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ON THE CHARAKTER OF THE DISTRIBUTION OF MANGANESE, VANADIUM, MOLYBDENUM AND TITANIUM IN PYRITES[1]

(Text-figs. 1—20)

Abstract: In this article the character of distribution of Mn, V, Mo and Ti in separated pyrites is discussed. The prevailing part of analytic data is original and only the smaller part of analyses is taken from literature. The discussion about relations of the distribution of the above mentioned elements is based on histograms and frequency curves. In the conclusion it is stated that almost all till now investigated microelements in pyrites (Co, Ni, Cu, Zn, Mn, V, Mo, Ti), isomorphous as well as unisomorphous, show in essentials lognormal or near to lognormal distribution.

In the foregoing works of the authors (B. Cambel, J. Jarkovský 1966) it has been stated that microelements as Co, Ni, Cu and Zn have in essentials lognormal character of distribution with positive asymmetry, regardless if they are isomorphous or unisomorphous. The difference is only that isomorphous elements in pyrite (cobalt, nickel) reacted very sensitively on the change of genetic conditions of pyrite, whereas unisomorphous elements as zinc and copper did not show such sensitive reaction during the process of rise or recrystallization of pyrite. It can be shown by the fact that the character of Ni and Co distribution in pyrites from various types of deposits changes.

In this article similarly as in the foregoing one we compare the differences in relations of distribution at manganese, vanadium, molybdenum and titanium in the basis genetic types of pyrite as in syngenetic more or less metamorphosed pyrites or in hydrothermal-epigenetic pyrites. We are based particularly on the results of pyrite analyses from Czechoslovakia, carried out by the authors (B. Cambel, J. Jarkovský 1967) and we take over the data of Mn, presented by F. Hegemann (1943), of V by H. Lange (1957). The analyses of V and Ti by C. M. Wright (1965) and of Mo in pyrites by Z. Michalek (1958) are included.

In graphs partial histograms of microelements contents in pyrites from individual deposits in ČSSR or from individual types of deposits are presented. In table 1 data of the frequency of elements contents in pyrites divided into 13 concentrations groups are presented. These data are illustrated also graphically in comparative graphs (text-fig. 1 — Mn graph, text-fig. 2 — V graph, text-fig. 3 — Mo graph, text-fig. 4 — Ti graph). Closer explanations are given with table 1 and with the text-figures.

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[1] This article is the continuation of the study on relations of distributions of Ni, Co, Cu and Zn in pyrite, published in „Geologický sborník 1966, 18, 2" and we recommend the readers to study the mentioned article. The relations of distribution of Ni and Co are presented separately in the monographic work by the authors „Pyrite Geochemistry of Some Deposits in ČSSR", which will come out in the Publishing House of the Slovak Academy of Science in 1967.

Table 1. Comparative table of frequency values of elements contents in pyrites 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
Mn	1	—	6	1	5	9	8	10	39	37	51	201	—	96	463
	2	15	—	1	14	10	7	26	12	42	12	42	—	136	317
	3	15	6	2	19	19	15	36	51	79	63	243	—	232	780
	4	—	1	—	—	—	—	2	—	12	7	16	—	54	92
	5	2	1	2	2	7	3	11	26	42	26	70	1	46	239
	6	—	—	—	3	2	—	4	6	23	4	38	—	203	283
	7	2	1	2	5	9	3	15	32	65	30	108	1	249	522
	8	17	8	4	24	28	18	53	83	156	100	367	1	535	1394
V	1	—	—	—	—	—	1	1	5	12	180	77	—	227	503
	2	—	—	—	—	1	5	4	8	25	200	133	—	300	676
	3	—	—	—	—	1	—	3	—	2	61	27	1	144	239
	4	—	—	—	—	2	5	7	8	27	261	160	1	444	915
Mo	1	—	—	1	—	—	1	—	1	7	62	231	23	224	550
	2	—	—	1	—	—	1	—	1	10	66	265	47	224	615
	3	—	—	—	1	—	—	—	2	2	5	73	65	155	303
	4	—	—	1	1	—	1	—	3	12	71	338	112	379	918
Ti	1	1	7	9	3	15	11	18	42	62	87	156	3	89	503
	2	1	7	9	3	15	11	19	44	78	89	156	3	89	524
	3	3	4	10	4	7	2	11	13	21	14	69	12	69	239
	4	4	11	19	7	22	13	30	57	99	103	225	15	158	763

Explanations to the Mn rubric: 1 — syngenetic metamorphosed pyrites presented by B. Cambel, J. Jarkovský (1967); 2 — analyses of syngenetic pyrites mentioned by F. Hegemann; 3 — 1 + 2 + foreign analyses mentioned by B. Cambel, J. Jarkovský (1967); 4 — concretionary pyrites in unmetamorphosed sediments and coal analyzed by the authors and by F. Hegemann; 5 — hydrothermal pyrites of ČSSR and foreign pyrites mentioned by the authors; 6 — hydrothermal pyrites analyzed by F. Hegemann; 7 — addition of 5 + 6 + analyses by F. Lange (1957); 8 — total addition of all pyrites given under the numbers 3, 4 and 7.

Explanations to the rubric of V, Mo and Ti: 1 — metamorphosed syngenetic pyrites of ČSSR and some foreign pyrites mentioned by B. Cambel, J. Jarkovský (1967); 2 — the same + analyses on V by H. Lange (1957), with Mo the analyses by Z. Michalek (1958) are added and with Ti the analyses by C. M. Wright (1965); 3 — hydrothermal pyrites of ČSSR including some foreign pyrites analyzed by the authors in 1967, with Mo the analyses by Z. Michalek (1958) are added; 4 — addition of all analyses given under the numbers 2, 3.

Manganese

According to accessible data from literature, particularly the opinion of F. Hegemann (1939, 1941), Mn forms heterogeneous admixture in pyrite. According to L. H. Ahrens (1965) it may be admitted on the basis of values of ionization potentials that a very small part of Mn could be bound also isomorphously in sulphides.

Text-fig. 1. Graph of Mn contents in pyrites (according to tab. 1) divided into concentration groups. Further explanations are given with table 1.

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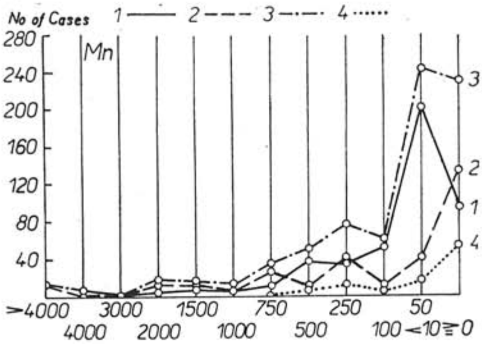

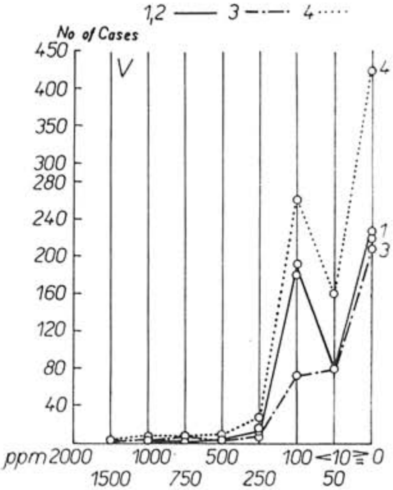

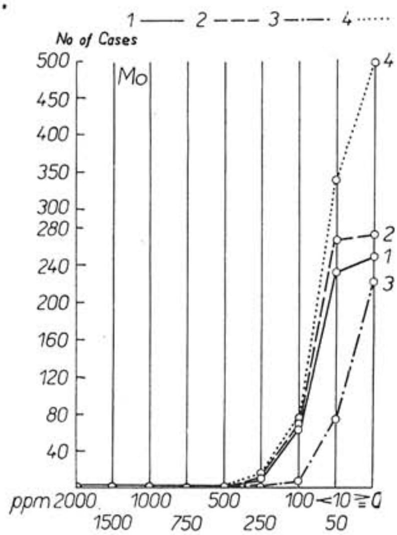

Text-fig. 2. Graph of V contents in pyrites (according to table 1) divided into concentration groups. Explanations are given with table 1.

Text-fig. 3. Graph of Mo contents in pyrites (according to table 1) divided into concentration groups. Explanations are given with table 1.

Text-fig. 4. Graph of Ti contents in pyrites (according to table 1) divided into concentration groups. Explanations are given with table 1.

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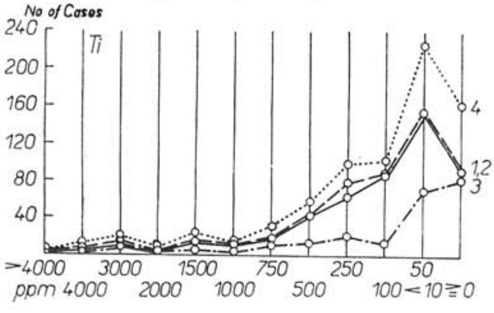
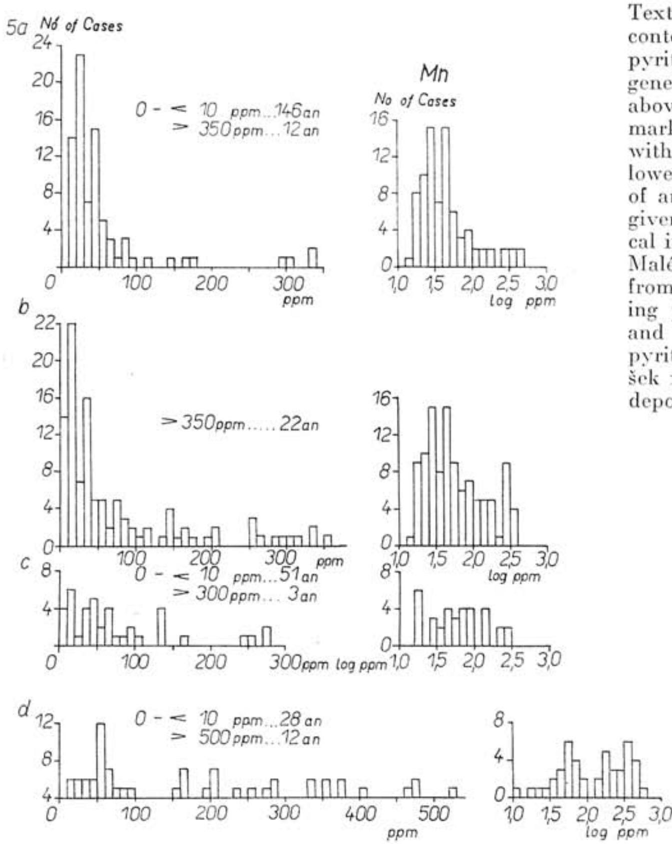


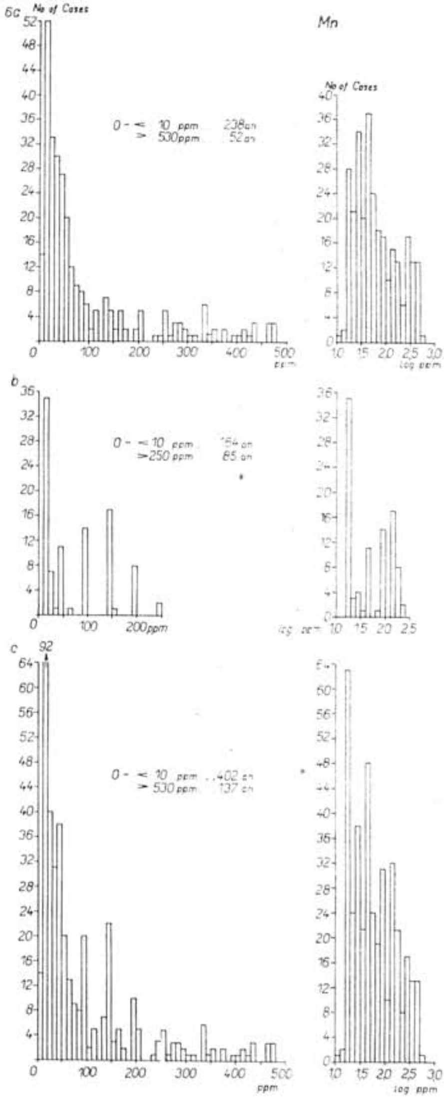


Text-fig. 5. Histograms of Mn contents in pyrites from various pyrites deposits in ČSSR of syngenetic origin. The upper number above the individual histograms marks the number of analyses with trace to zero values, the lower number marks the number of analyses with values over that given by corresponding analytical information. a — pyrites from Malé Karpaty Mts.; b — pyrites from Malé Karpaty Mts. including pyrites from Heľpa, Polhora and Žiarska dolina Valley, c — pyrites from the Smolník-Mníšek region; d — pyrites from the deposit Chvaletice and from the Zlaté Hory region.

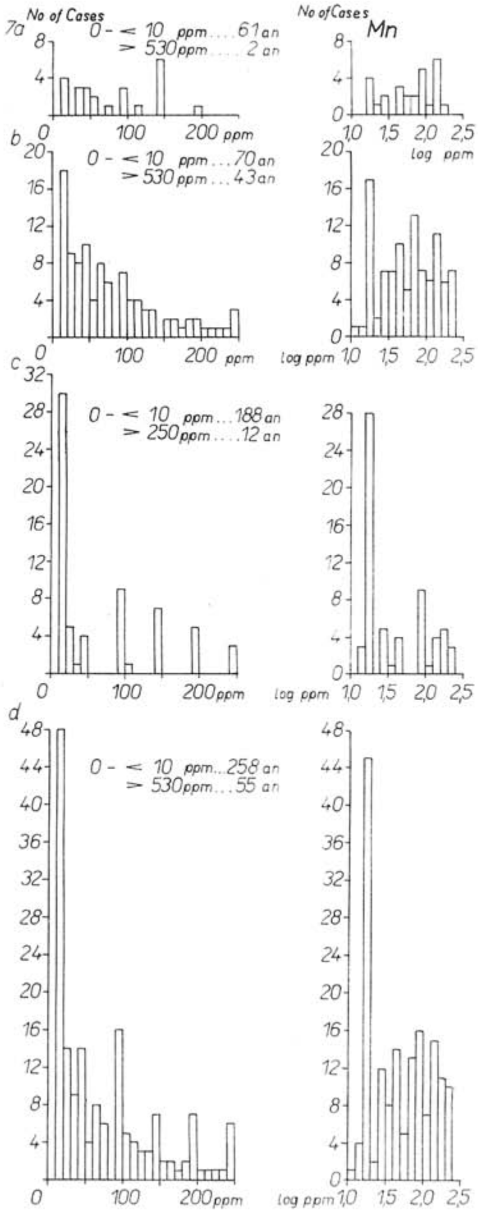
This conclusion is also supported by the results of separation carried out by B. C a m b e l, J. J a r k o v s k ý (1967). The repeated phase separation of pyrite was carried out in a mixture of diluted HCl (1 : 1) + HF. During the separation a certain small part (thousandths to hundredth of $^0/_0$) was unseparable. We suppose that this fact could support the opinion of L. H. A h r e n s on partial isomorphy of Mn in pyrite.

On text-fig. 5 showing histograms of Mn contents from various metamorphosed deposits in ČSSR similarly as on text-fig. 6 with histograms from hydrothermal deposits it may be seen that the majority of Mn has lognormal distribution. Mn of pyrites from Smolník and Mníšek (text-fig. 5c) and from Chvaletice including those from Zlaté Hory (text-fig. 5d) only doesn't show lognormal distribution character. It is due to the fact that in Smolník only a small part of pyrites contains Mn and in Chvaletice and Zlaté Hory, particularly at the last deposit, which is Mn-bearing, a part of pyrites contains anomal Mn quantity.

On text-fig. 6 attention is needed to be called to histogram 6b and on text-fig. 7 to histogram 7c, in which analytical data by F. H e g e m a n n (1943) are presented. It is evident that analytical values of Mn contents were probably rounded off because they concentrate in certain regular intervals of Mn contents. This fact upsets to a considerable extent also the character of other histograms, in which the results of F. H e-

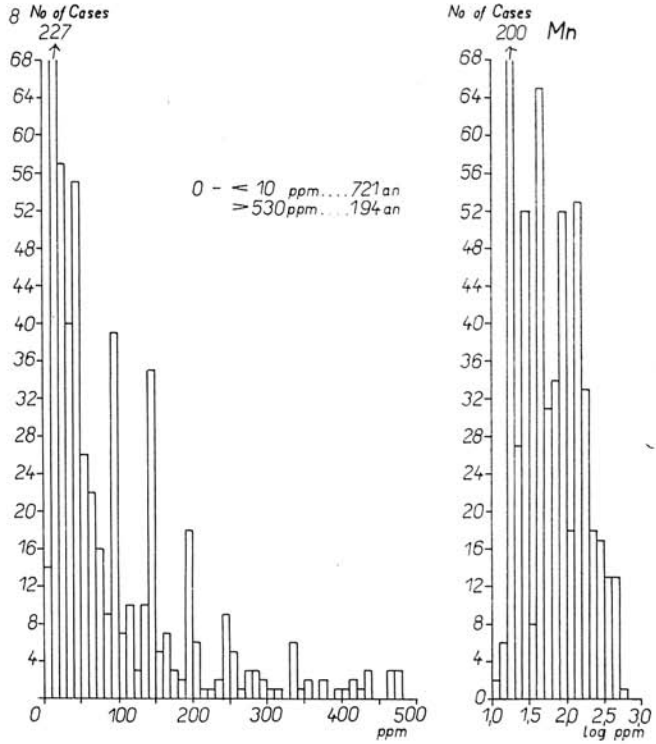


Text-fig. 6. Histograms of Mn contents in pyrites from various syngenetic pyrite deposits analyzed by the authors and by F. Hegemann (1943). a — syngenetic pyrites of ČSSR; b — syngenetic pyrites analyzed by F. Hegemann; c — summary histogram of the analyses by the authors and by F. Hegemann.



Text-fig. 7. Histograms of Mn contents in pyrites from hydrothermal deposits and from concretions in unmetamorphosed sediments. a — concretionary pyrites in unmetamorphosed sediments of ČSSR (coal, clays) and analyses of pyrites of similar character, presented by F. Hegemann; b — hydrothermal pyrites of ČSSR; c — hydrothermal pyrites analyzed by F. Hegemann, d — summary histogram b + c.

gemann are included. The construction of frequency curves which form the histogram contours and are given on text-figs. 17 to 20 is made difficult in this way. Generally as to the text-figs. 5, 6, 7, 8 it can be ascertained that syngenetic as well as hydrothermally epigenetic pyrites show equal character of Mn distribution, very close

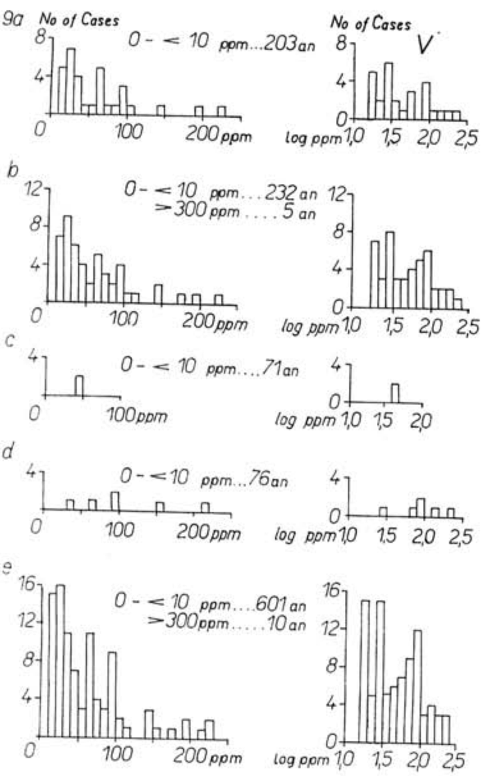


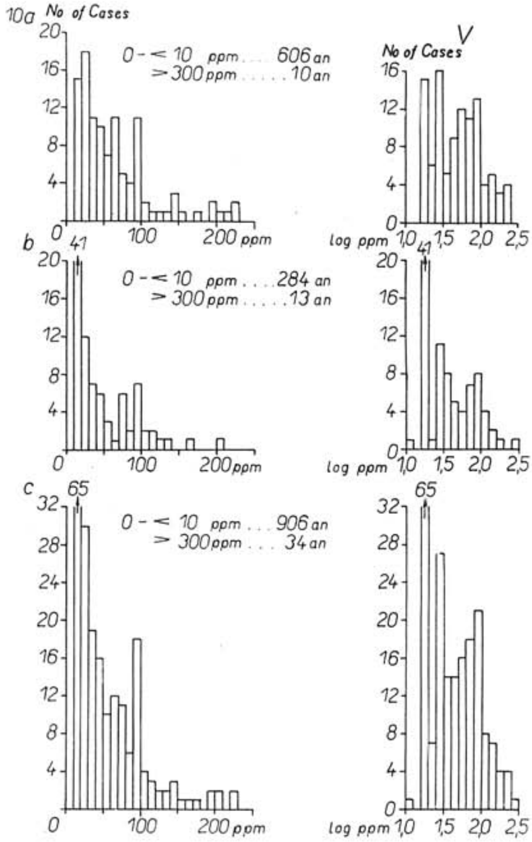
Text-fig. 8. Summary histogram of Mn contents in all pyrites analyzed by the authors and and by F. H e g e m a n n.

to the lognormal one. We may also ascertain that Mn in pyrites has relatively high percentage of cases of zero value. From 1394 cases (tab. 1) Mn was not found in 535 and values over 500 ppm appeared 160 times. The values plotted into the diagrams vary between 500 ppm and more than 10 ppm (tex-fig. 1) and make together 706 analyses. The histogram includes less than a half of cases. Text-fig. 1 shows two marked tops of the resultant curve 8 indicating most frequent Mn contents at the values of 250 to 100 ppm and maximal number of cases concentrating between the values of 10—49 ppm. The authors made on the whole about 800 pyrite analyses on Mn. The results confirm more frequent Mn content in syngenetic (232 analyses from 780 show no Mn, i. e. 30 % of cases) than in hydrothermal pyrites (249 analyses from 522 show no Mn, i. e. 47 % of cases).

V a n a d i u m

The problem of the crystallochemical position of V in pyrite was dealt with by few authors because so far only few such analyses were made. M. F l e i s c h e r (1955)





Text-fig. 9. Histograms of V contents in pyrites from pyrite deposits of syngenetic character in ČSSR. a — pyrites from Malé Karpaty Mts.; b — pyrites from Malé Karpaty Mts including pyrites from Heľpa, Polhora and Žiarska dolina Valley; c — pyrites from the Smolník and Mníšek region; d — pyrites from the Chvaletice deposit and Zlaté Hory region; e — summary of the above mentioned histograms.

Text-fig. 10. Histograms of V contents in syngenetic and epigenetic pyrites. a — analyses of syngenetic metamorphosed pyrites of ČSSR including analyses by C. W. Wright (1965); b — analyses of hydrothermal pyrites of ČSSR; c — summary histogram a + b.

presents only 18 analyses on V in pyrite. More analyses were made by H. Lange (1957). These analyses as well as those by C. M. Wright (1965) we took into consideration. Earlier works already (C. W. Carstens 1943, F. Leutwein 1941) mentioned that hydrothermal pyrites did not have V in contrast to syngenetic pyrites. H. Lange ascertained, however, that pyrites from the mine Einheit Harz considered as hydrothermally-epigenetic by him, contained V as common constituent, which fact he ascribed to the enrichment of pyrite on V during the ascent of hydrotherms through sedimentary sequences.

According to our results the conclusions of C. W. Carstens and F. Leutwein can be also confirmed when the difference in V contents between syngenetic and epigenetic pyrites is not too great. On the whole the number of cases of analyses without V content from Czechoslovak syngenetic pyrite deposits is 227 from 503 analyses, i. e. 45 % of cases. At hydrothermal deposits 144 cases from 239 do not contain V, i. e. 60 % of cases. Some deposits have pyrites almost without V content. Such deposit is Smolník and partly also Chvaletice and mineralizations in the Zlaté Hory region.

As to the crystallochemical position of V in pyrite we have ascertained by means of phase separation with gradual diminishing of pyrite grain and with the effect of the mixture of acids HCl (1 : 1) + HF a systematic decrease of V content (B. Cambel, J. Jarkovský 1967). Accordingly it may be concluded that V forms a constituent of the heterogeneous admixture in pyrite, most likely in the way of inner adsorption with gradual crystallization of pyrite.

The graphs 9 and 10 show that also with high number of spectrochemical pyrite analyses there is not the possibility of getting sufficient number of concrete data on V content for making histograms because of high number of analyses with zero and trace values. In spite of all that we can ascertain that V is characterized within the interval of concentration from traces to 200 ppm by a type of distribution close to the lognormal one.

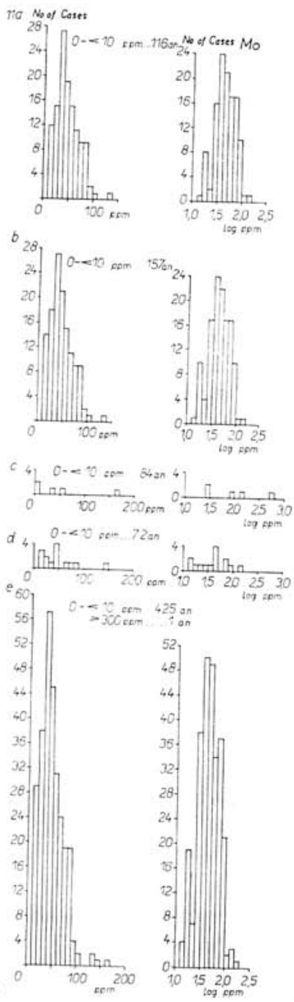
Molybdenum

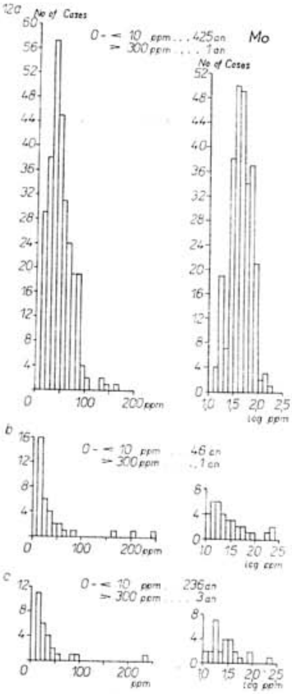
The study of molybdenum in pyrites was carried out only during the recent period. The majority of analyses (about 100) are given by Z. Michalek (1958) and in the work by B. Cambel, J. Jarkovský (1967) about 800 analyses are presented. Fewer analyses are given in other works, e. g. S. T. Badalov et al. (1966). According to the conclusion of Z. Michalek are pyrites forming at higher temperature characterized by low Mo contents (about 2 ppm), whereas Mo content in pyrites formed at lower temperature is increasing but does not exceed 100 ppm. Our results confirm the more frequent and also relatively higher Mo contents in sedimentary pyrites in contrast to hydrothermal pyrites as it follows from the enclosed text-fig. 3 as well as from tab. 1. From 615 analyses of pyrite of syngenetic origin presented by the authors together with the analyses by Z. Michalek Mo is absent (or present only in traces) in 251 cases, i. e. 40 %. Among 303 analyses of hydrothermal pyrites in 210 cases trace to zero Mo content was ascertained, making almost 70 %. From the text-fig. 3 it is evident that the maximum of cases with Mo content lies in the concentration interval of 10—49 ppm.

According to our opinions as well as to data in literature, e. g. A. B. Isajeva (1960) is Mo present in pyrite in the shape of heterogeneous admixture as fine dispersed molybdenite, most likely bound by inner adsorption. Thus the possibility of forming anomal mixture crystals in the shape of epitaxitic intergrowth, however, cannot be excluded absolutely.

As the made histograms show (text-figs. 11, 12, 13) Mo is the only element, which in contrast to other elements has the character of distribution rather close to normal. Particularly all metamorphosed syngenetic pyrites except those from Smolník and Chvaletice that contain Mo in few cases have symmetrical character of distribution with great excess. Only Mo in hydrothermal pyrites and concretionary pyrites from metamorphosed sediments shows approximately lognormal character of distribution (text-fig. 12b, c). Moreover it is necessary to remark that histograms of hydrothermal pyrites without Mo are made from relatively few cases.

This fact can prove the influence of just genetic-conditions on systematic uniform





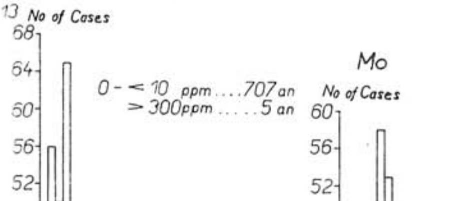
Text-fig. 11. Histograms of Mo contents in syngenetic pyrites. a — pyrites from Malé Karpaty Mts.; b — pyrites from Malé Karpaty Mts. including pyrites from Heľpa, Polhora and Žiarska dolina Valley; c — pyrites from Smolník and Mníšek; d — pyrites from Chvaletice and the Zlaté Hory region; e — summary of the above mentioned histograms.

Text-fig. 12. Histograms of Mo contents. a — in syngenetic pyrites of ČSSR including analyses of similar pyrites by Z. Michalek (1958); b — of concretionary pyrites from clays, carbonates and coal in ČSSR and similar pyrites analyzed by Z. Michalek; c — of hydrothermal pyrites in ČSSR analyzed by the authors.

and relatively low Mo content in crystals of syngenetic pyrites. Such a specific distribution was particularly effected by syngenetic-volcanogeneous-submarine metallogeneous processes combined sometimes with later metamorphosis. The source of Mo has to be sought in the simultaneous rise of surrounding sediments and pyrite mineralization and the milieu influenced intensively the content of microelements in pyrite during the process of its recrystallization. On the other side the hydrothermal process caused lesser regularity in the distribution of Mo and some other elements. In the majority of cases the hydrothermal transport caused variable representation of some elements related to the difficulty in their migration in hydrotherms. This is particularly valid for Mo contents. The above mentioned attests to the possibility of concluding syngenetic or epigenetic origin of pyrite mineralization on the basis of the character of distribution and abundance of Mo contents.

Titanium

The geochemistry of Ti in pyrites on the basis of quantitative analyses was studied so far minimally. M. Fleischer (1955) who has summarized the results on micro-elements contents in sulphides till 1955 presented only 21 analyses of pyrites on this element. Our results (B. Cambel, J. Jarkovský 1967) which provide for about 800 analyses on Ti content in pyrites show higher Ti contents in syngenetic metamorphosed pyrites in contrast to hydrothermal pyrites (tab. 1 and text-fig. 4). From 524 analyses of syngenetic metamorphosed pyrites in 89 cases Ti was not ascertained, i. e. only in 19 % of cases. In hydrothermal pyrites from 239 analyses Ti was not ascertained or found only in traces in 81 cases, i. e. 34 % of cases.



Text-fig. 13. Summary histograms of Mo distribution in all pyrites analyzed by the authors and by Z. Michalek.

As tab. 1 and text-fig. 4 show hydrothermal pyrites have maximal amount of cases with zero and trace values, whereas syngenetic pyrites reach maximum of cases within the interval of 49 to 10 ppm Ti.

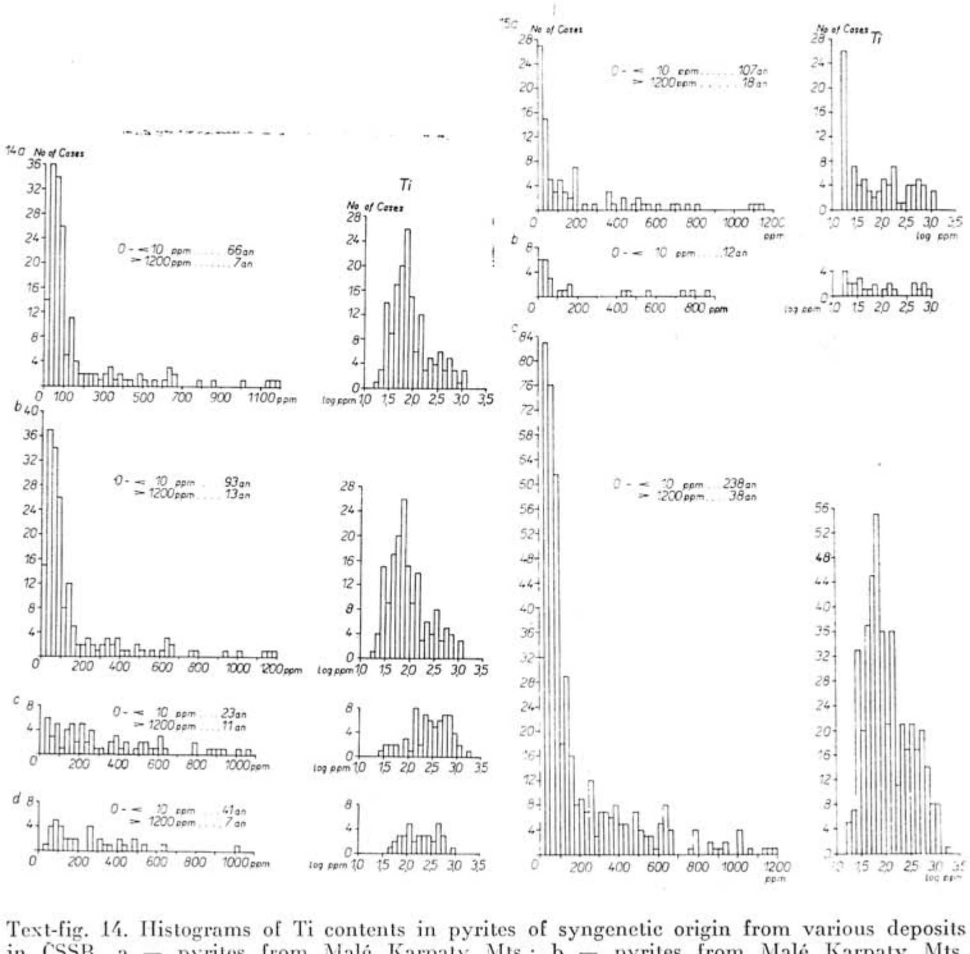
As to the way of representation of Ti in pyrites this question has not been treated separately in literature. According to our opinion there is one of heterogeneous forms of Ti representation in pyrite.

On the whole Ti is one of the elements which are present in pyrite almost in all cases and the histograms therefore show clearer the character of distribution. On text-fig. 14 histograms of Ti from metamorphosed syngenetic pyrite deposits in ČSSR are given. It is evident that only the Smolník and Chvaletice deposits have separate character of Ti distribution caused by more variable frequency of Ti contents. It can be seen clearly on the linear scale of these histograms. The comparison of text-figs. 14 and 15 shows no difference in the character of distribution and the lognormal type of distribution, similar to the syngenetic, also in hydrothermal pyrites. The type of distribution is most clearly characterized on text-fig. 16, where all the data of Ti contents are summarized, obtained by the authors and to a little degree taken from literature.

In a separate article we intend to present comparison of frequency curves of distribution of the individual elements, given in this as well as in the foregoing paper (B. Cambel, J. Jarkovský 1966), particularly in syngenetic and hydrothermally epigenetic pyrites. The frequency curves were made by drawing contours of summary histograms of contents of individual elements in syngenetic and hydrothermal pyrites. These comparative distribution curves not only determine the character of distribution but also make possible to know the number of analyses, from which the curve was formed, according to the size of the delimited surface or how many cases of contents of elements are found within the interval in the histogram.

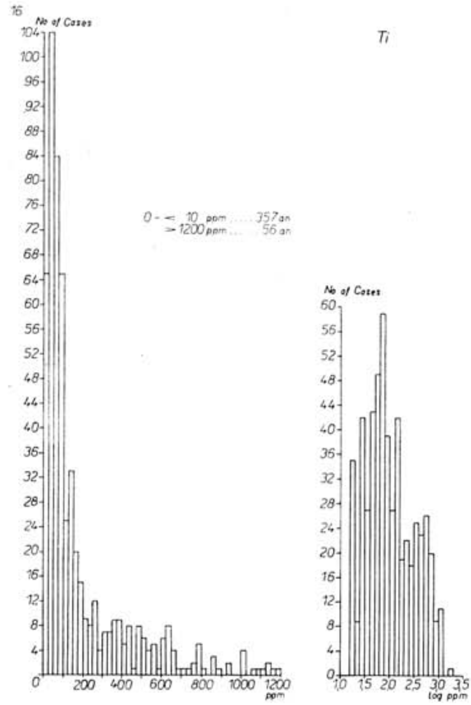
Text-fig. 17 shows that on the linear scale only Ni in syngenetic pyrites has deviations from lognormal type of distribution. It is the consequence of numerous analyses of highly metamorphosed syngenetic pyrites from the Malé Karpaty Mts. region and Helpa, placed here.

An exception is also made by Zn because its low contents (less than 100 ppm) are no more observable spectrochemically. Its frequency curve therefore shows decreasing tendency towards the low contents. On logarithmic scale only Ni shows anomaly,

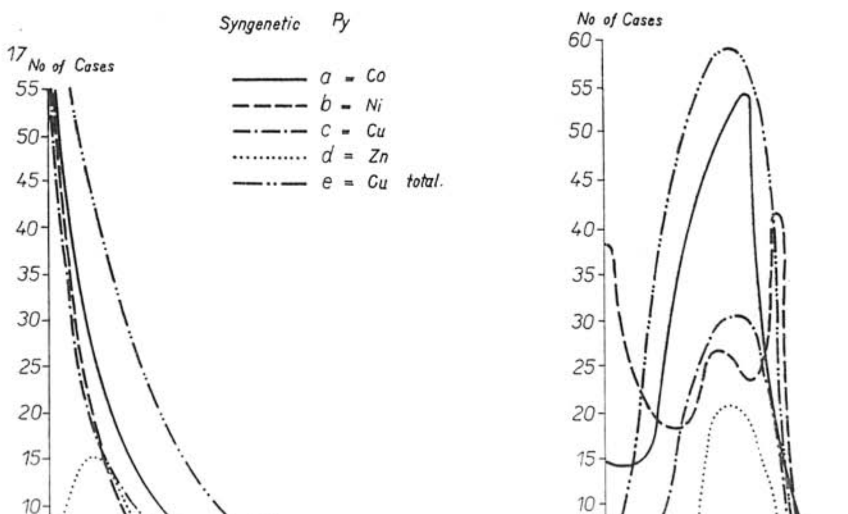


Text-fig. 14. Histograms of Ti contents in pyrites of syngenetic origin from various deposits in ČSSR. a — pyrites from Malé Karpaty Mts.; b — pyrites from Malé Karpaty Mts. including pyrites from Helpa, Polhora and Žiarska dolina Valley; c — pyrites from the Smolník and Mníšek region; d — pyrites from Chvaletice and Zlaté Hory region.

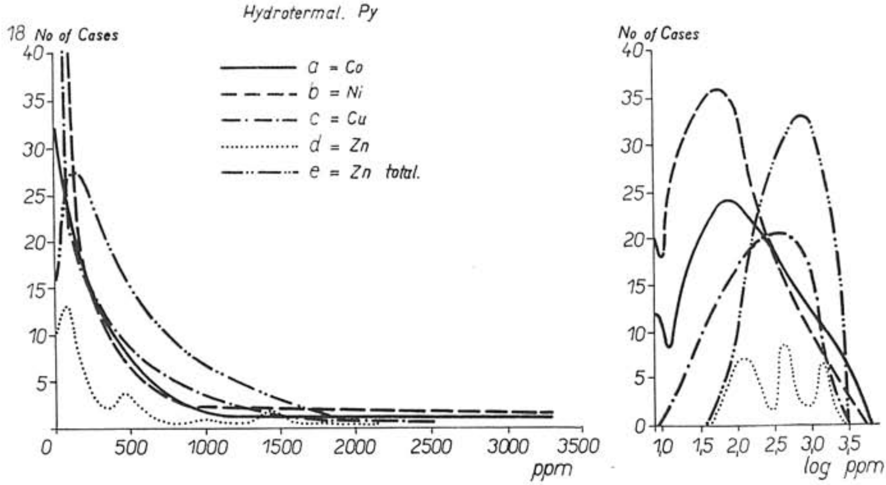
Text-fig. 15. Histograms of Ti contents in pyrites. a — in hydrothermal pyrites of deposits in ČSSR; b — in concretionary pyrites from clays, coal and carbonates in ČSSR; c — summary histogram of Ti contents in syngenetic pyrites mentioned by B. C a m b e l, J. J a r k o v s k ý (1967) and C. M. W r i g h t (1965).



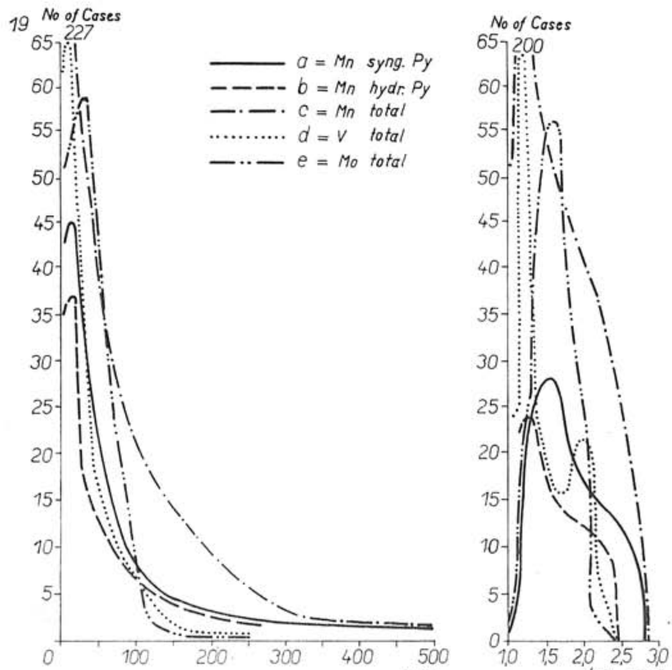
Text-fig. 16. Summary histogram of Ti contents in syngenetic and hydrothermally-epigenetic pyrites presented in the foregoing histograms (text-figs. 14, 15).



Text-fig. 17. Frequency curves of Co, Ni, Cu and Zn from metamorphosed syngenetic pyrites. a — Co from pyrites in ČSSR and pyrites mentioned by F. H e g e m a n n; b — Ni from pyrites in ČSSR and pyrites mentioned by F. H e g e m a n n; c — Cu from pyrites in ČSSR; d — Zn from pyrites in ČSSR; e — Cu from all types of pyrites.

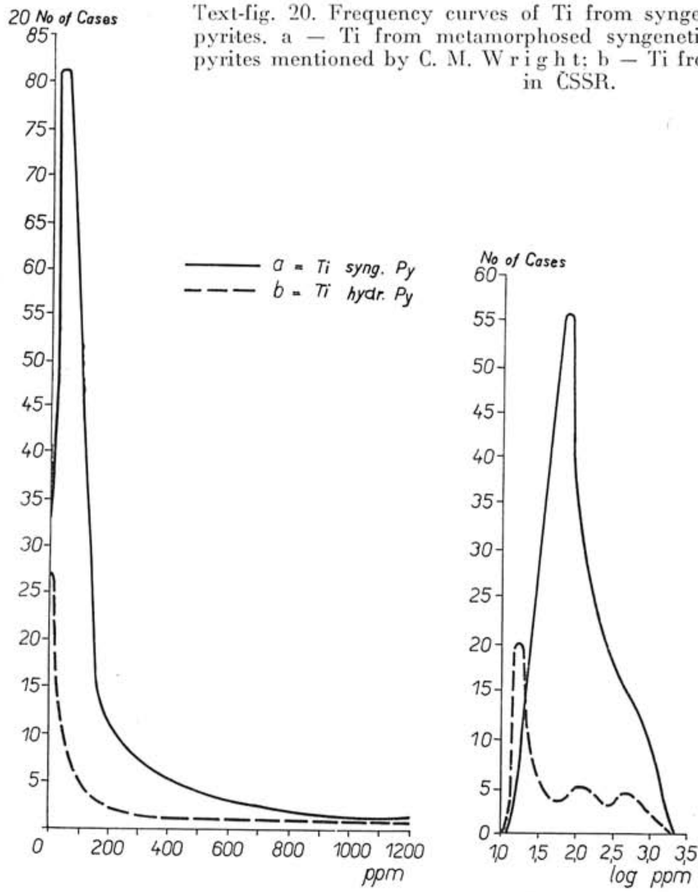


Text-fig. 18. Frequency curves of Co, Ni, Cu and Zn from hydrothermal pyrites. a — Co from pyrites in ČSSR and pyrites mentioned by F. Hegemann; b — Ni from pyrites of ČSSR and pyrites mentioned by F. Hegemann; c — Cu from pyrites in ČSSR and pyrites mentioned by F. Hegemann; d — Zn from pyrites of ČSSR and pyrites mentioned by F. Hegemann; e — Zn from all types of pyrites.



Text-fig. 19. Frequency curves of Mn, V and Mo from metamorphosed syngenetic and epigenetic pyrites. a — Mn from metamorphosed syngenetic pyrites in ČSSR; b — Mn from hydrothermal pyrites in ČSSR and pyrites mentioned by F. Hegemann; c — Mn from all types of pyrites; d — V from all types of pyrites; e — Mo from all types of pyrites.

having a curve with three tops. This is caused by summarizing of frequency curves of Ni in hydrothermal pyrites (positive asymmetry) and of the frequency curve of Ni from metamorphosed syngenetic pyrites of ČSSR (negative asymmetry — B. C a m b e l, J. J a r k o v s k ý 1966).



Text-fig. 20. Frequency curves of Ti from syngenetic and hydrothermal pyrites. a — Ti from metamorphosed syngenetic pyrites in ČSSR and pyrites mentioned by C. M. W r i g h t; b — Ti from hydrothermal pyrites in ČSSR.

On text-fig. 18, which shows contents of elements in hydrothermal pyrites a type of distribution very close to the lognormal can be seen. Zn also shows here a different character of distribution.

The comparison of frequency curves on text-fig. 17 and 18 indicates more irregularities in the character of distribution of elements in syngenetic pyrites from various deposits than in hydrothermal pyrites.

On text-fig. 19 are frequency curves of Mn, V and Mo. On the logarithmic scale only V shows frequency curves with two tops caused particularly by the abnormally high content of this element in some syngenetic pyrites.

Text-fig. 20 illustrates frequency curves of Ti from syngenetic and hydrothermal deposits. There is a type of distribution very close to the lognormal one with increased irregularity (positive asymmetry) of hydrothermal pyrites on the lognormal scale.

Translated by J. P e v n ý.

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