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GOLD IN PYRITES FROM THE VOLCANIC COMPLEX OF THE VTÁČNIK MTS.

(Tabs. 3, Figs. 8)

Abstract: Data on gold contents in pyrite from the profile of borehole of the Vtáčnik Mts. volcanic complex (the central Slovakia) are presented in this work. The average gold contents ($\bar{x}$) in pyrite from the 17 analyses represent the value of 0.133 $g.t^{-1}$. In the upper level of borehole (97 — 604 m) the average contents are < 0.02 g. t^{-1} and in the lower part of borehole (708.5 — 1397.5 m) the average gold contents have increased to value of 0.22 $g.t^{-1}$. In this work the authors observe also correlation of gold to arsenic which is positive. Positive relation of gold was registered also in the cases of Co, Ni, Cu, Zn, Ti. According to data of scanning electron microscope gold forms the isometric formations of globular and crystalline shape mostly of 0.5 to 1 μm size. Most probably, electrum especially in pyrite from deeper parts of borehole is concerned. Contents of gold have been determined using the method of atomic absorption spectroscopy with detection limit of 0.02 $g.t^{-1}$.

Резюме: В работе документированы данные о содержании золота в пирите из профиля буровой скважины вулканического комплекса горного массива Втачник (центральная Словакия). Среднее содержание золота ($\bar{x}$) в пирите из 17 анализов представляет величину 0,133 г. $т^{-1}$. В верхнем уровне буровой скважины (97—604 м) среднее содержание $<$ 0,02 г. $т^{-1}$ и в нижней части буровой скважины (708,5 — 139,5 м) среднее содержание золота повысилось до величины 0,22 г. $т^{-1}$. Авторы в работе исследуют и корреляцию золота к мышьяку, которая положительной. Положительное отношение золота было отмечено в случаях Co, Ni, Cu, Zn, Ti. В соответствии с данными растрового электронного микроскопа золото образует изометрические формы шарообразного и кристаллического вида размером преимущественно с 0,5 по 1 μм. Это касается вероятнее всего электрума особенно в пирите из более глубоких частей буровой скважины. Содержания золота были определены при помощи метода атомной абсорбционной спектроскопии с границей определительности 0,02 г. $т^{-1}$.

Gold in pyrites has been studied in horehole from the Vtáčnik Mts. which was localized near the village Prochoť (Fig. 1). Borehole penetrates the Neogene volcanis complex to 1400 m depth. In this profile of borehole changes of the gold contents in pyrite could be observed from the surface to considerable depth. Pyrite is present in rocks of the whole profile of borehole in the form of impregnations, coatings on cracks and in thin veinlets.

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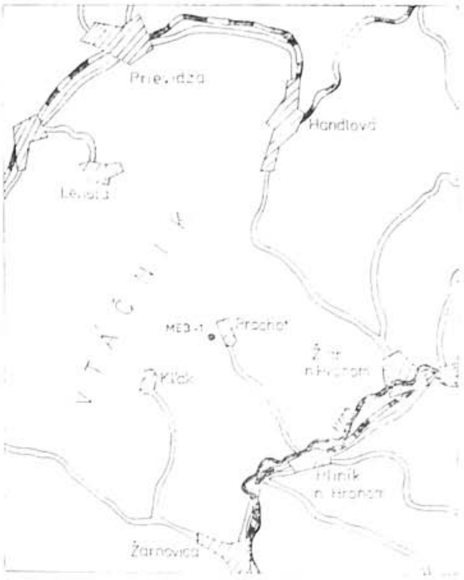

Fig. 1. Scheme of localization of borehole MEB-1.

Volcanic complex in profile of borehole is built up mainly of products of the surficial volcanic activity. Lava bodies of pyroxenic andesite take part in its structure, they alternate with volcanoclastic material. Volcanoclastic material is considerably variable. Positions of volcanic breccias, epiclastic volcanic breccias, as well as positions of tuffs and tuffites hawing marks of expressive sorting of material vary in it. Owing to the changes, it is difficult to determine original structures in the rocks of profile of borehole. According to petrographic analyses A. Mihálik o v á (1980) has determined also diorite porphyries in the profile of borehole. Geological profile of volcanic complex is represented graphically in Fig. 2.

Petrographic characteristics of rocks

The rocks in the whole profile of borehole are altered in various intensity. In the process of alteration hydrothermal and hypergene alterations took part in the rocks.

In the process of hydrothermal alterations dark minerals – pyroxenes are most intensively altered in the rocks. Pyroxenes are totally altered to chlorite, while plagioclases (andesine – labradorite) are almost fresh and they are only partly sericitized and carbonatized. Chlorite is most abundant secondary mineral and epidote, sericite, quartz, pyrite and carbonates are accompanying minerals. The basic matter of rocks is altered too, as well as primary minerals (J. F o r g á č – A. B r l a y, 1981). Formation of galenite, sphalerite and chalcopyrite which form rare clusters and fillings of thin veinlets along with quartz and carbonates (A. B r l a y et al., 1980) occurred in this process. Dislocation of ore mineralization is shown in Fig. 2.

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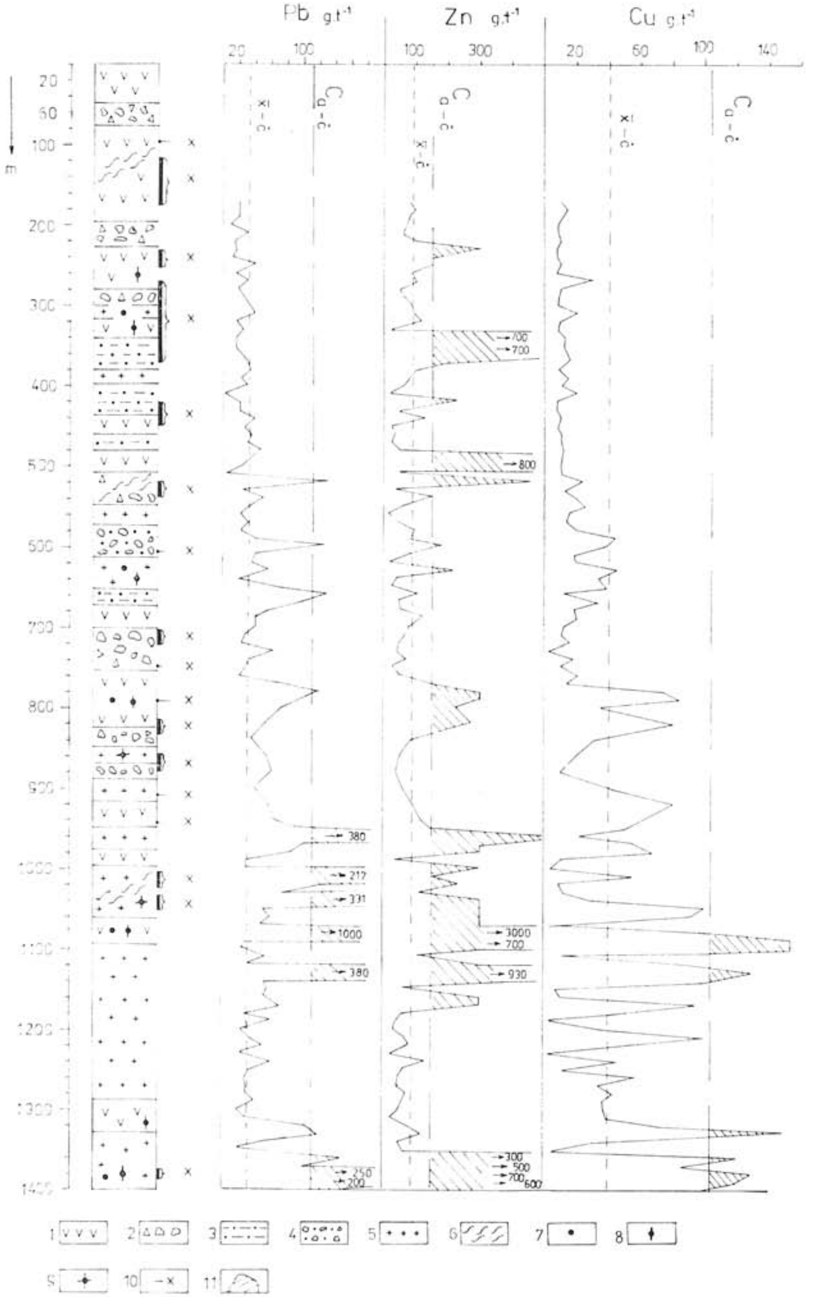
Fig. 2. Geological profile of borehole MEB-1 according to J. F o r g á č – A. B r l a y (1981).

Explanations: 1 – pyroxenic andesite, 2 – andesite breccias, 3 – lithoclastic tuff, 4 – pumice tuff, 5 – diorite porphyry, 6 – tectonic breccia, 7 – occurrence of galenite, 8 – occurrence of sphalerite, 9 – occurrence of chalcopyrite, 10 – places of sampling, 11 – anomalous concentrations of elements in the rocks, $\bar{x}$-c – medium value in unaltered andesites from the central Slovakia, c_a-c – limit of anomaly reckoned from unaltered andesites from the central Slovakia.


Pb g.t-1
Zn g.t-1
Cu g.t-1
20
100
100
300
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60
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800
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1300
1400
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212
331
1000
380
250
200
700
700
800
3000
700
930
300
500
700
600

In hypergene process leaching of rocks and further their disintegration and formation of secondary sulphates and clay minerals were occurring. There are Fe and Al sulphates – alunite, jarosite and alunogen in the upper parts. From the clay minerals montmorillonite, less frequently kaolinite were formed in the upper parts and illite is dominating in the lower parts. Alterations took part by means of intensive leaching to cca 500–600 m depths. In deeper parts they can be observed in cracks and in grinded secticns.

Distribution of gold and arsenic in pyrite

Distribution of gold in pyrite has been studied on the basis of data given in Tab. 1. Totally 17 determinations of gold in pyrite have been done using the

Table 1
Table of Au and As contents in pyrite from borehole MEB-1

Depth m	Au	As	Depth m	Au	As
97	< 0.02	< 1000	745	0.10	< 1000
105	< 0.02	< 1000	790	0.46	4000
150		< 1000	805	0.22	1170
177		< 1000	828		1700
235	< 0.02	< 1000	845	0.15	5500
265		< 1000	862		< 1000
353	< 0.02	< 1000	882		< 1000
374		< 1000	910	0.13	< 1000
424	< 0.02	< 1000	943	0.25	1350
443		< 1000	1004	0.20	3000
522	< 0.02	< 1000	1017		2750
530		< 1000	1031	0.17	2240
604	< 0.02	< 1000	1050		3300
708.5	0.10	< 1000	1385	0.42	1170
722		1170	1397.5		—

Explanations: Gold contents were determined using the method of atomic absorption spectrometry with detection limit of 0.02 $g.t^{-1}$, arsenic contents were determined using emission spectral analysis with detection limit of 1000 $g.t^{-1}$. For determination of gold in more cases 2–3 samples were joined in order to obtain necessary amount of sample material for analysis (1 g). These cases are marked by braces. Au and As contents in the table are in $g.t^{-1}$. Dash (–) means that As determination was not realized.

Table 2
Table of Au and As average contents in pyrites from individual depth parts of borehole MEB-1

Depth m	$\bar{x}$ Au	n	$\bar{x}$ As	n
97 — 604	0.008	7	400	7
708.5— 745	0.10	2	657	3
790 — 910	0.24	4	1938	7
943 —1397.5	0.26	4	2452	6

Explanations: Table is made up of data given in Tab. 1. Average Au and As contents from individual depth parts of borehole are in question, whereby n denotes number of analyses. Data given in Tab. 1 by mark < (less than) were adapted for Au to value of 0.008, which represents 2/5 from the value of 0.02 and for As to value of 400, which represens 2/5 from the value 1000. Contents are given in $g.t^{-1}$.

method of atomic absorption spectrometry. The average gold contents ($\bar{x}$) in the studied pyrites are altogether 0.133 $g.t^{-1}$. In the upper part of borehole (97—604 m) the average contents of this element are < 0.02 $g. t^{-1}$, but in the lower part of profile of borehole (708.5—1397.5 m) the average contents have risen up to the value of 0.22 $g.t^{-1}$ which refers to the fact that Au mobility from the rock surrounding to metallogenetic phase represented mainly by pyritization is substantially higher in deeper levels of borehole. One of the reasons of increased accumulation of gold in pyrite from the lower part of profile of borehole is, as it is shown by data in Tabs. 1 and 2 and Fig. 3., the risen contents of arsenic in pyrite from the lower level of borehole. While at depths of 97 – 604 m the

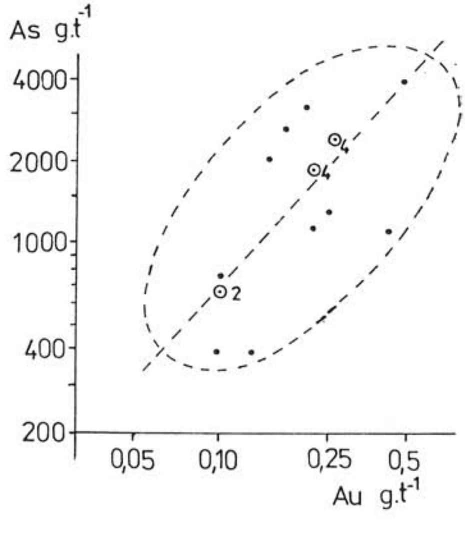

Fig. 3. Correlation diagram of gold and arsenic contents in pyrites from hydrothermally altered volcanites of the Vtáčnik Mts.
Explanations: Full dots in diagram denote value of correlation of contents of individual couples Au/As. Dots with circles denote values of correlation of average Au/As contents according to data from Tab. 2. Numbers in diagram signify number of data from which the average contents of couples Au/As were reckoned. Correlation Au/As with data on gold contents < 0.02 $g.t^{-1}$ and with data on arsenic contents < 1000 $g.t^{-1}$ couldn't be given in diagram.

average contents ($\bar{x}$) of arsenic in pyrite are < 1000 $g.t^{-1}$, in the lower part of borehole the contents of As are 1891 $g.t^{-1}$. Positive relation of gold to arsenic is known in geochemistry. But it has not been observed in our country on example of pyrite in structural boreholes of neovolcanic regions.

Problems of the forms of gold transportation in hydrothermal solutions are dealt besides others by V. N. Sorokin (1973). Investigation of dispersed and stockwork-dispersed pyrite-arsenopyrite and pyrite gold ores from the investigated deposits in the U.S.S.R., as it is given by quoted author, makes possible to presuppose that they were formed at active participation of arsenic and that gold was probably transported in form of sulphur-arsenic complex compounds. It is natural, that increased Au and As contents and their positive correlation were caused also by the risen thermodynamic conditions, especially temperature.

When comparing the increased gold contents in pyrite (Tab. 1) with documentation given in Fig. 2 where the places of anomalous Pb, Zn and Cu contents in the rocks from the borehole are marked, we can state that tendency of the increased gold contents becomes evident in those places where the increased contents of mentioned polymetallic elements in parent rocks of pyrite have been ascertained. Presence of galenite, sphalerite and chalcopyrite in profile of borehole is concerned (J. Forgáč – A. Brlay, 1981).

Relation of gold to other microelements in pyrite

Relation of gold to other investigated microelements in pyrite results from Tab. 3, data of which are graphically demonstrated in Fig. 4. Positive relation of gold especially to Ni, Co, Cu, but also to Zn and Ti results from the graph. Lead and manganese practically don't show any relation to gold, but they indicate negative correlation. The mentioned relations are caused by higher or lower increase of element contents (Co, Ni, Cu, Zn, Ti), eventually by uneven distribution of elements (Pb, Mn) in pyrite from the deeper parts of profile of borehole (708.5–1397.5 m). Relation of gold in pyrite from the upper part of borehole (97–604 m) to investigated microelements couldn't be studied owing to its very low contents which are lower than the limit of analytical detection (< 0.02 $g.t^{-1}$).

From this follows, that gold in pyrite manifests positive relation mainly to the elements crystallochemically similar to iron (Co, Ni). Cu manifests partial crystallochemical relation to the elements from iron group too, especially to Fe, Co, Ni (A. G. Burns, 1970; J. Jarkovský, 1977, 1980). Contents of Co, Ni, Cu rise with depth in pyrite from volcanic complex Vtáčnik, whereby manganese contents tend to decrease with depth of sample localization. As far as titanium is concerned, it is remarkable, that this element has positive relation to gold too, though heterogeneous component in pyrite is in question (J. Jarkovský – J. Forgáč – D. Jančula, 1981). Positive relation to gold is manifested by Zn too. Probably fine unseparable inclusions of sphalerite, the quantity of which is rising with depth, is concerned. The fact that small part of Zn occurs in pyrite in form of anomalous mixed crystals can't be excluded in pyrite from the deeper level of profile of borehole, where higher temperature of hydrothermal solutions is expected (B. Cambel – J. Jarkovský, 1967).

Table 3
Table of average Au, Co, Ni, Cu, Zn, Ti, Pb, Mn, Ag contents in pyrites from four depth levels of profile of borehole MEB-1

Depth in m	$\bar{x}$ Au	n	$\bar{x}$ Co	$\bar{x}$ Ni	$\bar{x}$ Cu	$\bar{x}$ Zn	$\bar{x}$ Ti	$\bar{x}$ Pb	$\bar{x}$ Mn	$\bar{x}$ Ag	n
97 — 604	<0.02	7	93	13	41	260	1674	65	93	<10	7
708.5— 745	0.10	2	146	38	36	120	1350	374	117	<10	3
790 — 910	0.24	4	231	42	57	146	1838	143	162	<10	7
943 —1397.5	0.26	4	193	56	51	248	2747	304	37	9.8	6

Explanations: Data on Co, Ni, Cu, Zn, Ti, Pb, Mn, Ag contents are taken over from the work J. Forgáč – J. Jarkovský (1981); n denotes number of analytical data. Data on gold contents were obtained using atomic absorption (AAS), the other elements were determined using spectrochemical method (SPA).

It is evident from data in Tab. 1 that in the upper part of borehole at depths of 97–604 m from borehole MEB-1 concentration of gold is relatively very low in comparison with average Au contents (0.22 $g.t^{-1}$) in pyrite from the lower part of borehole (708.5–1397.5 m). This problem is remarkable and for the time being it can't be explicitly explained. We suppose that hydrothermal solutions leached heavy metal elements including gold which was numerously concentrated in sulphide phase – in pyrite from parent rooks. We are of opinion that

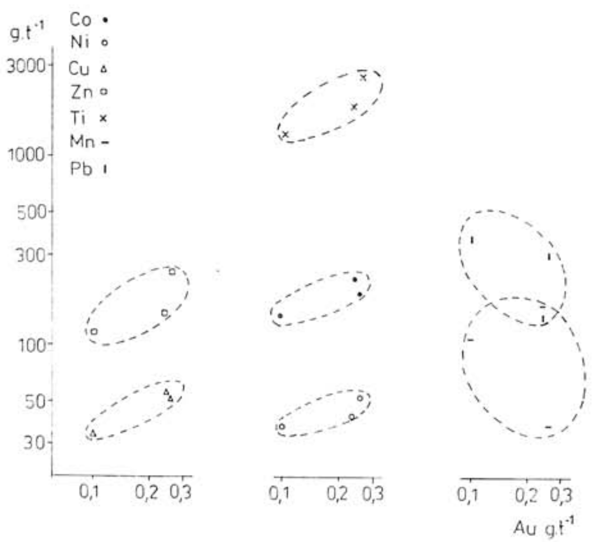

Fig. 4. Correlation diagram of average Au, Co, Ni, Cu, Zn, Ti, Mn, Pb contents in pyrites, numerical data of which are given in Tab. 3
Explanations: Data from depth level 97 – 604 m are not expressed in the graph.

Fig. 5. Globularly rounded, colloform enclosures of electrum in pyrites occuring on the borders of block structure, SEM, × 6000 (1004—1017 m).

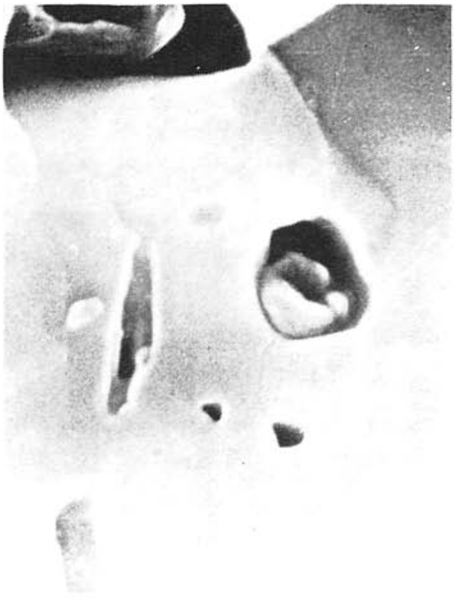

Fig. 6. Globular forms of electrum with marked microtexture (by striation), SEM, × 30 000 (805—828 m).

original volcanic rocks already contain primarily less Au, Co and Ni in the upper part of volcanic complex in comparison with deeper zones.

Forms of gold occurrence in pyrite

When studying forms of gold occurrence in pyrite we have based partly on study by means of scanning electron microscope, partly on confrontation of obtained results with analogies from our own investigations in other localities, as well as with results of undestructive neutron activation analysis and atomic absorption spectroscopy.

By means of scanning electron microscope two forms of gold occurrence were demonstrated in studied pyrites. Dispersions of submicroscopic size 0.5—1.5 μm of globular or slightly elongated formations, sometimes with slightly marked submicrotexture reminding of parallel stration are the most frequent form. This type usually occurs in zones of borders of pyrite inhomogeneity, i. e. on the borders of blocks, and therefore it can be considered according to Čuchrov's classification (1955) for syntactic (Figs. 5, 6).

Phenomenon of block structure of pyrite which is typomorphic for the certain type of this mineral has been already proved in the previous works (M. Harman, 1966, 1979). Character of arrangement of neighbouring more or less differently oriented structural units of crystal lattice of various size within the framework of pyrite monocrystal is concerned. With studied pyrite a highly developed type of crystallization of blocks is generally in question, which is especially marked in deeper parts of borehole. Blocks

Fig. 7. Cubic (octahedral) electrum in pyrite from the lower part of borehole, × 2250 (1385–1397.5 m).

Fig. 8. Crystalline inhomogeneity (sphalerite ?) in pyrite, SEM, × 9000 (1385–1397.5 m).

are relatively big (over 20 μm), which proves the fact that crystallization of original matrix has progressed to such measure that presuppositions for good crystalline limitations of complete pyrite grains have been created.

Globular or slightly elongated morphology of particles is typical of colloform origin which corresponds well with the similar forms of gold occurrence (electrum) observed by electron microscope in pyrites from locality Govežda (Bulgaria) described by V. N. Velčev (1965), or from Kremnica veinstone of Helena and Krížna veins of Kremnica vein system (M. Böhmer – M. Harman, 1969).

Occurrence of these forms of gold is mainly bound to the central and lower parts of borehole, which is in correspondence with our observation, that transportation of complex compounds leached from parent rocks and their first phase of crystallization in pyrites along with other elements (Co, Ni, As, Zn, Ag etc.) are in question. Expressive increase of silver contents along with gold (according to spectrochemical analyses from < 10 g.t^{-1} in the upper parts up to 33 g.t^{-1} Ag in the lower parts of borehole), as well as analogies from other localities in the West Carpathians enable to presume that electrum is at stake.

In the lower part of borehole where according to obtained results share of gold and polymetallic elements reaches the higher values, evolution of forms of gold has occurred, which show marks of better crystallographic limitation, viz. cubic forms, usually combination of cube (001) and octahedron (111) of 4 μm size (Fig. 7). Evolution of this form of gold was conditioned in the deep parts of borehole most likely by more optimum thermodynamic conditions (temperature) and by increased contents of polymetals. Also for this type of morphology, analogies from Kremnica metallogenetic district can be found, where such electrum occurs in zones with more varied associations of ore minerals.

Besides gold also enclosures of independent crystalline phases of other minerals (most likely sphalerite) were found in pyrite grains from deep parts of borehole by electronmicroscopic study, wholly in accordance with our presumptions (Fig. 8).

Finally, heterogenous occurrence of gold (electrum) and zoning of its occurrence are proved indirectly by the results obtained by means of undestructive neutron activation analysis (analyzed in central laboratory ČSUP in Stráž pod Ralskem). From this analysis considerable oscillation of gold contents in the studied pyrites follows in comparison with results obtained by atomic absorption. Reasons of different values of both methods can be explained by unevenness of occurrence of gold (electrum) enclosures (inhomogeneities) in pyrite, as well as by different weight of weighed portion taken for analysis by both methods. While for atomic absorption weighed portion of 1 g weight was used, for neutron activation weighed portion tenfold lower (100 mg) was taken, which could cause increased gold contents in consequence of locally risen concentration of enclosures in some pyrite grains. With atomic absorption whole gold contents got into solution regardless of form of its occurrence in pyrite.

Analytical method of Au determination in pyrites

Atomic absorption spectroscopy with electrothermic atomization was used for gold determination in the studied pyrite samples. Atomic absorption spectrometer Perkin-Elmer model 303 in conjunction with graphite cell NGA-74 served for the mentioned purpose. Height of absorption signal was recorded at resonance line 242.8 nm by means of line recorder PE model 56. Discharge lamp with hollow cathode supplied by current of 15 mA was used as a source of monochromatic radiation.

With regard to low gold contents in the studied samples and possible interferences of accompanying elements, it was necessary to separate gold and to
cathode supplied by current of 15 mA was used as a source of monochromatic
B. Cambel – V. Streško – O. Černeková-Škerenčáková, 1980) it was ascertained that in this sense methylisobuthylketone and dibuthylsulphide in toluene belong to the most advantageous organic solvents.

Working process given in the following text in a shortened form was chosen in the presented work:

0.5 – 1 g of softly grinded sample was mixed and thoroughly grinded with ammonium nitrate in ratio 2 : 1. After 30 min. of annealing above moderate flame of a lamp (about 300 °C), the acquired mixture was placed into muffle-furnace, where it was annealed at 650 °C for 1 hour. It is necessary to follow carefully this temperature because at presence of arsenic an alloy with gold originates, melting point of which is only a little higher as the given temperature necessary for removal of sulphides. Adapted sample was decomposed by hydrobromic acid and bromine. Insoluble part was separated by centrifugation and from the acquired solution gold was extracted into 5 ml of methylisobuthylketone. The obtained gold solution of 50 μl capacity was dosed into a graphite pipe placed in inert atmosphere of argon of the above mentioned device.

Concentrations of gold were ascertained from the measured absorption signals using the method of calibration curve. Same procedure as with solutions of samples was done with comparative solutions of gold. It was possible to determine 0.02 $g.t^{-1}$ of gold from 1 g of weighed portion of pyrite sample by described method.

Conclusions

1. In this work the authors document data on Au contents in pyrites from hydrothermally altered volcanic rocks from the Vtáčnik Mts.

2. Gold contents increase along with arsenic with depth of sampling from borehole MEB-1 (Tabs. 1, 2, Fig. 3).

3. The authors document also relation of gold to other microelements in pyrite (Co, Ni, Cu, Zn, Ti) which is positive. In the case of Pb and Mn, correlation was practically not ascertained (Tab. 4, Fig. 3).

4. The authors touch also the question of low gold contents in pyrite from 97—604 m depth of profile of borehole. This question requires a further special study.

5. Form of gold occurrence in pyrite has been an object of investigation on scanning electron microscope (Figs. 5—8). It results from documented microphotographs that ascertained isometric microinclusions of globular and crystalline shape mostly of $0.5 - 1$ μm size represent most likely gold with silver ingredient (electrum).

6. The authors give also basic conditions of atomic absorption spectroscopy, data on gold contents in pyrite with detection limit of 0.02 $g.t^{-1}$ have been ascertained by this method.

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