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## THE CONTENTS OF GOLD IN PYRITES OF VARIOUS GENESIS

(Figs 2, Tab. 8)

**Abstract:** The authors carried out determination of gold contents in 67 samples of pyrites from the West Carpathian and other regions of Czechoslovakia as well as in further 40 samples, from which pyrites were separated out. The samples were selected from various genetic types of deposits. The authors have established that the contents of gold are characteristic of individual genetic types. For syngenetic pyrites from the region of the Malé Karpaty Mts. (the contents of gold are low) arithmetic mean is thousandths  $\text{g.t}^{-1}$ , for hydrothermal plutogenic ones the contents are highest (in tenths  $\text{g.t}^{-1}$ ). Whereas the syngenetic pyrites have mostly equal contents of gold, plutogenic and subvolcanic ones have distribution of gold most uneven. The syngenetic pyrites contain gold in dispersed state and almost no difference between the gold contents in pyrites, in rocks or ores, from which the pyrites were separated out, is observed on the contrary, hydrothermal pyrites are concentrators of gold, having as a rule evidently more than the samples, from which pyrites were separated out. The authors have found out that on the basis of the content of gold genetic conclusions may be drawn successfully.

**Резюме:** Авторы определили содержание золота в 67 образцах пиритов из области Западных Карпат и других областей ЧССР как и в дальнейших 40 образцах из которых были пириты высепарованные. Образцы были отобраны из разных генетических типов месторождений. Авторы определили что содержания золота являются характеристическими для отдельных генетических типов. Для сингенетических (из области Малых Карпат) содержания золота низкие (арифметическое среднее в тысячных  $\text{г/т}$ ), для гидротермально плутогенных содержания самые высокие (в десятых  $\text{г/т}$ ). Тогда как у сингенетических пиритов содержания являются самыми равномерными, у плутогенных и субвулканических распределение золота самое неравномерное. Сингенетические пириты содержат золото в рассеянном состоянии и разница между содержанием золота в пиритах в породах или-же рудах, из которых были пириты высепарованные почти не заметна — наоборот, гидротермальные пириты являются концентраторами золота, как правило содержат его очевидно больше чем образцы из которых был пирит высепарован. Авторы определили что на основании содержания золота возможно делать успешные генетические выводы.

About the occurrence of gold, its contents and behaviour under natural conditions there are still always little data. In the last years were microelements in sulphidic minerals studied intensively by us. More profound investigations were carried out in pyrites, pyrrhotites and chalcopyrites. In these works data about the occurrence and content of gold are usually missing or seldom only. The cause lies in insufficient sensibility of commonly applied analytic methods. For this reason, in the presented work in the first place we had to devote to selection of suitable method, which would provide sufficiently reliable results. The applied method is worked out in detail in the diploma work (Černeková, 1978) and the results of this method were presented

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at the Vth seminar about atomic absorption spectrometry in Červený Kláštor (Streško 1978).

Regarding to the relatively wide-spread occurrence of pyrite at deposits of various genetic type in the first stage of investigations we were focused on the study of gold in pyrites and where it was possible, also the contents of gold in ore and rock, from which pyrite was separated out, were determined. The aim of this approach was to clear up whether the main bearer of gold is pyrite or other mineral environment or pure gold as independent component of raw ore.

In selection of the studied samples it was necessary to obtain pyrites of various genetic types from several representative localities, mainly from the West Carpathian region. Due to the limited capacity and difficulties in separation 65 samples from various localities were analysed only.

All the analysed samples were divided into the following groups:

Type I. Hydrothermal-subvolcanic pyrites

Type II. Hydrothermal-plutonogenic pyrites

Type III. Hydrothermal-sedimentary and syngenetic highly metamorphous recrystallized pyrites (accompanied by quartz and pyrrhotite)

Type IV. Syngenetic-sedimentary pyrites/ often found in dark metamorphosed schists with content of metapyroclastics (amphibole)

Type V. Syngenetic-sedimentary, hydrothermal-syngenetic or hydrothermal-remobilized pyrites (in places concretionary, of unclear and combined genesis)

Type VI. Pyrites from skarns

Type VII. Sedimentary-concretionary pyrites from coal, with diagenetic remobilization

It is necessary to remark that this division into 7 groups is too narrow to express all genetic specifications of individual depositional accumulations. This concerns mainly types III. and V., in which the individual ore mineralizations cannot be unambiguously interpreted genetically. In type III two subtypes, quartz-sulphidic pyrites with chemogenic quartz-hydrothermal syngenetic ores (anal. no. 35, 36, 40, 41) and syngenetic, highly metamorphic ores with pyrrhotite or quartz are connected. The process of metamorphic recrystallization and hydrothermal remobilization could, however, have played an important role here so that the ores are close to hydrothermal Au ores in content and unequableness of contents. The degree of proportionality of action of these two processes: metamorphic recrystallization and displacement of ore constituent by means of solutions is difficult to establish precisely.

In genetic type V essentially all unclear genetic types of deposits are included, in which the syngenetic-sedimentary (including hydrothermal-sedimentary) one is most probable (Smolník, analyses no 60, 61). In other types metamorphic recrystallization, primary hydrothermal action as well as endogenous or exogenous origin of ore component is unclear, just as it is difficult to decide, which phenomena and characteristics of ores are the result of superimposed, subsequent processes and which are primary. The other above mentioned genetic ore types, also in small amounts of analysed samples, provide a good characteristic of gold content, valid for the whole genetic group.

Table 1  
Coefficients of concentration of gold according to Ščerbakov (1976)

Rocks	Coefficient	Rocks	Coefficient
ultrabasic	0.28	granitoid rich in Ca	0.005
gabbroid	0.02	granitoid rich in K	0.02
granitoid	0.05	clay and clay shales	0.0063

*Gold in rocks, minerals and ores*

Gold belongs among elements seldom found in earth crust. The contents of gold in meteorites are much higher than in earth crust and vary 0.05—1.44 g.t<sup>-1</sup> and in chondrites 0.16—0.22 g.t<sup>-1</sup> (Borisenko, 1972). Very interesting are the coefficients of gold concentration, which indicate the ratio of gold content in rocks regarding to the content in chondrites (Tab. 1), mentioned in the work by Ščerbakov (1976). These coefficients characterize fractionation and differentiation capacity of elements and the ability of their migration in the process of formation of ore deposits. Besides that they make possible to show the general character of vertical division of elements. According to Ščerbakov the average content of gold in the whole mass of our Earth is 0.4 g.t<sup>-1</sup>.

From laterary data is evident that in general we may observe decreasing gold content from ultrabasic toward acid rocks. A greater dispersion of gold content was observed in ultrabasic rocks. According to Borisenko (1972) gold occurs in natural objects in various forms, as admixture of native gold or electrum. Its particles may also be sorbed in formation of rocks-forming or ore minerals in form of dispersed atoms. On the basis of the results of the mentioned author gold contents in ultrabasic rocks vary from 0.001 to 0.1 g.t<sup>-1</sup>. On the contrary, Kaširin (1975) has found in granites lower gold contents, from 10<sup>-4</sup> to 10<sup>-2</sup> g.t<sup>-1</sup>. On the basis of the mentioned facts and own results, some authors (Rožkov, 1973); Muškin (1974); Ščerbakov (1976) range gold to elements concentrating in deep sub-crustal areas or even in the core of earth. The data about higher contents of gold in harzburgite-dunite order in contrast to the gabbro-peridotite formation confirm the hypothesis about a deep-seated subcrustal source of this metal according to Golovnja (1977). Korobjenikov (1979) carried out 1400 quantitative analyses of gold in vein rocks of various regions in the USSR. The author confirmed increasing tendency of gold contents from vein rocks of acid composition to basic rocks. According to Anošin (1977) concentration of gold in vein rocks was observed in hydrothermally altered types only. The data about gold contents in the work by Nikitin (1974) point to higher values in sedimentary ferric minerals originated in the sea. The average content for this type of rocks is 0.005 g.t<sup>-1</sup>.

The occurrence of gold in metabasites of the West Carpathians is studied by Cambel and Spišiak (1979), who have found out the average values of this element in the individual mountain-ranges. The obtained contents varied 0.012—0.030 g.t<sup>-1</sup>. These data, compared with the foregoing authors, are

Table 2  
Contents of gold in rocks according to various authors

Rock	Au content in g.tl <sup>-1</sup>		Literature	Locality
chondrite	0.22	(14)	Baedecker, Ehman, 1965	Urals peninsula Kola
ultrabasites	0.10—0.05	(76)	Borisenko, 1972	
kimberlites	0.0039	(14)	Rožkov, 1973	
eclogite	0.0044	(15)	Golovnja, 1974	
eclogite-kimberlite	0.0007—0.0045	(25)	Golovnja, 1974	„Obnaženaja” North Jakutia
coarse-grained dunites	0.024	(6)	Golovnja, 1977	Massif Raj. iz
chromite ores	0.066	(24)	Golovnja, 1977	„
harzburgites	0.0083	(2)	Golovnja, 1977	„
biotitic granites	0.0047	(15)	Kaširin, 1975	Konstatntin Massif
beretisized granites	0.0054	(15)	Kaširin, 1975	(Lena gold-
vein series	0.0027—0.021	(34)	Kaširin, 1975	bearing region
biotitic granites	0.0013	(28)	Kaširin, 1975	Džegbakar Massif, Lena gold-bearing district
biotitic and biotite amphibole granites	0.0016	(46)		
diorite prophyrites	0.0064	(1400)	Kaširin, 1975	Vitim-Engažim Massif Lena-
lamprophyres	0.0050	(1400)		gold-bearing district
syeno-diorites	0.0065	(1400)		vein rocks
granite-aplites	0.0031	(1400)	Korobjenikov, 1979	of various districts
granite and acid effusives	0.00012—0.00058		„	of the USSR
gabbroid		(28)	„	
diorites	0.0064	(14)	Ščerbakov, 1970	„
chlorite-amphibolic schists	0.0035	(14)	„	„
	0.028—0.540	(76)	„	
			Šilin, Osipov, 1979	

Explanations: the values in parentheses with contents of gold mean the amount of analyses, from which was calculated the average

somewhat higher. The applied analytical method and way of calculation of average values could have played some part here. The survey of literature data about gold contents in individual rocks is given in Tab. 2.

The basis for the study of forms and contents of gold in rocks is the study of this element in individual minerals. The contents of gold in rock-forming minerals were established by Ščerbakov and Perežogin (in Polanski, Smulikowski, 1978), as richest in gold magnetite has been shown with the content 0,048 g.t<sup>-1</sup>. Higher contents were also observed in olivine, pyroxena and xuartz (0,011—0,016 g.t<sup>-1</sup>). As Mantei and Brownlow (1967) mentions, magnetite need not always contain higher gold contents compared with the accompanying minerals.

Table 3  
Contents of gold in pyrites according to various authors

Original sample	Au content g.t <sup>-1</sup>	Literature
accessory pyrites	0.0355	Jusupov, 1977
pyrites of endogenic deposits	23.3	Jusupov, 1977
pyrite from deposits of gold-bearing quartz	211.0	Jusupov, 1977
hydrothermal pyrites	3.8—6.4	Jusupov, 1977
pyrites from metasomatic deposits of Kuznec Altaj	0.215—0.840	Jusupov, 1977
pyrite from kimberlites „Obnaženaja” North—Jakutia	0.0019— (1)	Rožkov, 1977
pyrite from gabbros	3.8—6.4 (17)	Zvereva, 1973
pyrite from propylitized gabbro-anorthosites	6.4	Zvereva, 1971
pyrite from beresitized quartz diorites	0.17	Zvereva, 1971
pyrite from Witwatersrand, porous, South Africa	245.9 (14)	Utter, 1978
pyrite from Witwatersand, compact, South Africa	257.7 (12)	Utter, 1978
pyrite from Witwatersand, idiomorphic	166.8 (16)	Utter, 1978

Explanations: the values in parentheses with contents of gold mean the amount of analyses, from which was calculated the average

The contents of gold in minerals are mainly depending on the contents of gold in original rocks and on the structure of the competent mineral. On the basis of her own investigations Zvereva mentions that the contents of gold in dark rock -forming minerals are equal and independent from the amount of present iron and manganese. Similarly no connection between gold and the presence of several petrogenic elements has been found (Golovnja, 1974). The gold is probably found, regarding to its high ionization potential, in individual minerals in form of submicroscopic native particles.

According to the latest results of Osipov and Šilin (1979) gold contents in amphibolites display direct dependence with magnesium and indirect with iron. According to these authors gold contents in amphibolites are depending on the contents of so called mantle gold and gold released as consequence of remelting of the earth crust. Although no minerals-concentrators of gold have been found, Korobjenikov (1979) mentions that the main bearers of gold are plagioclases, quartz and amphiboles. On the contrary, Jusupov — Abdurachmanov (1977) consider pyrite as concentrator of gold. In Tab. 3 the average contents of gold in pyrites of various genesis are mentioned.

In our country Němec (1974) dealt with establishing of gold in pyrites. Higher contents were established in pyrites from hydrothermal polymetallic veins and gold-bearing quartz veins (Tab. 4). The author points out that the higher contents of gold indicate native gold in competent mineral association in the majority of cases. Lower contents of gold were found in pyrites of uranium mineralization.

Table 4  
Contents of gold in pyrites [Němec, 1974]

Paragenetic type	Locality	Amount of samples	Au g.t <sup>-1</sup>
polymetallic	Horšovský Týn	—	1.2
	Sřibro	4	0.5—6
	Příbram	3	0.9—1.1
hydrothermal	Kutná Hora	12	0.9—2.9
	Pohled near Hav. Brod.	—	1.0
	Bartoušov	—	2.0
veins	Nová Ves near Rýmař.	—	11
	Banská Štiavnica	—	0.9
	Borotice near Libčice	—	5
auriferous quartz veins	Slavosice	—	0.35
uranium formation	Dolní Rožinka	—	2.0
fluorite-barite veins	Běstvína	8	0.9—11
polymetallic and pyrite	Zlaté Hory	3	0.5—2.5
seratiform deposits	Suchá Roudna near	—	1.8
of unclear genesis	Bruntálu		
pegmatites	Dolní Bory	2	1.4—2.5

*Explanations:* lines in the rubric — amount of samples was not mentioned in the original work

Petrovskaja (1973) has found out that gold may be concentrated in chalcopyrite at deposits of the pyrite-chalcopyrite association. At Pb—Zn deposits gold is concentrated in galena, then in pyrite, chalcopyrite and sphalerite. Only at sulphidic deposits the above mentioned authores observed preferential concentration of gold in pyrites. Concentrating of gold in sphalerites is pointed out by Siličev, Belozerceva (1975), explaining the mentioned observation by change of physical-chemical conditions in the moment of sphalerite crystallization. Native admixtures in crystal lattice of sphalerite probably formed with intense destruction of gold-bearing complexes.

#### Migration and concentration of gold

The opinions of behaviour of gold under natural conditions are different. Petrovskaja (1973) mentions that in magma gold accumulated in the process of magma differentiation or was sorbed from the surrounding rocks or subcrustal emanations, which came into contact with the intrusions with their movement. At the beginning of magmatic process gold was equally distributed in the melt. Concentration and carrying of gold from magma chambers took place with cooling off of the melt and increasing pressure of volatile components only. Further migration and precipitation of gold was depending on the change of composition and temperature of hydrothermal solutions, which were closely linked with transportation and accumulation of quartz, sulphur, alkalies and haloids with their ascent. The forms of gold transportation under hydrothermal conditions may be various regarding to chemical properties of gold and diversity of geological processes at various levels of depth.

It is probable that gold was transported by diluted water solution of acid or basic character. Concerned is the chloride-basic character of solutions with a higher or lower content of sulphuric compounds and carbon dioxide. One of the theories is



migration of gold in form of chloride complexes in acid solutions. The stability of these complexes, however, lowers at 200 °C. As Baranova, Barsukov (1977) mention, the presence of pure chloride complexes is possible in very acid solutions only (below pH 1). For the mentioned reason transfer of gold in form of hydroxide-chloride and hydro-sulphide complexes is more probable. The mentioned authors dealt in detail with their stability. Weisenber (in Petrovskaja, 1973) experimentally confirmed solubility of gold in basic solutions at temperature 150–250 °C, pointing to the possibility of hydrothermal migration of gold. Other experiments attest that gold can be transported also in form of thiosulphide complexes. Their stability is, however, small and it is not probable that they would take part in the transfer of gold in the hydrothermal process.

The precipitation of gold in gold-bearing quartz veins took place in the terminal stage of the ore-forming process under conditions of temperature less than 300 °C and at pressure below 150 MPa (Letnikov, Vilov, 1975). Studying vein-deposits of gold in the pyrite-arsenopyrite association Sorokin (1973) came to the conclusion that in early stages of the hydrothermal process arsenic could have replaced sulphur. This way sulphur-arsenic complex compounds originated, by means of which gold could have been transported. The author also points to siderophyllic properties of gold and close migration properties of arsenic and gold.

Colloids of gold also deserve attention, formed under conditions of small depths together with colloids of quartz. They did not take part in longer migration of gold, however, can be characteristic of the individual periods of the action of solutions.

Very little studied are gold-organic complexes, to which Goleva, Krivenko (1970) called attention in migration in natural waters under exogenic conditions.

The association of gold with tellurium is explained by the origin of polytellurides at low concentrations of sulphur. Regarding to instability of the mentioned complexes native gold originates as product of their decomposition (Smidt in Petrovskaja, 1973). Native gold brings some genetic information on the character of ore solution, from which gold precipitated at certain level of depth. Further on, the low nativity of gold is characteristic of deposits with juvenile source and on the contrary, high nativity of gold is in palingene sources of ore solution (Košman, Jugaj 1972; Levitan, Berzon 1977).

To questions unclear up also the role of metamorphism in migration and concentration of gold belongs. Some authors admit carrying away of gold from rocks at high grades of metamorphism (Petrov, 1972), other authors, on the basis of the study of samples with various grade of metamorphism point out (Šochin, 1974) that gold is supplied with metamorphism. According to Pčelincev (1973) only repeated scattering of gold, its higher dispersion etc. may occur as a consequence of metamorphism. The contents of gold in metamorphosed rocks are depending on the contents of gold in original rocks and not on the grade of metamorphism.

Miller and Fišer (1973) pointed to the role of manganese in dissolution of gold in the zone of sulphide deposits with presence of sulphate and chloride ions under exogenic conditions. Transportation with surface waters can take place by surface waters in colloidal or fine-dispersed form and/or in form of thiosulphide or little studied organic complexes (Goleva, 1970). The mentioned author denies the possibility of gold transfer in form of chloride complexes and mentions that it is possible in rare, very acid fumarole waters.

### *Forms of occurrence of gold in minerals*

Only very few authors hold the opinion that gold is found in sulphide minerals in form of sulphur compounds. These theories mainly result from the absence of visible gold particles in gold bearing sulphides. Maslenceckij (in Petrovskaja, 1973) established the formula of sulphuric compound of gold as  $Au_2S_3$ . Such forms of occurrence of gold are, however, unstable and must have decomposed immediately after their origin.

Several authors hold the theory of the existence of solid solutions of gold in sulphides (Schweigart, 1965). Zvereva (1971) points out that with regard to the high potential of gold ionization and the oxidation–reduction potential in  $Au^+$  ( $Au$  and  $Au^{+3}$ )  $Au$  system gold probably occurs in form of neutral molecules.

On the basis of certain correlation between gold and iron, copper, manganese, vanadium and relations between the contents of iron and gold in some minerals Ščerbakov (in Mantei, 1967) holds the theory of isomorphous occurrence of gold in minerals. Similarly Joralemov (in Petrovskaja, 1973) admits isomorphous replacement of the mentioned two elements also in spite of differences in their atomic radii (Au — 0,14 nm and Fe — 0,12 nm).

Of great importance in solution of this question are experimental syntheses of gold-bearing sulphides. Most detailed observation was carried out by Maslenickij (in Petrovskaja, 1973), with heating of mixture of elementary sulphur, ammonium, chloride, compound of iron and solution of gold resulting in growth of large and well developed crystals of pyrite containing 300 g.t<sup>-1</sup> gold. In thin section the prevailing part of gold was found in form of fine dispersions.

We have no convincing evidence of isomorphous replacement of other elements by gold. Similarly, it is not possible to speak unambiguously about the presence of solid solutions in gold-bearing sulphide. The possibility of their existence at certain degree of development of the ore-bearing process is, however, admitted, also when gold in sulphides is formed by independent microinclusions. (Petrovskaja, 1973).

### *Selection of samples*

At the beginning of the work we mentioned intentions and facts decisive for selection of samples for investigation of gold. Most samples were taken from the collection of authors and several of them were already studied geochemically also from the viewpoint of contents of other microelements. The mentioned fact makes possible to draw further correlative conclusions on dependence of gold and other elements, which will be solved in a particular work.

The fundamental problem of establishing of gold in pyrites or ores is connected with the degree of purity and monomineralness of analysed pyrite. The homogeneity of analysed sample can also be of not little influence on the final results. The occurrence of gold particles in pyrite crystals, also when trying for perfect homogenisation of sample before the analysis, often does not lead to reliable analytical results. In this fact one of the great problems of detection of gold in geological materials lies, which is necessary to take into consideration with interpretation of achieved results. Partial elimination of the mentioned influence can be carried out with raising the weighed portion of sample taken for analysis.

### *Separation of samples*

Separation of samples was carried out in the separatory laboratory of the Geological Institute of the Slovak Academy of Sciences under leadership of Ing. M. Žabka. The analysed samples were different in their specific gravity, mineral content and character of pyrite and association of accompanying minerals. Therefore it was necessary to apply several approaches of separation so that purest pyrite but also the largest amount of this mineral for analysis should be obtained.

The samples containing relatively pure pyrite, only with a small amount of accompanying minerals, were crushed by hand in Platner's mortar and separated under binocular microscope.

Other samples were crushed on jaw breaker. The insufficiently crushed part was then ground on roller mill and sorted on sieve of size 0,40 mm. The screen undersize fraction was then treated on table, pyrite came into



heavy fraction. With small amount of screen undersize fraction placer mining on a large watch glass was used. This way pyrite concentrate was obtained. When also other sulphides were found in it in large amount flotation with foamer DOWTROT and with collector Z-200 in environment with pH 7,5—7,6 was used to remove them. Further on, magnetic separation on isodynamic magnetic separator COOK was used. The mentioned way of separation was made twice, with current 1,5A and 2,5A. Pyrite passed into the nonmagnetic portion. Nonmetallic minerals were removed in heavy liquid (bromoform).

The purity of separated pyrite was controlled under binocular microscope and by qualitative spectrochemical analysis (J. Chudý, Geological Institute of the Faculty of Natural Sciences at the Comenius University). As the results have shown, purity of pyrite was relatively good because petrogenic elements did not exceed concentration 1% and sulphide minerals of other elements were found in negligible amount.

### *Analytical method*

After valuation of data from literature two different ways of decomposition of sample with extractational enrichment in methyl isobutylketone (MIBK) (Streško, 1979) or dibutylsulphide (DBS) in toluene (Rubeška et al.) were selected. In verifying the reliability of the mentioned working approaches good correlation of final results was achieved. More precise results were obtained with the second approach and therefore this way practically all samples were analysed.

The weighed portion of sample 2—10 g with grain size 150—200 mesh was thoroughly mixed and rubbed with ammonium nitrate in ratio 2 : 1. The mixture is annealed in porcelain crucible, first at 400°C 30 min. and then 1 hour at 650°C. In case the sample contains arsenic loss of gold with formation of alloy with low melting point can occur. For this reason it is necessary to anneal the sample at lower temperature for a longer time. After cooling of the sintering mixture this is rubbed and under permanent mixing decomposed by hydrobromic acid and bromine. The insoluble residue is separated twice with centrifugation and from the obtained solution gold is extracted into DBS in toluene. In the organic layer gold was established by the method of atomic absorption spectrometry with application of flame or electrothermic atomisation. In electrothermic atomisation the device Perkin—Elmer model 303 with graphite cell HGA-74 was used. As source of radiation was a discharge lamp with hollow cathode supplied by current 15mA. Measuring was made with resonance line of gold 242,8 nm. Argon was used as inert gas. The conditions of the individual phases were established from decomposition and atomisation curves as follows: drying 100°C, charring 800°C, atomisation 2400°C.

The analysed solution of gold was dosed into graphite cell by means of micropipette Brand (FRG). The pipetted volume was depending on the content of gold and varied within the limits from 10 to 50  $\mu$ l. The detection limit (lowest point of calibration curve) of the applied working method was 0,002  $\mu$ g/ml gold, i.e. 0,1 ng with pipetted volume 50  $\mu$ l. In solid sample, using 10 g of weighed portion, this value corresponds to 0,001 g.t<sup>-1</sup>

Regarding to inaccessibility of standard reference materials correctness of the method was verified by independent working approach (extraction into MIBK). In compiling of the correlation graph good accordance of results obtained by both working approachs was achieved. More detailed results are mentioned in the diploma work [Černeková — Škerenčáková, 1978]. Preciseness of detection was traced in one sample, in which with average content  $0,023 \text{ g.t}^{-1}$  gold relative standard deviation 25,6 % was achieved.

#### *Comparison of results obtained by other working approaches*

A part of the studied samples from the Little Carpathians was analysed also at the Institute of Geochemistry of the Siberian Academy of Sciences in Irkutsk. On the basis of ore mineralization of original samples these were divided into three groups and designated with letters A,B,C. The samples designated with letter "A" were practically free of sulphide minerals visible with eye. The samples with letter "B" contained distinctly certain amounts of these minerals. In the last group designated with letter "C" samples were analysed, in which sulphide minerals predominated — typical ores of the pyrite formation were concerned. The original samples were separated in separation laboratory of the Geological Institute of the Slovak Academy of Sciences with application of gravition method. This way two fractions were obtained — heavy and light portion. In the original sample and in light portion the contents of gold were established by means of atomic absorption spectrometry in graphite cell at the Institute of Geochemistry of the Siberian Academy of Sciences in Irkutsk. Closer conditions of the analysis have not been sent.

On the whole 13 samples were analysed, from each the original sample and light portion (Tab. 5). 9 samples from them belonged to group "B" and 4 samples to group "C". In the first group of samples B, in the majority of cases, gold (in 6 samples) remained in the original sample and in the light fraction the portion of gold did not essentially sink. In the second group of analysed samples (C) in two samples a higher content of gold in the original sample and in two samples in light fraction was established.

The above mentioned results confirm that pyrite or sulphides are the main bearers of gold in rocks but the content of gold in pyrites and rock is almost equal. Native gold in form of gold particles is practically not represented except for pyrite. The rich pyrite ores (C) are of similar character as dark schists containing less pyrite (B). This essentially testifies to equal genetic conditions of samples rich and poor in sulphides. It agrees with the opinion that pyrite is enriched in gold where also the rock or mineral paragenetic environment is characterized by such properties. It should be remarked that hydrothermal pyrites with content of antimonite in the Malé Karpaty Mts. have 10—100 times higher contents of gold (analyses no. 7 and 8), testifying to a different genetic character of Sb mineralization from pyrites of the pyrite formation.

Besides atomic absorption spectrometry also the method of neutron activation was applied for detection of gold in some original samples from the Malé Karpaty Mts. The achieved results together with our ones and the results of the Institute of Geochemistry of the Siberian Academy of Sciences

Table 5

The results of gold establishing in original samples and in light fractions  
Analysed at the Institute of Geochemistry A. Sc. USSR in Irkutsk

Sample No.	Type of sample	Locality	Au content g. t <sup>-1</sup>	
			origin. sample	light frac.
40 B	with pyrite dark schist	MK—Karol upper	0.0055	0.0090
42 B	with pyrite dark schist	MK—Karol lower	0.0022	0.0015
43 C	sulphide ore	MK—Karol lower	0.0014	0.0090
47 C	sulphide ore	MK—Ján III	0.0067	0.0030
47 B	dark schist	MK—Ján III	0.0065	0.0104
52 B	dark schist	MK—Augustín upper dump	0.0147	0.0145
53 B	graphitic schist	MK—Augustín upper dump	0.0075	0.0052
55 C	sulphide ore	MK—Augustín borehole KU-3	0.0022	0.0056
70 B	graphitic schist	MK—Pezinok borehole KU-4	0.0062	0.0930
71 C	sulphide ore	MK—Pezinok dump	0.0090	0.0024
77 B	quartz-sulphide ore	MK—Pezinok dump	0.0032	0.0018
79 B	quartz-sulphide ore	MK—Pezinok	0.0024	0.0015
80 B	amphibolite with pyrite	way behind the District Health Centre MK—Pezinok	0.0051	0.0009

Table 6

Comparison of gold establishing results in original samples with atomic absorption spectrometry and neutron activation

Sample No.	Locality	g. t <sup>-1</sup> Au		
		NA ÚL—ČSUP	AAS IRKUTSK	AAS GŮ—PFUK
40 B	MK—Karol upper	<0.01	0.0090	0.0010
42 B	MK—Karol lower	0.126	0.0015	0.0030
43 C	MK—Karol lower	0.060	0.0090	0.0020
47 C	MK—Ján III.	0.131	0.0030	0.0010
55 C	MK—Augustín upper	<0.01	0.0050	0.0010

Explanations: NA — neutron activation

AAS — atomic absorption spectrometry

ÚL—ČSUP — Central Laboratory of Czechoslovak

Uranium Industry Stráže

GŮ—IRKUTSK — Institute of Geochemistry A. Sc. USSR in Irkutsk

GŮ—PFUK — Geological Institute of Natural Science Faculty of Comenius University

in Irkutsk are mentioned in Tab. 6. In all concrete values obtained with neutron activation, compared with atomic absorption spectrometry, these are different and in two cases almost 100 times higher. In samples 40 B and 55 C gold has not been established, i.e. it was below the detection limit of the applied method [0,01 g.t<sup>-1</sup>]. The values obtained by atomic absorption, also when in different laboratories, are getting closer to one another in spite of application of different working approaches.

### *Discussion and conclusion*

The results of analyses of 67 samples of pyrites from deposits of various genetic types and 40 analyses of samples, from which pyrite was separated, are the basis for geochemical interpretation. The chemical analyses are summarized in Tab. 7, in which the samples are subdivided according to individual genetic types of pyrites so as it was mentioned in the introductory part of this work. Besides that a table of arithmetic and geometric means of gold contents according the individual deposits, groups of deposits or mountain ranges and according to individual genetic types was compiled.

From the achieved results the following conclusions may be drawn:

1. The results confirm that certain contents of gold are characteristic of certain genetic types of deposits or certain deposits (Tab. 8). Plutogenic and subvolcanic pyrites show a greater dispersion of gold content than syngenetic types, which fact is in the first place valid for pyrites from one deposit area and one genetic group but partly also in general.

2. Syngenetic ore mineralizations of the pyrite formation are poorer in gold than plutogenic and subvolcanic genetic types but also here are exceptions, mainly in hydrothermal-plutogenic types. For instance, the deposit Alžbeta, some ore types of the Malé Karpaty Mts., some ores of the deposit Smolník and one sample from the deposit Zlaté hory. Also when their genesis has not been found out sufficiently, the variable and higher contents of gold in pyrites are closer to hydrothermal pyrites than to pyrites of typical syngenetic deposits.

The contents of gold in syngenetic pyrites display as to equability some analogy with Ni and Co contents, which elements are of isomorphous position and have equable distribution of contents. It may be concluded that gold in syngenetic pyrites is a fine-dispersed component of pyrite crystals and also similar to minerals of sediments with component sorbed (colloidal) from surrounding rocks. Therefore is not a great difference between the contents of gold in syngenetic pyrites of the Malé Karpaty Mts. and in schists, in which the pyrites are found. On the whole, gold contents in syngenetic pyrites from the Malé Karpaty Mts. region are very low (arithmetic mean 0,0029 g.t<sup>-1</sup> and in original samples [0,011 g.t<sup>-1</sup>].

3. As the results of gold detection in the studied pyrites show, the highest contents were found in pyrites from hydrothermal deposits (arithmetic mean 0,242 g.t<sup>-1</sup> and geometric mean 0,122 g.t<sup>-1</sup>). In original samples an orderly lower value of the geometric mean was established in this genetic type [0,039 g.t<sup>-1</sup>]. The arithmetic mean is not so much different [0,118 g.t<sup>-1</sup>], what is caused by considerable variation of gold contents in original samples. The highest contents of gold were found in hydrothermal- plutono-

Table 7  
Results of establishing of gold in pyrites in various genetic types.

I. Hydrothermal — subvolcanic pyrites				Content Au g.l <sup>-1</sup>	
Anal. No.	Locality	Samp. No.	Description of orig. sample	pyrite	original sample
1.	PV—Zlatá baňa mine	ZK-5	fine-grained pyrite in andesite	0.280	0.081
2.	BŠ—Zlatno	4	strip of compact pyrite in andesite	0.030	
3.	BŠ-Bieber vein	7	lumpy rodlike marcasite from vein	0.008	
4.	BŠ—Terézia vein	3	fine-grained pyrite in veiny quartz	0.340	
5.	BŠ—Bieber vein	8	veinlet of fine-grained pyrite in andesite	0.093	0.057
6.	BŠ—Viliam vein	9	crystals of pyrite disseminated in andesite [2—4 mm great aggregates]	0.065	0.033
	A. P.			0.136 (6)	0.057 (3)
	G. P.			0.072 (6)	0.053 (3)
II. Hydrothermal — plutogenic pyrites				Content Au in g.t <sup>-1</sup>	
7.	MK—Pezinok	259	chambers of pyrite in schistose rock and quartz	0.080	0.081
8.	MK—„Sb” drift	251	fine-grained pyrite in dark quartz	0.300	
9.	MK—Pernek	253	fine-grained pyrite with quartz and ankerite	0.080	0.001
10.	MK—Častá Mária mine	262	fine-grained pyrite with carbonates and quartz	0.127	0.032
11.	MK—Častá red. mine	283	chambers of fine-grained pyrite in carbonate rock	0.360	0.085
	A. P.			0.189 (5)	0.059 (4)
	G. P.			0.154 (5)	0.021 (4)
12.	NT—Dúbrava	157	disseminated pyrite in milky quartz, present scheelite	0.082	0.038
13.	NT—Flotation drift	130a	veinlet of pyrite in pink quartz, sulpho-salt Pb—Sb (?)	2.030+	
14.	NT—Lower Ignác drift	27	medium—grained pyrite	0.510	
15.	NT—Lower Ignác drift	29	medium—grained pyrite	0.590	
16.	NT—Dúbrava	38	fine—grained crystalline pyrite in quartz	0.700	
17.	NT—Dúbrava	32	fine—grained pyrite in quartz, present antimonite	0.140	
18.	NT—Dúbrava	96	clusters of medium—grained pyrite in quartz	0.050	
19.	NT—Dúbrava	9	fine—grained pyrite in quartz, occurrence of scheelite		
20.	NT—Dúbrava	131	fine to—medium—grained pyrite in quartz and Fe—dolomite, present tetrahedrite	0.600	
	A. P.			0.540	
	G. P.			0.582 (9)	
	A. P.+			0.349 (9)	
	G. P.+			0.401 (8)	
				0.281 (8)	

Continuation of Tab. 7

Content Au g.t. <sup>-1</sup>					
Anal. No.	Locality	Sample No.	Description of orig. sample	pyrite	orig. sample
21.	SGR—Droždiak vein	R-4	crystals of pyrite with chalcopyrite in schistose rock	0.180	0.018
22.	SGR—Droždiak vein	VZ-4	fine-grained pyrite with chalcopyrite in hydrothermally altered rock	0.137	0.078
23.	SGR—Droždiak vein	R-9	crystals of pyrite in coarse-crystalline siderite, present chalcopyrite and specularite	0.110	0.001
24.	SGR—Droždiak vein	R-12	lumpy sample with pyrite, quartz and specularite	0.040	
25.	SGR—Droždiak vein	R-13	raw ore with pyrite, chalcopyrite and crystalline siderite	0.001	0.001
26.	SGR—Droždiak vein	R-23	lumpy sample with pyrite, barite, chalcopyrite and siderite	0.140	0.017
27.	SGR—Droždiak vein	R-24	fine-crystalline pyrite with chalcopyrite in siderite, present quartz	0.320	0.560
28.	SGR—Droždiak vein	R-26	ore with pyrite, chalcopyrite, specularite and siderite	0.040	0.009
29.	SGR—Droždiak vein	R-28	ore with pyrite, chalcopyrite, specularite and siderite	0.200	0.400
30.	SGR—Zlatník vein	R-30	crystals of pyrite in coarse-crystalline barite, present chalcopyrite and tetrahedrite	0.010	0.025
31.	SGR—Droždiak vein	R-113	crystals of pyrite, chalcopyrite with cinnabar and tetrahedrite in barite	0.216	0.960
32.	SGR—Droždiak vein	R-185	fine-to medium crystalline pyrite with calcite, occurrence of tetrahedrite	0.440	0.005
33.	SGR—Droždiak vein	R-6121	compact pyrite with specularite	0.018	
34.	A. P.	ČM—Kutná Hora	compact pyrite in quartz	0.144(14)	0.212(12)
	G. P.			0.072(14)	0.021(12)
				0.170	0.480
	A. P.			0.293(28)	0.164(17)
	G. P.			0.137(28)	0.031(17)

*Explanations:* A. P. — arithmetic mean, G. P. — geometric mean, + — indicates the average without designated samples, N. T. — Low Tatra, B. Š. — Banško-štiavnicke rudohorie mts., P. V. — Prešov hills, MK — Malé Karpaty Mts., ČM — Czech-Moravian region, SGR — Spišsko-gemerské rudohorie mts., VEP — Veporides, — the numbers in parentheses mean the amount of analyses.

genic pyrites from Dúbrava (GP.—0,349 g.t.<sup>-1</sup>). A high content of gold (2,03 g.t.<sup>-1</sup>) was found in analysis no 13. This may be caused by fine dispersions of gold in quartz, which could not be separated with the separation method. The fact that in hydrothermal pyrites the average contents are higher



Continuation of Tab. 7

## III. Hydrothermal — sedimentary and strongly metamorphic crystallized syngenetic pyrites

Anal. No.	Locality	Sample No.	Description of orig. sample	pyrite	orig. sample
35.	MK—Augustín drift	MK-1	graphite—quartz sulphidic ore	0.140	0.001
36.	MK—Trench drift	1	fine—dispersed pyrite in sulphidic—quartz ore	0.022	0.027
37.	MK—Augustín drift	MK-2	sulphidic—quartz ore	0.060	0.001
38.	NT—HeĽpa	23	pyrite dispersed in amphibolic ore	0.106	0.055
39.	NT—HeĽpa	135	fine—grained—to medium—grained dispersions of pyrite in rock with quartz and metapyroclastic	0.100	0.007
40.	SGR—Bystrý potok	310	raw ore with pyrite and chalcopyrite and further sulphides	0.700+	1.50
41.	SGR—Bystrý potok A. P. G. P.	743	compact pyrite—pyrrhotite ore	2.00+ 0.446 (7) 0.101 (7)	0.265 (6) 0.015 (6)
	A. P.+ G. P.+			0.085 (5) 0.072 (5)	0.018 (5) 0.006 (5)
IV. Syngenetic — sedimentary pyrites — weaker-stronger metamorphosed					
42.	MK—Pernek	430	fine—grained pyrite in amphibolite	0.001	0.025
43.	MK—Rybníček	3	disseminated 1—2 mm pyrite in metapyroclastics	0.009	0.001
44.	MK—Pyrite drift	10	disseminated fine—grained pyrite in chloritic schists	0.005	0.005
45.	MK—Karol — upper	40-B	fine dispersions of pyrite in graph. schist	0.001	0.001
46.	MK—Karol lower	42-B	fine dispersions of pyrite in graph. schist	0.001	0.001
47.	MK—Ján III	47-C	pyrite ore	0.001	0.001
48.	MK—Ján III	49-A	pyrite of microscopic dimensions in the sedimentary rock of dark grey colour	0.005	0.001
49.	MK—ore district	52-B	fine—grained pyrite in dark schist	0.004	0.021
50.	MK—Augustín upper	55-C	rich pyrite ore in dark rock	0.001	0.001
51.	MK—Karol lower	43-C	pyrite layer in dark schist	0.002	0.002
52.	VEP—HeĽpa	208	sulphidic pyrite-pyrrhotite ore with prevalence of pyrite	0.001	0.012
53.	VEP—HeĽpa	185	fine dispersion of pyrite in dark schist	0.006	0.020
54.	ČM—Chvaletice	27	crystals of pyrite in graph. schist	0.001	0.055
	A. P.			0.003(13)	0.011(13)
	G. P.			0.002(13)	0.005(13)
	A. P. MK			0.003(10)	0.006(10)
	G. P. MK			0.002(10)	0.002(10)

Continuation of Tab. 7

V. Syngenetic-sedimentary, hydrothermal-sedimentary or remobilized pyrites often concretionally recrystallized

Anal. No.	Locality	Sample No.	Description of orig. sample	Content Aug. t <sup>-1</sup> pyrite	orig. sample
55.	VEP-mine Mútnik community Hnúšťa	28	pure compact pyrite in talc	0.013	
56.	VEP-mine Mútnik community Hnúšťa	45-S	coarse—crystalline, pure pyrite from talc schist	0.040	
57.	VEB-Čiško mine	631	disseminated pyrite in hydrothermal quartz in sericite—chloritic schist	0.001	0.001
58.	VEB-Čiško mine	605	disseminated pyrite in hydrothermal quartz in sericite—chloritic schist	0.001	0.001
59.	SGR-Smolník	24	fine—grained pyrite dispersed in chloritic phyllite	0.137	
60.	SGR-Smolník	26	2—4 mm large crystals of pyrite dispersed in chloritic phyllite	0.105	
61.	ČM-Zlaté Hory	25	fine—grained pyrite dispersed in light—grey rock	1.700+ 0.285 (6) 0.027 (6)	
	A. P. G. P.			0.049 (5) 0.014 (5)	

## VI. Pyrites from skarns

62.	VEB-Kokava nad Rimavicou	39	coarse—crystalline pyrite	0.057	
63.	BŠ-Vyhne, Mária mine A. P. G. P.	11	medium—crystalline pyrite with veinlets of quartz	0.046 0.051 (2) 0.051 (2)	0.037

## VII. Sedimentary pyrites from coal, remobilized concretions

64.	Komořany near Most	248	pure concretions of pyrite	0.012	
65.	Duchcov	3	radial radiate crystals of marcasite	0.013	
66.	Duchcov	2	fine—grained crystalline pyrite	0.020 0.015 0.015 0.014	
67.	Duchcov A. P. G. P.	2/6	concretions of pyrite		

than in average samples may also indicate that in this genetic type of samples gold is preferentially concentrated just in pyrites. This tendency is also to be seen from the course of histogram. (Fig. 1).

Table 8

Genesis of pyrite		Number of analyses	A. P.	G. P.
I. Hydrothermal-subvolcanic (HS)	pyrite	3	0.136	0.072
	orig. sample	6	0.057	0.053
II. Hydrothermal-plutonogenic (HP)	pyrite	28	0.293	0.137
	orig. sample	17	0.164	0.031
Nízke Tatry Mts.—Dúbrava	pyrite	9	0.582	0.349
Dúbrava without sample 130 a				
(2,030 g. t <sup>-1</sup> Au)	pyrite	8	0.401	0.281
Malé Karpaty	pyrite	5	0.189	0.154
	orig. sample	4	0.059	0.021
Rudňany	pyrite	14	0.144	0.072
	orig. sample	12	0.212	0.021
III. Hydrothermal-sedimentary and strongly metamorphic crystallized syngenetic pyrites (HS—SM)	pyrite	5 (7)	0.085	0.072
	orig. sample	5 (6)	0.018	0.006
IV. Syngenetic-sedimentary more or less metamorphosed	pyrite	13	0.0029	0.0020
Malé Karpaty	orig. sample	13	0.0110	0.0050
	pyrite	10	0.003	0.002
	orig. sample	10	0.006	0.002
V. Syngenetic-sedimentary hydrothermal-sedimentary or remobilized often concretionally recrystallized	pyrite	6	0.285	0.027
without Zlaté Hory	orig. sample	1	—	—
VI. Pyrites from skarns	pyrite	5	0.049	0.014
	pyrite	2	0.051	0.051
VII. Sedimentary-concretionary pyrites from coal remobilized	pyrite	4	0.015	0.014
Hydrothermal pyrites together:	pyrite	39	0.242	0.122
Syngenetic-sedimentary together:	orig. sample	25	0.118	0.024
	pyrite	20	0.101	0.005
+ average without Zlaté Hory	orig. sample	14	0.010	0.005
1,700 g.t <sup>-1</sup> Au	pyrite	19	0.016+	0.003

4. In the genetic type of hydrothermal deposits samples from three fundamental regions of the Low Tatra, Malé Karpaty Mts. and Spišsko-gemerské rudohorie mts. — Rudňany were analysed. It is evident from the calculated average contents that in the mentioned three regions gold content decreases in the following order: Low Tatra, Malé Karpaty Mts. and Spišsko-gemerské rudohorie mts. In the individual samples gold contents are, however, highly variable.

5. Hundred times lower contents of gold in contrast to hydrothermal-plutonogenic ones were found in syngenetic — sedimentary pyrites [type III] A. P. — 0,003 g.t<sup>-1</sup>, G. P. — 0,002 g.t<sup>-1</sup>). In original samples similar values were found [A. P. — 0.001 g.t<sup>-1</sup>, G. P. — 0,005 g.t<sup>-1</sup>]. As visible from the results, gold contents in pyrites and original rocks are almost equal and no variation of gold contents in individual samples was observed. The mentioned facts may be characteristic of stable PT conditions of the marine environment, in which pyrite originated.

6. Considerable variation in contents of gold was observed in syngenetic, hydrothermal-sedimentary or highly recrystallized pyrites (types III). Concerned are samples, mostly subjected to strong metamorphism, which could have resulted in redistribution of gold in the given environment. The average contents would be misrepresented very much by the anomalous result of the sample from Bystrý Potok, therefore we did not take it into account in calculation.

7. Similar variation of gold contents display also pyrites from syngenetic-sedimentary and hydrothermal — remobilized pyrites (Type V). The highest content was found in pyrite from Zlaté Hory ( $7,7 \text{ g.t}^{-1} \text{ Au}$ ). The mentioned

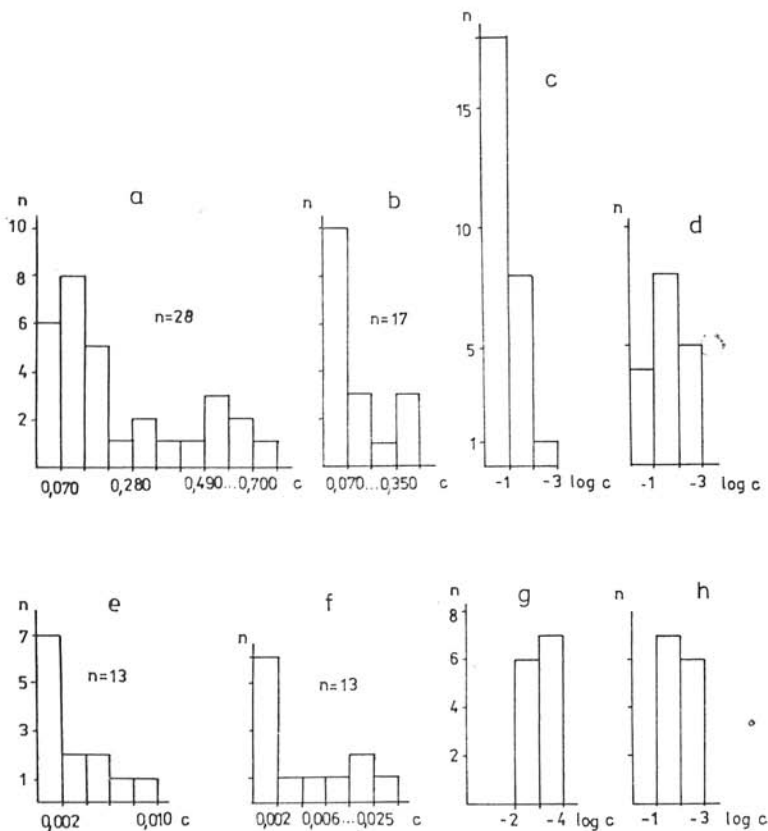


Fig. 1. Histograms of distribution of Au contents in pyrites and original samples from some genetic types

Explanations: a — conc. of Au in pyrites from hydrothermal-plutonogenic types, b — conc. of Au in original samples from hydrothermal-plutonogenic types, c — log. of concentration of Au in pyrites from hydrothermal-plutonogenic types, d — log. of concentration of Au in original samples from hydrothermal-plutonogenic types, e — conc. of Au in pyrites from syngenetic-sedimentary types, f — conc. of Au in original samples from syngenetic-sedimentary types, g — log. concentration of Au in pyrites from syngenetic-sedimentary types, h — log. of concentration of Au in original samples from syngenetic-sedimentary types.

result agrees with the content of gold established by N ě m e c (1974) at the same locality.

8. In analysed samples of pyrites from skarns the arithmetic and geometric means completely agree. More profound geochemical conclusions were not possible to draw for the small number of analysed samples. Similar results were also obtained in the analyses of pyrites from coal. The average contents are somewhat lower in contrast to the preceding genetic type.

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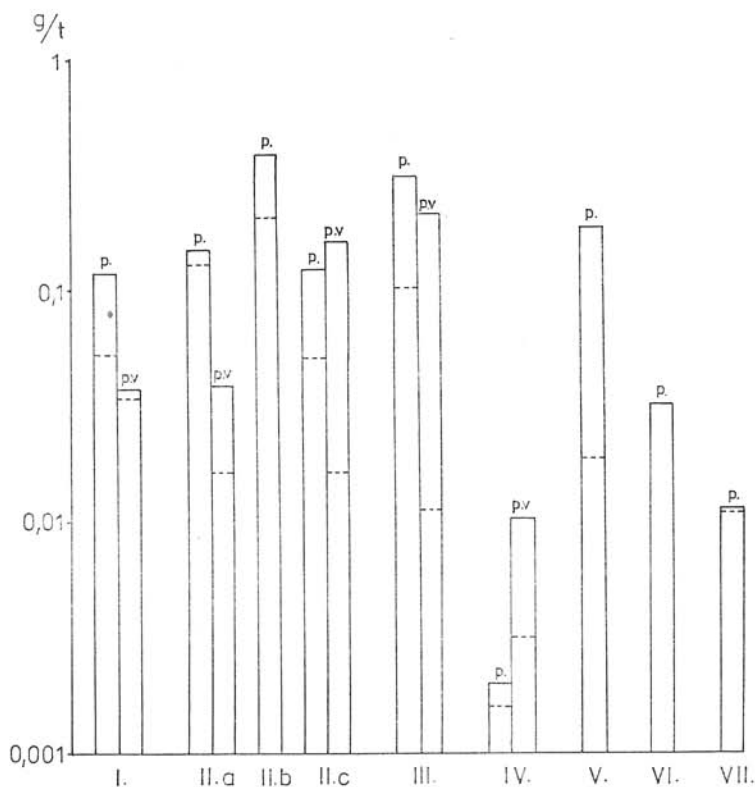


Fig. 2. Comparison of average contents of gold in pyrites and original samples from traced genetic types

*Explanations:* I, II.a, II.b, II.c, III, IV, V, VI, VII- individual genetic types, see p. 140  
 p — pyrites, p.v. — original samples, ———— — arithmetic mean, ---- geometric mean.

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