GEOLOGICKÝ ZBORNÍK — GEOLOGICA CARPATHICA 31, 1—2, BRATISLAVA, JUNE 1980, PP 49—63

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GEOCHEMICAL AND CRYSTALLOCHEMICAL ASPECTS OF THE DISTRIBUTION OF Mn AND Cu IN PYRITES AND PYRRHOTITES.

(Figs. 8, Tab. 2)

Abstract: The paper deals with the question of distribution and modes of occurence of Mn and Cu in pyrites and pyrrhotites, as well as with their mutual relations from the geochemical and crystallochemical point of view. The entrance of Cu into the crystal structure of pyrite is documented by the obtained data based upon the data from the foreign literature.

Резюме: Статья занимается вопросом распространения и форм выступания Mn и Cu в пиритах и пирротинах и их взаимных соотношений с геохимической и кристаллохимической точек зрения. На основании полученных данных, подкрепленных данными из зарубежной литературы, документирует возможность вступления Cu в кристаллическую структуру пирита.

At the geochemical study of microelements in pyrites and pyrrhotite we arimed first of all at the elements Ni and Co, for they occur in the mentioned sulphides mainly in isomorphic form. The evidence of this statement was recently given by means of X-ray microanalysis (B. Cambel, J. Jarkovský, J. Krištín, 1977).

Further elements occurring systematically, or almost systematically are Mn and Cu. The form of their occurrence at eleveated contents, can have heterogeneous character, as determined in pyrites from Chvaletice also by X-ray microanalysis (J. Kantor, J. Krištín, 1973; B. Cambel, J. Jarkovský, J. Krištín, 1977). In the first we studied the mode of Mn occurrence in pyrites and pyrrhotites by fractional separation (B. Cambel, J. Jarkovský, 1967). On the example of the pyrite from Chvaletice and of the pyrrhotite from Helpa we found that the spectochemically determined small contents of Mn remained both in pyrite and pyrrhotite also after repeated separation and they practically could not be removed by separation. Thus it can be concluded that up to a certain concentration level of Mn both in pyrite and pyrrhotite a crystallochemical relation to the structure of pyrite is preserved.

The problem has still remained open and it could not be successfully solved even by meant of X-ray microprobe because of its limited detection power. Therefore we described in pyrite and pyrrhotite the Mn, V, Ti Mo as scattered elements without more detailed determination of their mode of occurrence (B. Cambel, J. Jarkovský, J. Krišín, 1977). Among the listed elements only Mn is present nearly systematically in all genetic types of pyrite and pyrrhotite. At a more comprehensive study connected with a further microelement Cu, which is also systematically present in pyrite and pyrrhotite, we found by the method of column diagramms a negative correlation of the element pair Mn—Cu almost in all genetic types of pyrites and pyrrhotites.

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On the whole the realtions are as follows:

a) With the growing content of Cu in pyrites and pyrrhotites, the content of Mn falls more or less.

b) If pyrite and pyrrhotite occurs together in one sample, the content of Mn grows in the pyrrhotite whereas it simultatenously falls in pyrite. On the contrary, copper is more concentrated in pyrite and less in pyrrhotite.

The relation of Cu to pyrite can be explained also from the theoretical point of view on the basis of Jahn-Teller's effect or on the basis of As-presence in the structure of pyrite. If we start from the position of Mn and Cu in the periodic system of elements, as well as from the ionic and covalent character of sulphidic compounds formed by both the mentioned elements, it is necessary to state that Mn as siderophil element forms in its compounds the bond with more ionic character (e.g. alabandine MnS) than the typical chalcophil element Cu (e.g. in chalcopyrite $CuFeS_2$). It follows that Mn will be more concentrated in pyrrhotite which is in the fact also a covalent compound but having a higher part of ionic bond in comparison with pyrite. On the contrary Cu is more concentrated in pyrite than in pyrrhotite, because the pyrite contains in its structure a greater part of covalent bond than the pyrrhotite. Apart from that copper is more electronegative element than Mn. The values of electronegativity for Mn^{2+} is 180, for Fe^{2+} is 185 and for Cu^+ is 235 (A. S. Povarennych, 1963).

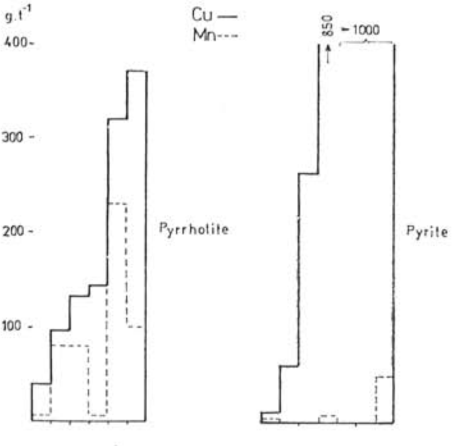


Fig. 1. The column diagrams of Cu and Mn contents in pyrrhotites and pyrites from Slavošovce (the contact of Gemerides with Veporides). *Explanations:* The data are represented according to the growing Cu contents, the figures on the horizontal axis represent the number of analysis.

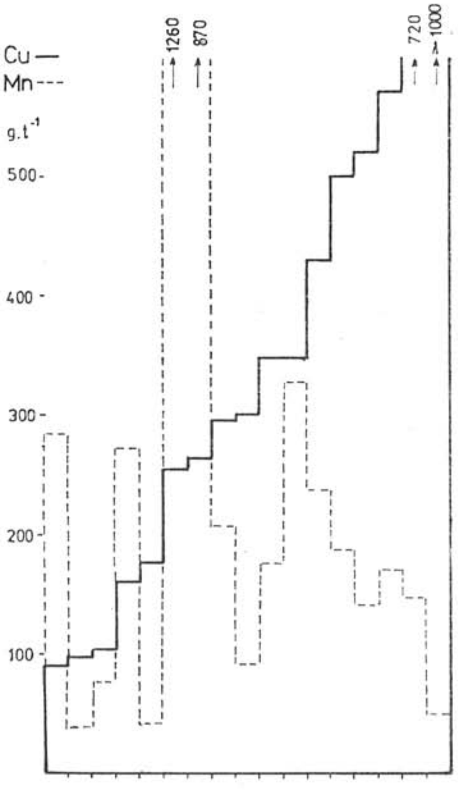


Fig. 2. The column diagrams of Cu and Mn contents in pyrrhotites from the Malé Karpaty Mts. *Explanations* like in the case of the Fig. 1.

A geochemical and crystallochemical relation of Mn and Cu to pyrite and pyrrhotite follows from the presented considerations. The same is proved in our works (B. Cambel, J. Jarkovský, 1967—1969), by numerous data a part of which is documented in the form of column diagrams (Fig. 1, 2). The relation of Cu to pyrite and of Mn to pyrrhotite is evident and was proved in the great majority of analysed samples of the mentioned sulphides. Exceptions are only in the case of unsufficiently separated samples.

It is however necessery to state, that the described relation concerning the contents of Mn and Cu in pyrites and pyrrhotites depends upon the specific geochemical conditions of the formation of the corresponding deposits or occurences, as well as upon the rock medium in which the studied sulphides were formed. So e.g. the pyrites from Chvaletice show relatively high contents of Mn similarly, like the pyrites from Heľpa. On the contrary, the pyrites from Malé Karpaty Mts. contain relatively small concentrations of Mn etc.

It is natural that in the case of very low contents of Mn and Cu in pyrites (e g. sedimentogenetic unmetamorphosed pyrites) this relation of the lowering of Mn-contents and of the growing of Cu-contents in pyrites can be discerned only by difficulties issuing from the relatively low spectrochemical detection power of both the elements, mainly of Mn.

The influence of physico-chemical and geochemical conditions on the distribution of Mn and Cu in pyrites.

At the study of Mn and Cu contents in pyrites from one deposit, the possibilities to follow the relation of these elements in pyrites from the spatial mainly vertical distribution are performable. In the recent years we pointed in collaboration with Železorudné bane n. p. (Iron ore mines) in Rudňany our attention on the study of the spatial distribution of elements in economically important minerals — siderite, baryte and chalcopyrite — from the Rudňany deposite. Beside of these minerals we also studied the distribution of the elements systematically present in the pyrite from the said deposit. The Rudňany deposit has been opened and accessible till the 19th horizon which fact, has enabled the possibility to follow the distribution of microelements in pyrite with the depth of the deposit.

As it follows from the table of spectrochemical data containing concentrations of Ni, Co, Mn and Cu in pyrites from the Rudňany deposit (Tab. 1), the contents of Co, Ni, Cu grow with the depth of the deposit and the content of Mn falls. This effect is conditioned almost by physico-chemical factors.

The presented relations are significantly characterized by the column diagrams of Mn and Cu contents in pyrites from the 10th and 16th horizon of the Droždiak vein (Fig. 3). They show that the growth of Cu contents with the depth of the deposit and the fall of the Mn ones.

As far as Ni and Co in the pyrites from the 10th and 16th horizon of the Droždiak vein in Rudňany, with the growing content of Co, the content of Ni grows with the deph, too. The same picture is reprosented also by the whole collection of analytical data for Mn and Cu in pyrites from Rudňany (35 analyses), (Fig. 4). It proves that beside of geochemical and physico-chemical factors, also crystallochemical factors, which we shall yet deal with later,

Table 1

The table of average spectrochemical data of Ni, Co, Cu and Mn contents in pyrites from the deposit Rudňany ($g.t^{-1}$).

The whole collection (35 analyses)

Element	$\bar{x}$	$\bar{x}_G$	Min. content	content Max.
Mn	293.2	60.3	4	3000
Cu	709.0	330.2	4	1700
Ni	930.0	735.0	117	2570
Co	1044.7	544.5	30	5100
The Droždiak vein (24 analyses)				
Mn	125.6	44.3	4	710
Cu	834.9	618.7	74	1700
Ni	1087.8	967.9	178	2570
Co	1358.4	897.0	186	5100
The Droždiak vein 10th horizon (7 analyses)				
Mn	215.0	176.6	50	380
Cu	477.0	303.2	74	1100
Ni	840.0	817.1	490	1150
Co	535.1	481.2	186	890
The Droždiak vein 16th horizon (6 analyses)				
Mn	166	64.8	10	710
Cu	956.6	855.7	340	1700
Ni	1226.6	1187.1	930	1700
Co	1806.6	1310.5	430	5100
The Zlatnik vein (9 analyses)				
Mn	801.4	325	30	3000
Cu	402.4	73.8	4	1100
Ni	472.7	391.5	117	1020
Co	325.2	203.2	30	740

Explanations: X — arithmetical, X_G — geometrical mean.

play a significant role for the enrichment of pyrite by copper at the simultaneous fall of the Mn content.

During the process of distribution of Ni and Co in the deposit, the sulphidic mineralization originates at the given physico-chemical conditions and at the lack of pyrrhotite both the elements in question are enriched mainly in pyrite. At the absence of pyrrhotite, the pyrite is able to accept from the surrounding medium in its structure both the mentioned elements up to a certain value of concentration corresponding to the given genetic conditions. The relations of Co and Ni in pyrites from the Droždiak vein in Rudňany the 10th and 16th horizon) are graphically presented in the corresponding diagram (Fig. 5).

Crystallochemical aspects of the distribution of Cu and Mn in pyrites.

Copper in pyrite.

The geochemical literature is not too much rich in data on microelements in pyrite. The most dates were published by M. Fleischer in 1955 who gathered 785 in that time known analyses of pyrite performed by different authors. B. Cambel and J. Jarkovský (1967) evaluated 801 spectrochemical analyses of pyrites concerning Co, Ni, Mn, Ti, V, Mo. Apart from the listed elements, 531 analyses include also data an Cu, Zn, Pb, As, Ab, Bi, Sn, Ag, Au and Te.

The analyses gathered by M. Fleischer (1955) show that from the 785 data on the content of Cu, 63 % of cases cover the range from 10 to 10000 g.t^{-1}, 10 % of cases have more than 1 % Cu with the highest concentration of about 6 %, 14 % of cases have less than 10 g.t^{-1} and in 13 % of cases the presence of copper was not detected at all. It is explained that the ma-jority of the data, if not all, corresponds probably to heterogeneous admixtures of chalcopyrite to pyrite.

A similar and even more convincing frequency of Cu contents in pyrite results also from our analyses. Among the 531 published data completed by 35 analyses of pyrites from the Rudňany deposit, 94 % show the Cu contents from 10 to 5000 g.t^{-1}, 3 % from 5000 g.t^{-1} up to cca 5 % and only less than 3 % represent the Cu content lower than 10 g.t^{-1}. A certain crystallochemical relation of Cu pyrite is shown also by the fact that no inclusions of chalcopyrite were detected by the X-ray microanalysis in the studied samples in spite of its very good lateral resolu-

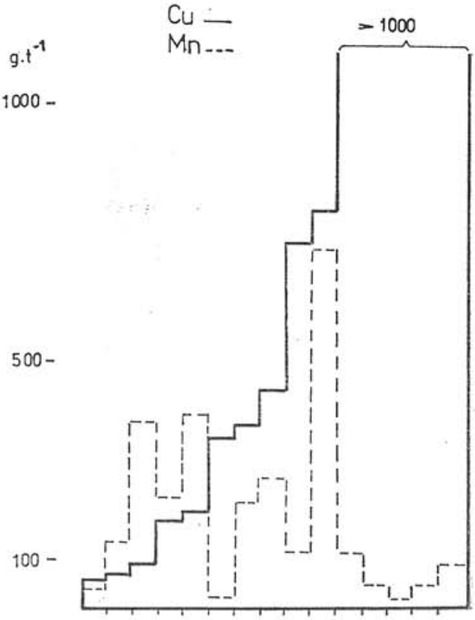


Fig. 3. The column diagram of the Cu and Mn contents in pyrites from the 10th and 16th horizon of the Droždiak vein in Rudňany. *Explanations* like in the case of the Fig. 1.

tion enabling to detect the mentioned inclusions having very small size ($1-2\ \mu m^2$.).

Direct proofs of Cu being the component of the crystal structure of pyrite follow from the data of some authors. G. Frenzel and J. Ottemann (1967) determined by means of X-ray microanalysis zonal pyrite with an elevated content (up to 10 %) of crystallochemically bound copper from the japanese deposit Nukundamu. A similar type of pyrite containing 1,5 % Cu was identified from Cerro de Pasco (Peru) by M. T. Einaudi (1968). Gelous pyrite from the deposit D. Fericelli (Romania) was studied by C. Lazar and J. Ottemann (1973). The crystallochemical formula of pyrite containing Cu, Ni and Co in its structure: $[(Cu_{0.064}\ Ni_{0.091}\ Co_{0.070}\ Fe_{0.816})\ S_2]$ is presented by S. Chiorboli and G. Mazzetti (1977). It corresponds to the low temperature paragenesis of pyrite with marcasite sphalerite, galenite and chalcopyrite from the Funtana Raminosa deposit (Sardinia).

At our comprehensive study of the distribution of Cu and Mn in pyrites, in the recent time we identified (J. Jarkovský, M. Chovan, J. Krištín, 1978) zonal pyrite having elevated content of Cu (up to 0,25 %) and As (up to 3 %) from the deposit Dúbrava (Nízke Tatry). It is anisotropic pyrite of the size up to 1 mm occurring in the deposit (The Predpekelná ore district) contained in the quarz — carbonate vein material in with tetrahedrite, horobetsuite association and chalcostibite.

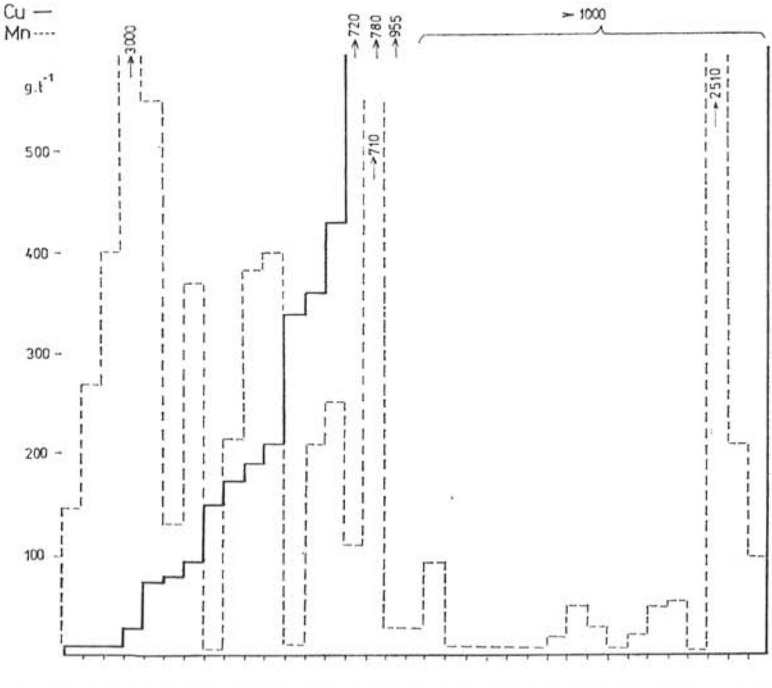


Fig. 4. The column diagram of the Cu and Mn contents in pyrites from different horizons of the Drožd'iak, Zlatník and Hrubá veins in the deposit Rudňany. Explanations like in the case of the Fig. 1.

In the mentioned pyrite three zones (I, II, III) corresponding to different contents and modes of occurrence of copper can be distinguished, as it can be seen from the records of the plane and line X-ray microanalysis (Figs. 6 and 7). The zone I containing up to 0,3 % of isomorphly bound copper represents the part of the pyrite grain which surrounds the inner zone II containing up to 0,1 % Cu. The zone described as III contains already microinclusions of Cu-As sulphosalts of less than 1 μm in diameter. According to the preliminary research of this interesting and in the Western Carpathians till now unique finding, we have to do with younger recrystallized pyrite which could under specific thermodynamic conditions accept in its structure a given amount of Cu as result of the elevated content of As in the structure of the mineral, as well as result of the mineralizing solutions. The analytical data obtained by the point analysis of the said pyrite are presented in the Tab. 2.

As it follows from the described facts, copper can occure in pyrite beside the heterogeneous form, also as crystallochemical component. It was proved also by experimental research performed by H. Shimazaki and L. A. Clark (1971) who demonstrated by hydrothermal synthesis (in the temperature range of 150 to 225 °C that CuS_2 formed in pyrite solid solutions. The zones in pyrite rich in copper represent solid solutions of CuS_2 limited by the set thermodynamic conditions. It was also proved by J. Kajivara (1969) who identified from the japanese deposit Hanawa Mine (Kuroko deposit type) a new Cu-Fe — disulphide named fukuchilite. This disulphide occurs in the mentioned deposit in the form of fine grained aggregate with pyrite and coveline and according to the results of the microanalysis it has the chemical composition corresponding to the formula: Cu_8FeS_3 and according to the röntgenometric data its structure is similar to the structure of pyrite.

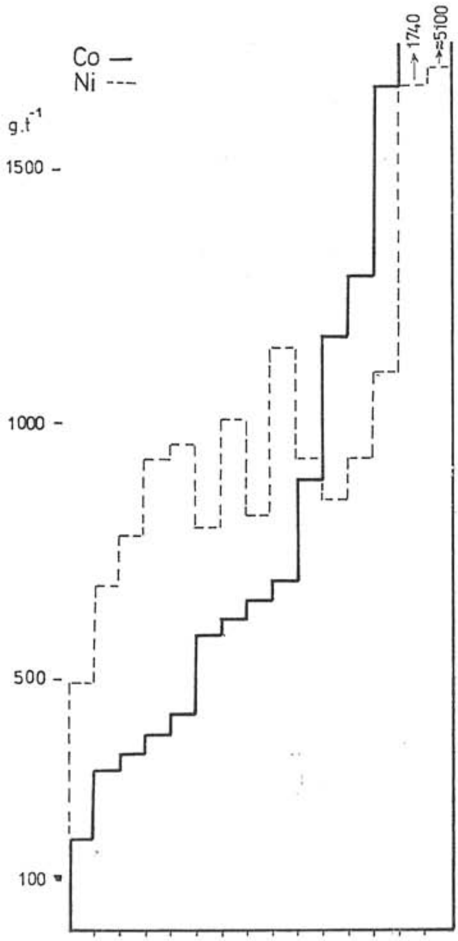


Fig. 5. The column diagram of the Co and Ni contents in pyrites from the 10th and 16th horizon of the Droždiak vein in Rudňany. *Explanations* like in the case of the Fig. 1.

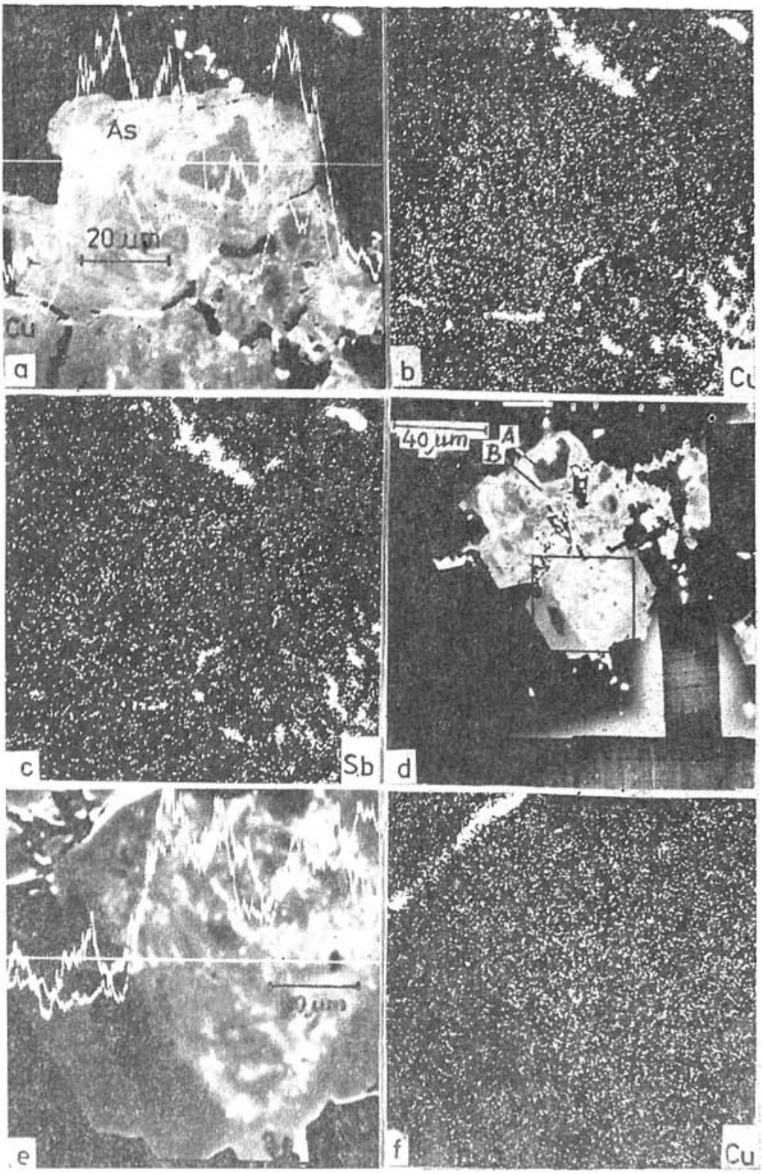


Fig. 6. The distribution of Cu, As and Sb contents in anisotropic pyrite from the antimony deposit Dúbrava (Nízke Tatry) recorded by the X-ray microprobe (J. Jarkovský, M. Chovan, J. Krištín, 1978). *Explanations:* The record „a" represents the composition of pyrite and none ore minerals (block) with the Cu and As distribution curve and with the line profile through which the measurement was performed. In the record „d" the places „A"; „B" are given where the Fe, Cu, As and S contents in pyrite were determined in 4 places by the point analysis. The corresponding values are documented in the tab. 2.

In our research we pointed our special attention to the study of the most significant microelements in pyrite and pyrrhotite i.e. of the cobalt and nickel. In the case of copper we determined frequent inclusions of chalcopyrite in pyrite. From this purpose we did not pay any deeper attention to copper occuring in the form of possible homogenous component in pyrite. This problem has been dealt with in the monography by B. Cambel and J. Jarkovský (1967), where the possibility of the formation of anomal mixed crystalls of copper in pyrite (F. Hegemann, 1941) is discussed.

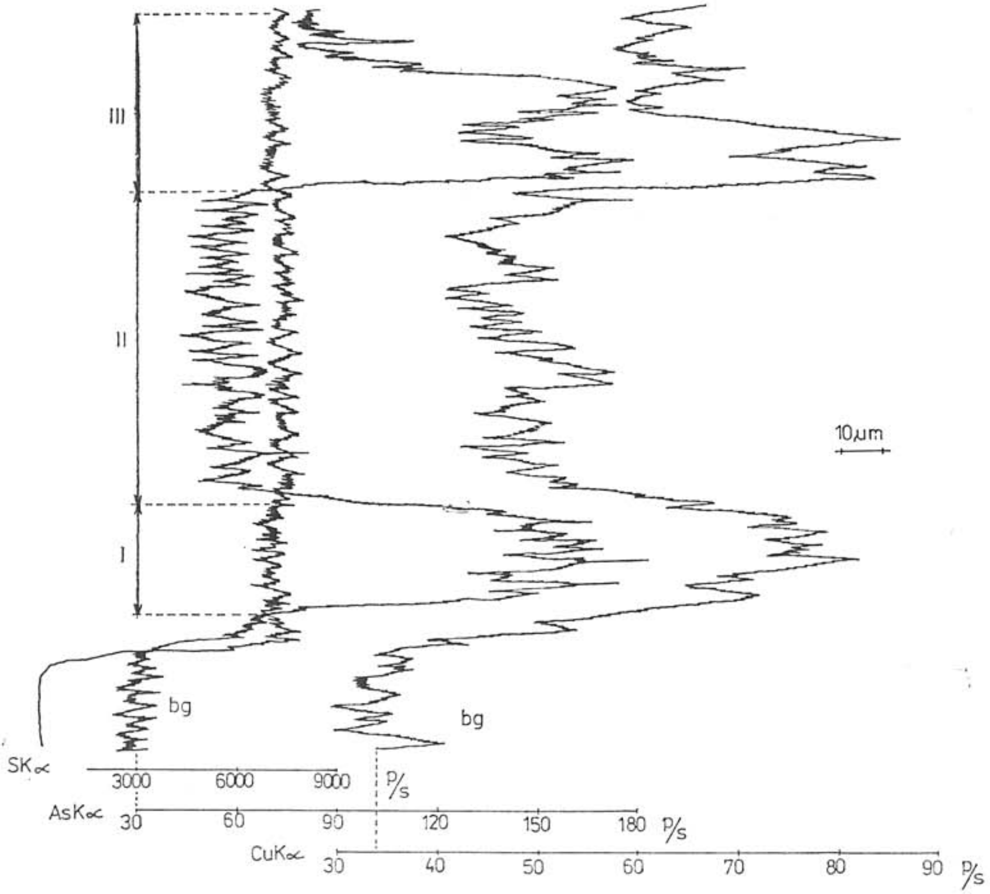


Fig. 7. The Cu and As distribution curve recorded using the apparatus JXA-5A under the 45° angle against the line presented in the Fig. 6. from the left to the right through an,,octaedric" plane of pyrite. Explanations: I the portion of pyrite around the zone of relatively pure mineral contains elevated Cu (cca 0,25 %) and As (cca 3 %) concentration. The size of the zone cca µm, II-the zone of relatively pure pyrite (cca 80 µm) in the from of comparatively well developed „octaedric" plane (Fig. 6)) with contents approx. 0,07 % Cu and approx. 0,5 % As, III — the changing of some zones in pyrite with microinclusions of Cu-As-Sb minerals of the size under 1 µu, bg — background.

Table 2
Table of X-ray microanalytical point analyses of Cu—As—pyrite from Dúbrava documented in the Fig. 6d

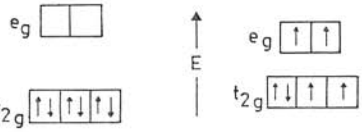
The place in the record	No of analysis	Mas %			
		Fe	Cu	As	S
A	1	45.1	0.08	—	52.8
	2	45.3	—	—	53.1
	3	45.4	0.07	0.17	52.9
	4	45.2	0.05	0.15	52.5
B	5	45.6	0.24	2.8	50.6
	6	45.0	0.16	1.8	51.2
	7	45.1	0.20	1.5	51.2
	8	44.8	0.12	0.6	52.3

The compounds of Cu^{2+} have mainly covalent character. There is no evidence of the free Cu^{2+} ion either in solutions or in solid state (J. Gažo and coworkers 1974). At the study of the question of isomorphic substitution one of the decisive factors for the entrance of elements into the crystal structure of the matrix mineral is the identity of the coordination number both for the central atom and the element by which it is isomorphly substituted. There exist different bounding possibilities of the Cu^{2+} atom apart from the more or less polar δ — bonds the Cu^{2+} atom can be in some compounds bound also by π — bonds, which usually are of dative character.

Cases when the Cu^{2+}compounds exist in the form of isomers having coordination polyhedrons of different deformation are known. Beside of the deformated octaedric coordination of the Cu^{2+} atom, tetragonal coordination is also known. The last is offen considered as the extreme case of the octaeder deformated in the form of the elongated tetragonal bipyramide in which the ligands on the z-axis are so far from the central atom, that the bonding interactions of these ligands with the central atom is practically lost. Tetragonal bipyramide, trigonal bipyramide and deformated tetraeder can also occur.

At the compounds of Cu^{2+}, as well as at the compounds of some transition metals with 6 identical ligands, the octaedric coordination is always deformated in a given degree. This effect was studied by H. A. Jahn and E. Teller and they formulated in 1937 the rule known as Jahn-Teller's effect: in consequence of the degeneration of its electron state, the configuration of none linear molecule is not stable and therefore a deformation of such a configuration occurs at which the degenerability is removed and the energy is lowered. In the case of octaedric Cu^{2+} complexes with the configuration (Ar) $(3d)^9$ it is necessary to state that the electron state $(t_{2g})^6$ $(e_g)^3$ of this ion is degenerated as consequence of the existence of two equivalent configurations on the level: $(d_x{}^2 - {}_y{}^2)^1$ $(d_z{}^2)^2$ and $(d_x{}^2 - {}_y{}^2)^2$ $(d_z{}^2)^1$ (Fig. 8). This degeneration is removed by the deformation of the octaeder by e.g. the elongation in the direction of the z-axis at which the state with an unpaired electron in the $d_x2 - {}_y2$ orbital becomes energetically lower. A similar situation occurs at the deformation by the shorting of the z-axis with the energetically lower state at the unpaired electron in the d_z^2 orbital.

From the quoted facts it is evident that copper in its Cu^{2+} compounds can under certain conditions behave similarly like the representants of the first series of transition elements Fe, Co and Ni with which it is in direct neighbourhood in the periodic system.



a) Weak Ligand Field b) Strong Ligand Field

Fig. 8. Schematic reprezentation of the two possible configurations of the same atom documenting the distribution of 6 „d" electrons in the low spin (a) and high spin (b) state (E. H. Nickel, 1969). *Explanations:* The small arrows give the direction of the electron spin, E — the direction of the energy growth.

It is necessary to state that from the point of view of the geochemical crystallochemistry named according to W. S. Fyte (1964), N. V. Belov and E. A. Pobedimskaia (1966) we can take in account also further knowledge and facts.

Beside of the content of Cu (1000 g.t^{-1}) the studied pyrite from Cerro de Pasco contains also a certain content of As (500 g.t.$^{-1}$) as it follows from the spectrochemical data by M. T. Einaudi (1968). As a matter of fact the pyrite from this locality does not occur with chalcopyrite but with luzonite by which fact the elevated part of the crystallochemically bound copper in this pyrite has been explained. The Cu^{2+} ion can be stabilized only in the deformated octaedric or in regular tetraedric coordination (chalcopyrite). If a certain, it can be even small, amount of As replaces S in pyrite, the d-electrons of the metal are bound with the atoms of arsenic (E. H. Nickel, 1968) so that the electron configuration Cu d^9 cannot be maintained. The configuration Cu^{2+} d^7 or d^8 then results. The described configuration is stabilised in regular octaedric position, so that the Jahn-Teller's effect is not manifest (D. Radcliffe, H. J. McSween, 1969).

According to the presence in the pyrite of the isomorphly bound As, it can be supposed that the Cu^{2+} ion can be preferently crystallochemically bound in this sulphide. According to the last cited authors, Cu^{2+} can be in pyrite crystallochemically bound on two kinds: as first: If S is substitude by As with the regular octaedric position of Cu^{2+} without the influence of the Jahn-Teller's effect and as second, if As is absent (e.g. bravoite and villamaninite) and Cu^{2+} can under the influence of Jahn-Teller's effect accept the deformated octaedric position.

The question of the stability of disulphidic phase of iron and copper

In connection with the determined data concerning the systematic presence of copper in the pyrites of different genesis, mainly in hydrothermal conditions of the deposit formation, the question of stability of the disulphidic phase of iron in natural conditions raises. This question was dealt with already by the cited authors H. Szimazaki and L. A. Clark (1971) at the synthesis of disulphidic phase $FeS_2 - CuS_2$. They state that the copper disulphide synthetized by R. A. Munson (1966) and by T. A. Bither et al. (1966, 1968) was obtained by the cited authors at very high pressures in the range from 15 kb (400 °C) up to 65 kb (400—1600 °C). In the structure of pyrite the cations are surrounded by 6 anions forming approximately regular octaedric position, whereas the anions are connected with 3 cations and with one anion. And so, as consequence of the manifestation of the Jahn-Teller's effect the Cu^{2+} ion occupies predominantly the octaedric position elongated in the direction of the z-axis (caused by assymetric occupation of the e_g orbital), whereas the structure of pyrite is characterised formerly by regular octaedric coordination.

It follows then that the CuS_2 — phase having the structure type of the pyrite can be stable only at high pressures. On the basis of the mentioned conclusions the question of the possibility of the formation of homogeneous copper in pyrite at low pressures can be raised. Some further circumstances inclusive the geochemical ones can however indicate that the disulphidic phase of iron and copper is without doubt metastable: the synthetic disulphidic phase of Fe and Cu prepared on hydrothermal way at 275 °C and tested dry at the same temperature was found as not stable. It came to its decomposition to pyrite, covelline and sulphur. The synthetically prepared disulphidic Cu-Fe phase showed a moderate zonality of individual grains and the products of the synthesis were sometimes reproduced with difficulties. At the valuation of the result of testing the products gained on the wet way, greater amounts of CuS_2 cannot be finally isomorphly built in at 300 °C. The formation of disulphide of iron and copper under hydrothermal conditions is however really stable, while the isomorphous mixture ability of CuS_2 in the pyrite must grow significantly with the fall of the temperature from 300 to 250 °C in the quantity from the zero up to approximately 70 molar %.

As it follows from the occurence of the natural sulphide of Fe and Cu (fukuchilite) presented by Y. Kajivara (1969) which structure is near to the structure of pyrite, this material consists from extremely small inclusions of pyrite and covelline in the form of a uniform distribution. Such a texture has been interpreted as the product of partial segregation of the original grains of fukuchilite. As the consequence of small inclusions of pyrite and covelline it is difficult to determine the composition of fukuchilite while the reflection power of pyrite dispersed in kuchulite is without doubt smaller than the reflexion power of greater pyrite grains which composition is assumed as FeS_2 following from the measurement of the lattice constant. On the basis of the results of the reflexion of the scattered pyrite small parts of segregated copper seem to be present.

Using the mentioned data of the cited authors an imagination concerning the character of the distribution of copper, as well as of its crystallochemic position in pyrite can be made. It is doubtless that copper in deposits has to pyrite a considerable geochemical affinity issuing form its crystallochemical properties.

If we, however, systematically did not record Cu in pyrite in homegeneous form by using the X-ray microanalyser it can be caused by the more or less metastable character of the bond of CuS_2 in this sulphide depending on geochemical conditions. Beside of that, the transition from the homogeneous to the heterogeneous form (segregation) is at relatively low Cu contents in pyrite continuous and therefore practically not observable by the microanalyser. Only at higher contents of homogeneous Cu, this element could be determined by the microanalyser J. Jarkovský, M. Chovan, J. Krištín, 1978).

Manganese in pyrite

In difference to copper, manganese is an often, but not systematic (according to the data of spectrochemical method) microcomponent in pyrites from different deposits and occurrences. Also from that fact it can be concluded that Mn, differing from Cu, does not manifest expressive sulphophil properties and its geochemical position in pyrite is therefore determined by its other properties. In the first place it is the chemical affinity to iron with which it forms the first series of transition elements beginning with scandium and ending with nickel. Also copper is ranged by some authors (e.g. R. G. Burns, 1970) to transition elements because it contains after nickel the most electrons in the 3d orbital and so it closes the first series of transition elements.

As it follows from the M. Fleischer's (1955) data and from our spectrochemical analyses, manganese in pyrite shows the following frequency of contents: From the 927 data concerning the Mn content gathered by Fleischer, 52 % of all cases show contents from 10 up to 5000 $g.t.^{-1}$, only less than 3 % of all cases have the contents lower than 10 $g.t^{-1}$ an even in 45 % of cases the Mn was not determined at all. The highest concentration of 1 % Mn was found only in one case.

From the 779 our published data completed by 35 analyses of pyrite from Rudňany (together 814), 53 % of cases have Mn in contents from 20 to 3000 $g.t.^{-1}$ 26 % of cases have contents smaller than 20 $g.t.^{-1}$, in 21 % of cases Mn was not determined at all and only 1 % of cases has the contents higher than 3000 $g.t^{-1}$ with the greatest concentration about 7000 $g.t^{-1}$.

From the statistical point of view the presented data are well comparable when the analytical under limit values are summarized with the „Zero" values. The frequency of Mn—contents in pyrite is then as follows. The Fleischer's data are the first and our date are the second (in brackets):

52 % 10 — 5000 $g.t.^{-1}$	(53 % 20 — 3000 $g.t^{-1}$)
48 % $<$10 — „0" $g.t^{-1}$	(46 % $<$20 — „0" $g.t^{-1}$)

As it can be seen the frequency determined from relatively great collection of geochemical data determined by different authors is not randomly, but lawfully distributed and it expresses the geochemical affinity of Mn to pyrite under the conditions of the formation of this mineral determined beside of ofther factors also by crystallochemical properties of Mn and Fe under the conditions of Fe — sulphidization.

If we analyse the numerous material of geochemical data, the following sequence of elements (V. V. Ščerbina, 1969) can be set according to their growing affinity to sulphur against oxygen: V—Mn—Sn—Fe—Co—Ni—Zn—Cd—Pb—Cu—Ag—Hg. From this sequence the differences of the behaviour of Cu and Mn under the conditions of pyrite formation are evident. The frequency of Mn — contents in pyrite is therefore considerably lower in comparison with Cu. On the contrary, the frequency of Mn in pyrrhotite is higher as compared with Cu as we give the corresponding evidence in other place.

Conclusion

1. The author studied comprehensively the geochemical and crystallochemical relations of Cu and Mn in pyrites and pyrrhotites from different genetic and deposit types of sulphidic mineralization from Western Carpathians using numerous spectrochemical data presented in monographical works by B. Cambel and J. Jarkovský (1968, 1969) completed by analyses published by foreign authors.

2. It was determined that the content of Mn falls in pyrites with the growing content of Cu. If the pyrite occurs together with pyrrhotite, Cu is concentrated more in the pyrite and Mn more in the pyrrhotite. It means that Cu has a closer crystallochemical relation to pyrite than to pyrrhotite. In the case of Mn situation is contrary. These relations can be argumented also from the theoretical point of wiev.

3. The crystallochemical relation of Cu to the pyrite is documented on the basis of some works of foreign authors, as well as on the basis of the own, till now unique finding in Western Carpathians (J. Jarkovský, M. Chovan, J. Krištín, 1978).

4. The deposite Rudňany can be demonstrated as the example documenting the signification of the study of Cu and Mn, as well as Ni and Co in pyrites. In this deposit the geochemical vertical zonality was proved on the basis of growing Cu, Ni and Co contents and falling Mn contents with the depth of the deposit.

5. It follows that pyrite as the most extended and the crystallochemically most stable sulphidic mineral in ore deposits can serve on the basis of Cu contents in pyrite in the given deposit or region, as available indicator for metallogenetic prognoze studies.

Translated by. E. Piško

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Manuscript received August 26, 1979