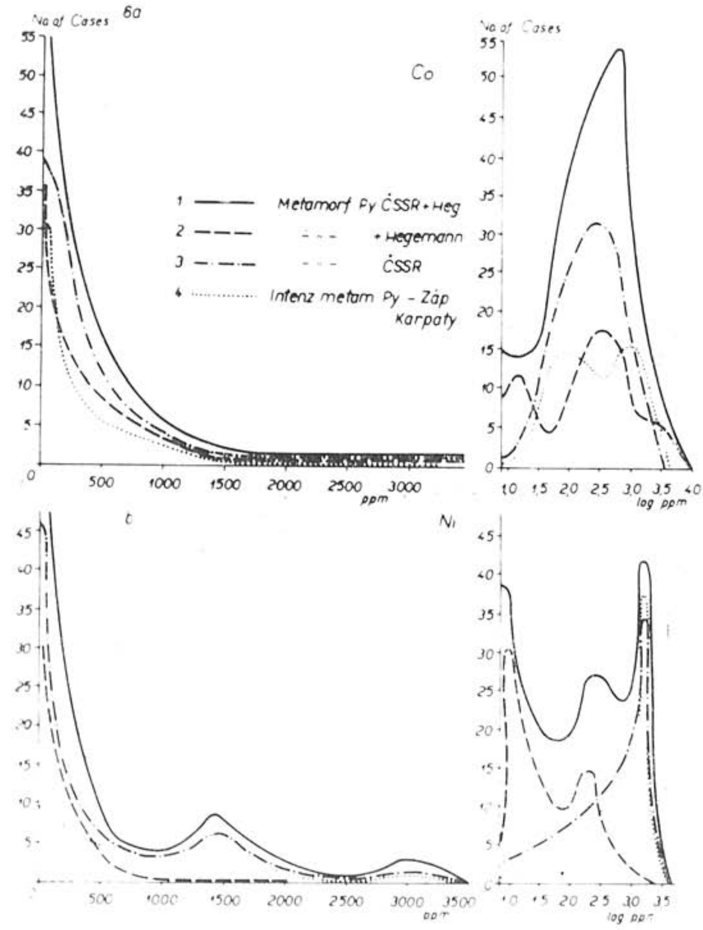


Fig. 6. Comparative histograms of Ni and Co frequency curves made on linear and logarithmic scale. The curves were made by drawing histogram contours. Explanations: 1 — pyrites of metamorphosed pyrite deposits in ČSSR + pyrites presented by F. H e g e m a n n being of the same genesis; 2 — metamorphosed syngenetic pyrites presented by F. Hegemann (1943); 3 — metamorphosed pyrites of pyrite deposits of ČSSR; 4 — intensively metamorphosed West Carpathian pyrites of Malé Karpaty Mts., Heľpa, Polhora, Žiar Valley.

distribution curves on logarithmic scale. The combination of negative excessive skewness (asymmetry) (syngenetic pyrites of ČSSR) and positive excessive skewness (asymmetry) (pyrites analyzed by F. H e g e m a n n) are seen there and in middle part of summary curve (full line) a top appear which is typical for frequency curves of Ni distribution in hydrothermal pyrites (fig. 7c).

The presented histogram indicates the importance and influence of the number of pyrite analyses and their selection from certain types of deposits for making summary distribution curves and for the determination of common distribution relations. It is evident that also the so called distribution relations are only relatively common and express relations dependent on factors mentioned in foregoing text (number of analyses, selection of samples and their locality, quality of analysis).

Fig. 7c shows Ni and Co distribution in pyrites of hydrothermal genesis. In these pyrites manifests clearly the typical character of lognormal division with positive skewness (asymmetry). The course of frequency curves on logarithmic scale only reveals certain differentiation in the distribution characteristic of pyrites of various groups of hydrothermal deposits presented in graph.

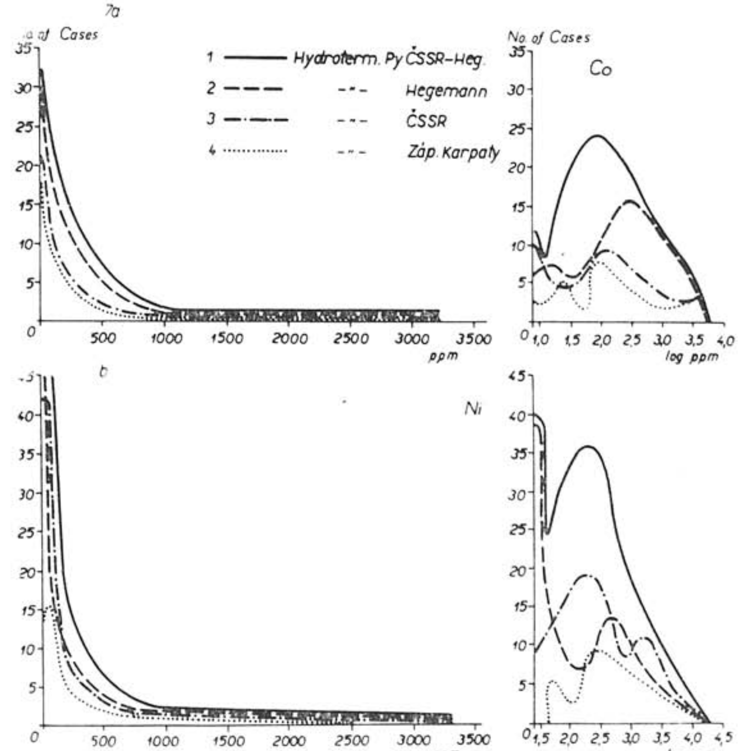


Fig. 7. Comparative histograms of Ni and Co frequency curves made on linear and logarithmic scale. The curves were made by drawing histogram contours. Explanations: 1 — hydrothermal pyrites of deposits in ČSSR and of those mentioned by F. H e g e m a n n (1943); 2 — pyrites of hydrothermal deposits presented by F. H e g e m a n n (1943); 3 — hydrothermal pyrites of ČSSR; 4 — hydrothermal pyrites of West Carpathians.

Evaluation of Zn and Cu frequency histograms

In figures 8 and 9 histograms of Zn and Cu contents from deposits of Malé Karpaty Mts., Helpa and Polhora, Smolník and Mníšek (8b, 9b), Chvaletice and Zlaté Hory (8c, 9c) are particularly presented as well as summary histogram of above mentioned partial histograms (8d, 9d).

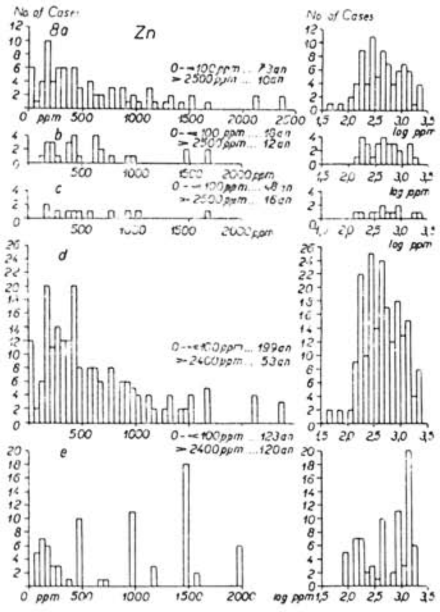


Fig. 8. Histograms of Zn contents in pyrites from various pyrite deposits in ČSSR of syngenetic origin and in pyrites presented by F. H e g e m a n n (1943) of the same genesis. Explanations: 8a — pyrites from Malé Karpaty Mts., Helpa and Polhora high metamorphosis, 8b — pyrites from Chvaletice and Zlaté Hory deposits, 8d — all metamorphosed syngenetic pyrites of ČSSR, 8e — metamorphosed pyrites analyzed by F. H e g e m a n n. The upper number above the individual graphs signifies the number of analyses with trace to zero contents. The lower number signifies the number of analyses above 2400 or 2500 ppm of the element.

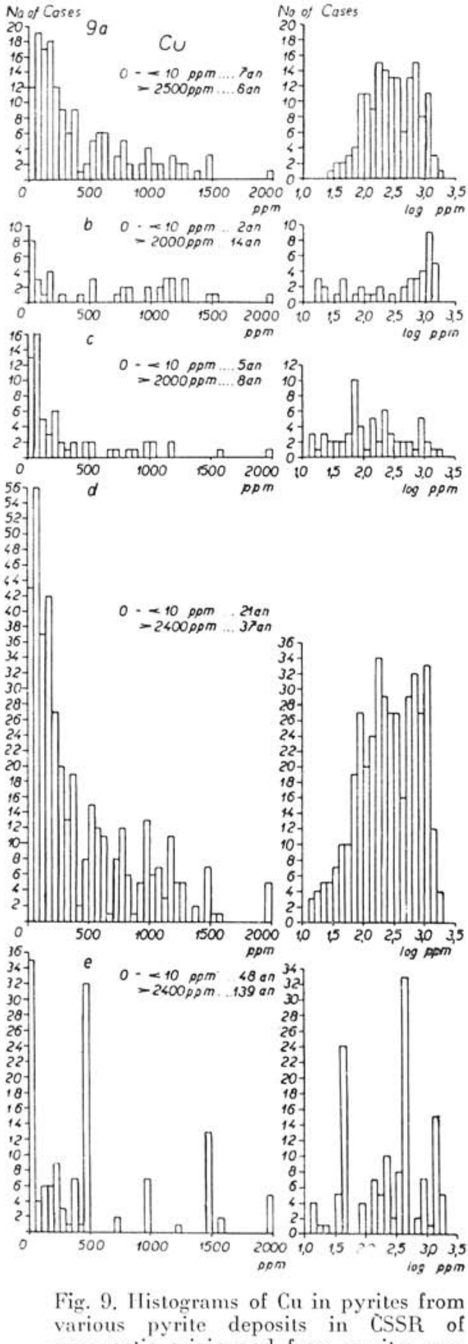


Fig. 9. Histograms of Cu in pyrites from various pyrite deposits in ČSSR of syngenetic origin and from pyrites presented by F. H e g e m a n n of the same genesis. Explanations: as to fig. 8.

The histograms show compared with Co and Ni histograms trace (<100 ppm) and zero values and extreme high values (above 2500 ppm) among numerous cases which were not plotted into histograms. It is the case e. g. in pyrite analyses from Chvaletice and Zlaté Hory and in numerous analyses of F. H e g e m a n n (fig. 11). Summary histograms of Zn distribution from above mentioned deposits show indistict positive asymmetric division being of indistinct lognormal character. High values of Zn contents are related with difficult separation of pyrite from Zn minerals.

Histograms of Cu in pyrites (fig. 9) in contradiction to Zn are characteristic by more lognormality and more analyses because trace (< 10 ppm) to zero values seldom occur in pyrites. On the contrary to that Cu values in pyrites are very high which is connected with consirable difficulties in the separation of pyrite from chalcopyrite (also in relation to sphalerite). High Cu values show particularly the analyses of F. H e g e m a n n, in which 139 analyses have vaules above 2500 ppm Cu (fig. 11).

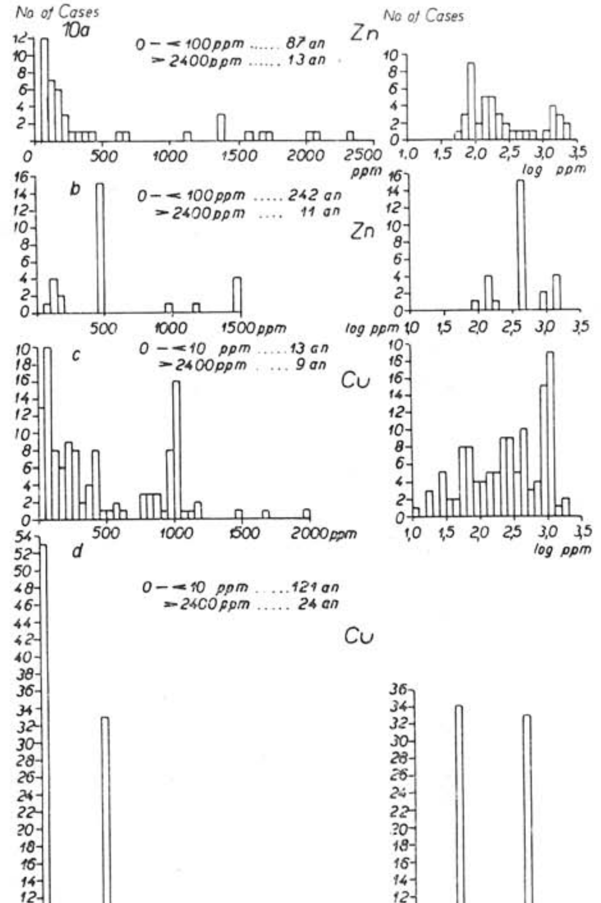


Fig. 10. Histograms af Cu and Zn contents in pyrites from hydrothermal deposits. Explanations: 10a + 10c — Zn and Cu in hydrothermal pyrites of ČSSR, 10b + 10d — Zn + Cu in hydrothermal pyrites presented by F. H e g e m a n n.

Fig. 10 presents histograms of Zn and Cu contents from pyrites of hydrothermal deposits in ČSSR (10a, 10c) and from pyrites of hydrothermal deposits given by F. H e g e m a n n (10b, 10d). It is evident that hydrothermal pyrites have lower Zn and Cu contents than syngenetic pyrites and that the number of cases with trace to zero contents increases, whereas the number with high contents of mentioned elements decreases there. These numerical data are presented particularly with histograms.

Fig. 12a shows summary histograms of Zn values in syngenetic metamorphosed pyrites from ČSSR and in pyrites presented by F. H e g e m a n n, fig. 12b shows histogram of Zn values in hydrothermal pyrites.

A part of fig. 12c present the sum of histograms of Zn distribution of all analyses mentioned by the authors and by F. H e g e m a n n. This histogram indicates that Zn has the character of middle expressive lognormal distribution with positive skewness (asymmetry) and on transformed logarithmis scale the symmetrical extension of distribution frequency is visible.

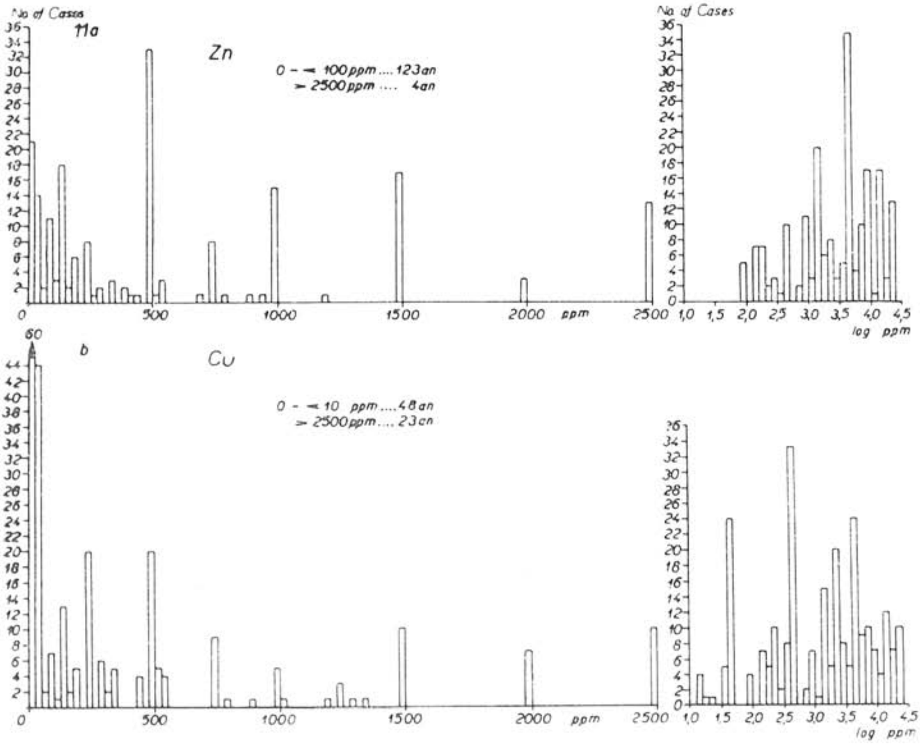


Fig. 11. Histograms of Zn and Cu contents in pyrites from syngenetic deposits analyzed by F. H e g e m a n n (1943).

Fig. 13a shows summary histogram of Cu frequency of syngenetic metamorphosed pyrites in ČSSR and of pyrites presented by F. H e g e m a n n, in fig. 13b a histogram of Cu of pyrites from hydrothermal deposits is made. Cu is in contradiction to Zn represented in more analyses and shows more expressive lognormal distribution with excessive positive inclination. No more expressive difference between the distribution of Cu in hydrothermal and in syngenetic pyrites is noticed there.

Fig. 14 illustrates the sum of Cu histograms given in fig. 13. The conclusion from the foregoing figure about the lognormal character of Cu distribution is confirmed there.

Conclusions

Ni and Co histograms of fundamental genetic types of pyrite (syngenetic pyrites and hydrothermal epigenetic pyrites) show only in main features a uniform but in detail different picture. Ni and Co have on linear scale also lognormal positive asymmetric distribution, whereas the division of values on logarithmic scale is essentially normal (symmetrical) but Ni has more irregular shape of frequency curves.

Our investigations show that one of the reasons of exceptional (normal) distribution of Co and Ni in pyrites is the high metamorphosis which caused additional redistribution of Co and Ni and in this way also the change of character of entire primary distribution of these elements. E. g. Co from Heľpa pyrites has distribution close to normal and similar distribution shows also Ni from Malé Karpaty pyrites. Certain irregularity in histograms made from analytic data of pyrites taken from several deposits was caused by manifold genetic conditions at these deposits. In the case of different character of Ni and Co distribution in different ore types, also in pyrites within one deposit. this circumstance can be probably ascribed to the fact (e. g. at Ni) that with higher Ni contents in pyrite one part of Ni represents the isomorphous constituent of pyrite and the other part represents the unisomorphous constituent. Two distribution types of the same element can therefore exist and combine under certain conditions also within one mineral.

The investigation of the character of Co and Ni as well as of Zn and Cu and of other

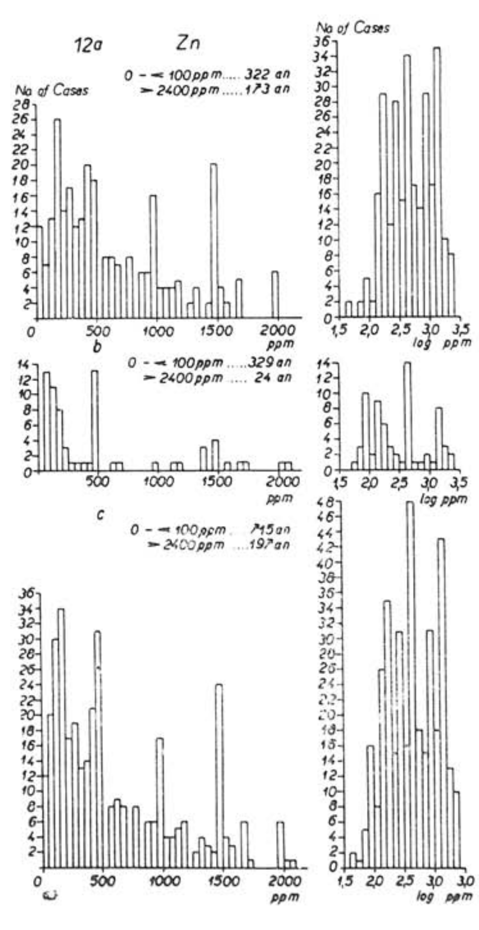


Fig. 12. Summary histograms of Zn contents values in pyrites: a — in syngenetic pyrites of ČSSR and in pyrites presented by. F. H e g e m a n n (1943) and C. M. W r i g h t (1965); b — in hydrothermal pyrites of ČSSR and in pyrites presented by F. H e g e m a n n; c — sum 1+2 l. e. of all pyrites types.

elements (Mn, Mo, V, Ti), about which we shall inform later, points to essentially lognormal character of the distribution with positive skewness (asymmetry) of all the named microelements in pyrite, regardless of being elements bound to pyrite by isomorphy or unisomorphy. The isomorphous or unisomorphous character of elements in pyrite therefore cannot be determined on basis of the distribution character according to hitherto existing investigations of the distribution of micro-elements in pyrite. The distribution of Co and Ni indicates very sensitive reaction of isomorphous elements in pyrite which can be considered as indicatory elements on the change of genetic conditions of pyrite and sensitive reflection of the influence of thermodynamic and other geological factors under the action of which the mineral arose or altered and recrystallized in their distribution. Such a sensitive reaction on the distribution and redistribution show among trace elements in pyrite Ni and Co only, whereas typical heterogeneous elements do not display such a sensitive differentiation of distribution

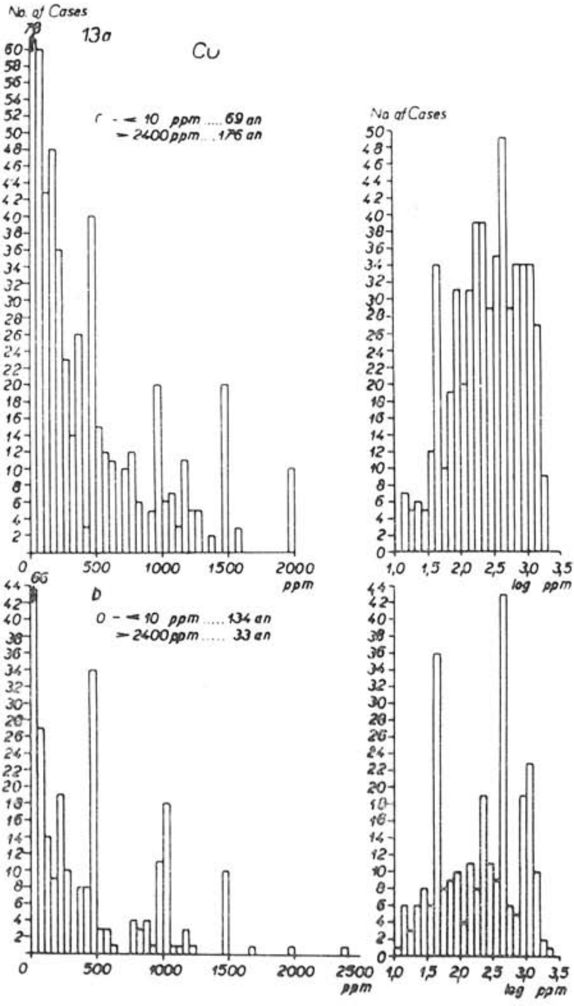
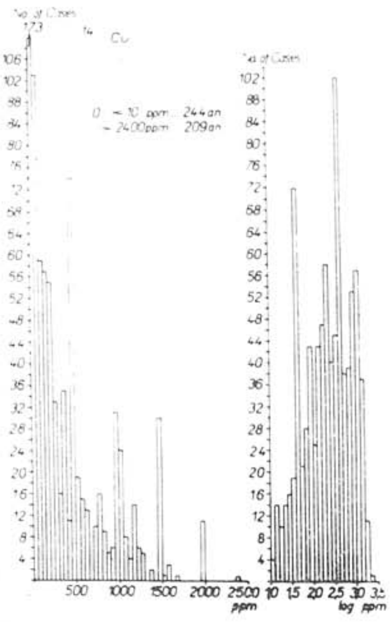


Fig. 13. Histograms of Cu contents expressed on linear and logarithmic scale. Explanations: a — metamorphosed syngenetic pyrites of ČSSR Hegemann. b — hydrother- and pyrites presented by F. mal pyrites of ČSSR and pyrites of hydrothermal deposits presented by F. Hegemann.

Fig. 14. Histogram of Cu contents in pyrites of all types of deposits analyzed by B. C a m b e l, J. J a r k o v s k ý and F. H e g e m a n n.



in relation to genetic conditions. It is evident from the histograms that heterogeneous elements in syngenetic pyrites as well as in hydrothermal pyrites show equal distribution character and also histograms from individual localities do not show such an expressive variability of distribution as Co and Ni. The above mentioned text is confirmed by the conclusion that isomorphous elements in pyrite (Ni and Co) similarly as unisomorphous elements (Zn, Cu and other) have essentially lognormal character of distribution but isomorphous elements display sensitive change of distribution character in relation to genetic conditions.

Translated by J. P e v n ý.

REFERENCES

A h r e n s L. H., 1954a: The lognormal distribution of the elements (A fundamental law of geochemistry and its subsidiary). Geochim. et Cosmochim. Acta 5. — A h r e n s L. H., 1954b: The lognormal distribution of the elements. II. Geochim. et Cosmochim. Acta 6. — A h r e n s L. H., 1957: Lognormal — type distributions. III. Geochim. et Cosmochim. Acta 11. — A h r e n s L. H., 1963a: Lognormal — type distributions in igneous rocks. IV. Geochim. et Cosmochim. Acta 27, 4. — A h r e n s L. H., 1963b: Lognormal — type distribution in igneous rocks. V. Geochim. et Cosmochim. Acta 27. — A h r e n s L. H., 1963c: Element distributions in igneous rocks. VI. Negative skewness of SiO_2 and K. Geochim. et Cosmochim. Acta 27. — A h r e n s L. H., 1964: Element distributions in igneous rocks. VII. A reconnaissance survey of the distribution of SiO_2 in granitic and basaltic rocks. Ceochim. et Cosmochim. Acta 28. — A h r e n s L. H., 1964: The significance of the chemical bond for controlling the geochemical distribution of the elements 1. Phys. Chem. Earth 5, 1. — A h r e n s L. H., 1966: Element distribution in specific igneous rocks. VIII. Geochim. et Cosmochim. Acta 30.

— A u b r e y K. V., 1956: Frequency-distributions of elements in igneous rocks. Geochim. et Cosmochim. Acta 9. — B a d a l o v S. T., B a s u t o v a S. M., G o d u n o v a L. I., Š o d n e v F. Š., 1966: K geochimii renija i molibdena v endogennych suľfidnych mestoroždenijach Srednej Asii. Geochimija 1, 99, Moskva. — C a m b e l B., J a r k o v s k ý J., 1966: The possibility of utilising of the nickel and cobalt in pyrites as indikators of ore genesis. Geol. sborn. Slov. akad. vied 17, 1, Bratislava. — C a m b e l B., J a r k o v s k ý J., 1967: Geochémia pyritu niektorých ložísk ČSSR. Vydav. SAV (in German with English summary) (in press). — Ď u r o v i č S., 1957: O lognormálnom rozdelení prvkov — I. Rozdelenie koncentrácií Ni, Cu a Mn v heľpianskom pyrotíne. Geol. sborn. Slov. akad. vied 8, 2, Bratislava. —
F r a n k - K a m e n e c k i j V. A., 1964: Priroda strukturnych primesej i vkľjučenij v mineralach. Izd. Leningr. universiteta, Leningrad. — H e g e m a n n F., 1941: Die isomorphen Beziehungen von Mn, Zn, Co, Ni und Cu zu Pyrit und Magnetkies. Zeitschr. f. Krist. 103. — H e g e m a n n F., 1943: Die geochemische Bedeutung von Kobalt und Nickel im Pyrit. Zeitschr. f. angew. Min. 4, Berlin. — C h a y e s F., 1954: The lognormal distribution of the elements — a discussion. Geochim. et Cosmochim. Acta 6. — K o l m o g o r o v A. N., 1941: On lognormal law of particle distribution at crushing. Compt. Rend. Ac. Sci. USSR 29, 2. — K m i n i a k o v á G., K i p i k a š o v á S., 1966: Zur Frage der Untersuchungen der Erzstrukturen. Geol. sborn. Slov. akad. vied 17, 1, Bratislava. — K y r š M., K ř i v á n e k M., 1960: Spolusrážení anorganických příměsí v mikrokoncentracích. Chem. listy 7, 54, Praha. — L a n g e H., 1957: Paragenetische und genetische Untersuchungen an der Schwefelkieslagerstätte „Einheit“ bei Elbingerode (Harz). Freiberger Forschungshefte C 33, Berlin. — M a r k o v A. A., 1917: On some limit formulae of the probability calculations. Bull. Acad. Imp. Sci. 6, 3, Petrograd (in Russian). — M i c h a l e k Z., 1958: Molybdenum in iron sulphide minerals. Bull. de l'Acad. polon. des sciences, Série des sci. chim., géol. et géogr. 6, 12, Warszawa. — M i c h a l e k Z., 1960: Nickel and cobalt in pyrites and marcasites. Bull. de l'Acad. des Sci. Série des sci. géol. et géogr. 8, 1, Warszawa. — M i l l e r R. L., G o l d b e r g E. D., 1955: The normal distribution in geochemistry. Geochim. et Cosmochim. Acta 8. — R a s u m o v s k y N. K., 1940: On the distributions of the metal concentrations in ore deposits. Compt. Rend. Acad. Sci. USSR 28, 9. — R a m u s o v s k y N. K., 1948: Lognormal law of the distribution of matter and its attributes. Leningr. Mining Inst. Bull. 20 (in Russian). — R i c h a r d s o n W. A., S n e e s b y G., 1922: The frequency distribution of igneous rocks. Mineralog. Mag. 19, 97.
R i c h a r d s o n W. A., S n e e s b y G., 1923: The frequency distribution of rocks. Mineralog. Mag. 20, 1. — R o d i o n o v D. A., 1961: K voprosu o logaritmičeski-normaľnom raspredeleniji soderžannych elementov v izveržennych gornych porodach. Geochimija 4. — S h a w D. M., B a n k i e r J. D., 1954: Statistical methods applied to geochemistry. Geochim. and Cosmochim. Acta 5. — V i s t e l i u s A. B., 1945: Frequency distributions of corosity coeficients and epigenetical processes in spirifer beds of the Buguruslan oilbearing region. Compt. Rend. Acad. Sci. USSR 49, 1. — V i s t e l i u s A. B., S a r m a t o v O. V., 1947: The stochastical basement one of geologically valuable probability distribution. Compt. Rend. Acad. Sci. USSR 58, 4 (in Russian). — V i s t e l i u s A. B., 1948a: On the quartz particles roundness in the sand of Belinsky Bank delta of the Volga. Compt. Rend. Acad. Sci. USSR 63, 1 (in Russian). — V i s t e l i u s A. B., 1948b: The measure of correlation between the numbers of the paragenesis. Mineralog. Soc. USSR, Bull. 77, 2 (in Russian). — V i s t e l i u s A. B., 1949: The calcium sulphates in Paleozoic beds of the east of the Russian platform. Geochem. Symposium Oil Inst. USSR 1 (in Russian). — V i s t e l i u s A. B., 1952: On the probability distributionsreply zo U. C. Dmitryevsky. Bull. Acad. Sci. USSR, ser. geol. 1 (in Russian). — V i s t e l i u s A. B., 1960: The skew frequency distributions and the fundamental law of the geochemical processes. The Journ.of Geol. 68, 1. — W r i g h t C. M., 1965: Syngenetic pyrite associated with a precambrian iron ore deposit. Econ. Geol. 60.

Review by J. K a n t o r.