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SULPHUR ISOTOPES OF THE STRATIFORM PYRITE DEPOSIT TURECKÝ VRCH AND STIBNITE DEPOSIT PEZINOK, IN THE MALÉ KARPATY MTS CRYSTALLINE, CZECHOSLOVAKIA

(*Figs. 1—29*)

Abstract: In the crystalline of the M. Karpaty Mts stratiform pyrite deposits occur within the volcanogenic-sedimentary sequence of Lower Paleozoic age. Spatial and genetical relations to the submarine diabase volcanism are apparent. For pyrite-sulphur δS^{34} values range —3.9 to —21.2 permil, and indicate bacterial reduction. Colloform-deposited and younger, crystalline pyrite are common, the latter displaying by 2—3 permil heavier sulphur. Extreme enrichment in S^{34} was found in mobilized pyrite veinlets (+19.6 to +21.9 ‰).

The stibnite mineralization is confined to the same productive sequences as the stratiform pyrite bodies. Though the latter may not contain Sb-ores, the stibnite deposits are usually pyrite rich. The following δS^{34} ranges were measured: stibnite (—2.2 to —6.5 ‰), arzenopyrite (—1.0 to —6.0 ‰), pyrite (—1.9 to —8.5 ‰), berthierite (—9.2 to —10.8 ‰), gudmundite (—5.9 to —13.5 ‰), and for pyrite whose appurtenence to the Sb — or syngenetic pyrite — mineralization is uncertain, δS^{34} varied between —3.1 and —18.4 ‰. Highest enrichment in S^{32} display Fe-bearing Sb-minerals indicating a link to the syngenetic pyrite deposits. The proposed schemes of „time and strata-bound Sb-W-Hg" — and hydrothermal mineralization are discussed.

Резюме: Слоеобразные пиритовые месторождения кристаллического массива Малых Карпат выступают в вулканическо-осадочном комплексе нижнепалеозойского возраста. Связ этих месторождений с субмаринным вулканизмом диабазового характера очевидна. Данные δS^{34} в пирите находятся в пределах от — 3,9 до — 21,2 ‰ и свидетельствуют об бактериальной деятельности.

Для минералов из Sb-месторождений находящихся в подобной геологической позиции были определены значения δS^{34} от —1 до —13,5 и в некоторых случаях до — 18,4 ‰. На отношение к сингенетическому пиритовому оруднению показывают отрицательные значения δS^{34} и обогащение изотопом S^{32} тех Sb-минералов, которые содержат железо. Предлагается дискуссия различных генетических схем.

Introduction

Important ore-deposits of the Malé Karpaty Mts. are confined to the Pezinok—Pernek crystalline. Outside this area a small deposit of copper-polymetallic ores is known in crystalline schists near the village Častá (N of Pezinok).

Copper and baryte mineralizations occur in melaphyre rocks of Permian-, sedimentary manganese ores in the Mariatal-schists of Liassic age. Though explored in the past they never reached economic importance owing to low grade and limited extent.

Mineral deposits of pyrite and antimony ores are the only ones attaining large dimensions in the M. Karpaty Mts. They are restricted to the Pezinok—Pernek crystalline located about 20 kms N of Bratislava.

This crystalline (of triangular shape) is flanked by postkinematic granitoids of Variscan age: the Bratislava Massif in the S, the Modra Massif in the N.

Two-mica quartz granodiorites prevail over two-mica granites in the Bratislava Massif. Leucocratic differentiates as well as pegmatites are common, too.

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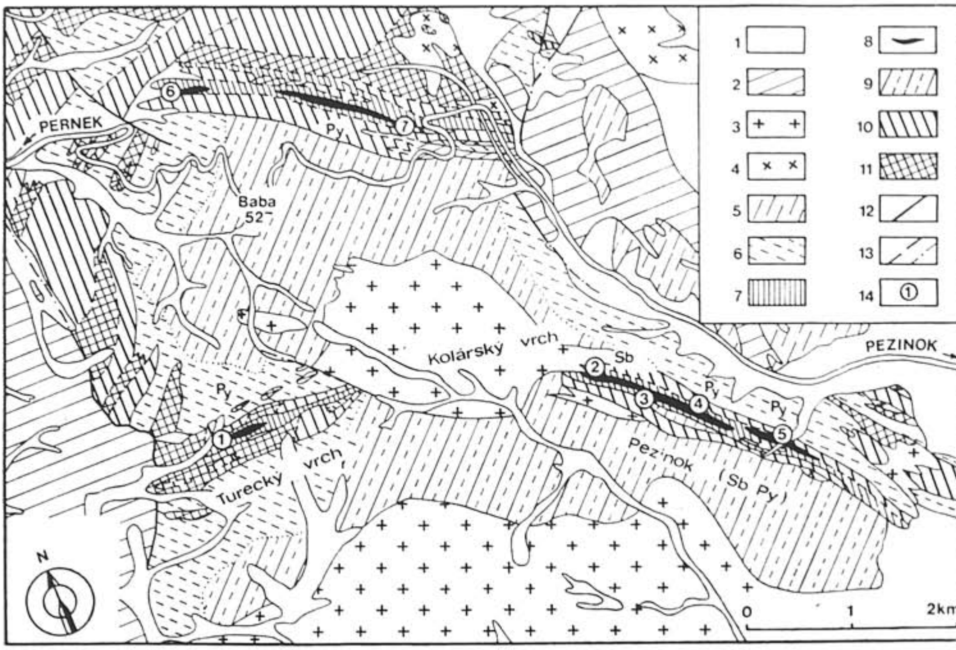


Fig. 1. Geological map of the Pezinok — Pernek area. After B. C a m b e l in Geological map of the M. Karpaty 1:50 000, 1972, slightly modified.
1. Quaternary 2. Mesozoic 3. Granitoids, Bratislava Massif 4. Granitoids, Modra Massif 3—4. Variscan 5. Sericite-chlorite and biotite phyllites (Harmónia unit) 6. Sericite-biotite-and biotite phyllites 7. Actinolite schists 8. Actinolite schists with stratiform pyrite bodies 9. Biotitic micaschistose gneisses and paragneisses 10. Amphibolites, medium to fine-grained 11. Amphibolites with prevailing pyroclastic material 5—11 Lower Paleozoic (to Upper Algonkian?) 12. Faults 13. Faults, supposed 14. Mines (adits): 1 — Rudolf, 2 — Kolárska, 3 — Stibnite, 4 — Pyrite, 5 — Ferdinand, 6 — Karol, 7 — Augustin.

The principal rocks of the Modra Massif are biotite granodiorites: two-mica granites and pegmatites occuring quite subordinately (B. C a m b e l — J. V a l a c h 1956, B. C a m b e l 1967).

The metasedimentary rocks of the crystalline belt consist of phyllites and schists (sericitic, chloritic, quartzose, biotitic, bituminous). By periplutonic metamorphism resulted micaschits as well as biotitic paragneisses, which are commonly garnetiferous.

Variable amounts of actinolite may be present, indicating original pyroclastic material in these schists that display often gradual transitions to black, bituminous (so called graphitic) schists and to metadiabasic rocks. The latter prevailing in the northern part of the Pezinok—Pernek area (B. C a m b e l 1958, R. Ž á k o v s k ý 1962).

Intrusive forms — gabbros, gabbrodiorites a. s. o. have been also described B. C a m b e l 1952, B. C a m b e l — G. K u p č o 1965) but are not marked in geological maps.

Biotitic paragneisses and micaschists, extending between the Bratislava granitoide massif and the ore zone Pezinok—Kolárský vrch—Turecký vrch (map. Fig. 1), are supposed to represent the oldest members of the crystalline (B. C a m b e l 1958).

They are overlain by the volcanogenic-sedimentary rocks of the so called first productive zone (Pezinok—Kolársky vrch. Konské hlavy—Turecký vrch). It consists of submarine diabasic extrusions and pyroclastics, alternating with pelitic and organo-detritic metasediments.

Within this zone large bodies of stratiform pyrite ores occur, apparently in genetic relation to the diabase volcanism.

In the NW part of the section Pezinok—Kolársky vrch is located the largest antimony deposit of the M. Karpaty Mts., it's SE part being dominantly mineralized by pyrite.

In the section Konské hlavy—Turecký vrch of the first productive zone only indications of Sb ores are known, though pyrite forms here large lense-shaped bodies, too.

The present paper deals with the distribution of sulphur isotopes in sulphides of both parts of the productive zone No. 1.

After B. Cambel (1958) the productive volcanogenic-detrital sequence has been succeeded by a younger detrital sedimentation, represented in the enclosed map by biotite phyllites, micaschits and paragneisses laying between the first productive zone in the south and the second one in the north.

The principal masses of metabasic rocks are concentrated in the northern part of the territory, to the N of the road connecting Pezinok with Pernek. They are believed to represent with the enclosed stratiform pyrite bodies, products of a younger volcanic phase (B. Cambel 1958).

In connection with this „younger" volcanogenic-detrital sequence three ore zones are distinguished: with stratiform pyrite deposits and Sb-mineralizations or deposits in each one. In the zone developed along the southern margin of the metabasite area lie the deposite Kristina, Nádej, Augustín and Karol. The other two zones occur outside the area illustrated on the geological map.

A somewhat different interpretation of the superposition of the rock sequences was given by J. Čillík — P. Sobolič — R. Žákovský (1959) and R. Žákovský (1962) who regarde all ore zones as penecontemporaneous.

Pyrite deposit Turecký vrch

The pyrite deposit Turecký vrch and the antimony deposit Pezinok—Kolársky vrch are located in the southern part of the Pezinok—Pernek crystalline about 1 to 2 kms N of the Bratislava granitoide Massif.

They are part of the so called first productive zone, which is by the granitoide intrusion of the Kolársky vrch divided into two segments. One of them (segment I. of B. Cambel l. c.) stretches from Pezinok NW to the hill Kolársky vrch in a total length of about 4 kms. It contains the largest Sb-deposit of the M. Karpaty Mts. as well as stratiform pyrite bodies.

The E-W trending continuation of the productive zone beyond the granitoide cupola (zone Ib of B. Cambel) may be followed in the surroundings of the hill Turecký vrch. Conformable pyrite sheets of larger dimensions, but only indications of Sb-ores were disclosed in this section by recent exploration.

The southernmost productive zone is regarded as older than the three northerly lying ones (B. Cambel 1959, 1967).

In all are the principal characteristics of the mineralization similar: The bodies are stratiform, lying concordantly within the ore bearing sequence. The latter consits of lithologically variegated beds with actinolite-, graphite-, sericite-, chlorite- schists in variable proportions, as the most important. Gradual transitions between the rock- and ore-types are common. Pyrite ores display at places pronounced banding and well preserved sedimentary textures (Fig. 5—15).

The largest accumulations of pyrite occur within, or in the close proximity of actinolite schists. Though syngenetic pyrite is never absent, it generally forms only minor ore-bodies in black „graphitic" beds (The term graphitic is used, though flakes of crystalline graphite occur only in higher metamorphosed schists of the area).

Certain diversity between pyrite deposits of the productive zones may result also from differences in the state of preservation of sedimentary structures and textures.

In the mineralizations of the Turecký vrch area features indicating synsedimentary deposition of pyrite are often preserved up to the minutest details. In the SE segment of the first ore-zone, in the deposits Pezinok—Kolársky vrch they become rarer, less pronounced, or even totally lacking.

Similar conditions are encountered in the second ore-zone. Feebly metamorphosed ores exhibiting synsedimentary textures, the sulphides being represented by pyrite only, occur in the NW part (surroundings of Karol-deposit).

Intense metamorphism produced abundant pyrrhotite and destroyed often the fine synsedimentary features. (Deposits Augustín, Rýhová, Nádej, Kristina in the SE part of second zone).

The pyrite mineralization of the Turecký vrch deposit, its relation to the host rocks is illustrated in the section (Fig. 2) after R. Žákovský.

For the characterization of the deposit sulphide sulphur isotope ratios of samples from the boring TV-6 were used.

Since 1956 pyrite deposits of the M. Karpaty Mts. are regarded as of exhalative-sedimentary origin and as genetically related to the submarina diabase volcanism of Lower Paleozoic age (St. Polák 1956, B. Cambel 1956).

Isotopic investigations revealed the important role of biogenic processes during the formation of the ores. Pyrite sulphur is considerably enriched is S^{32} which is usually produced by sulphate reducing bacteria (J. Kantor in B. Cambel — J. Kantor 1972).

In the past besides a syngenetic, submarine-exhalative also hydrothermal or liquation origin have been ascribed to the M. Karpaty pyrite ores.

Stibnite-deposit Pezinok—Kolársky vrch

The ore bearing complex Pezinok—Kolársky vrch is undrelain by an up to several hundred meters thick zone of biotite gneisses which are supposed to represent the oldest sediments of the crystalline and are penetrated by numerous pegmatite dykes and small granite bodies.

In its overlier — towards the central part of the crystalline — a less metamorphosed sequence of biotitic, micaschistose gneisses and phyllites is developed.

Argillaceous and bituminous sediments with variable proportions of pyroclastic material and actinolite schists alternating in a variegated sequence are the proper host rocks to the mineralizations. Stratiform pyrite bodies are confined mainly to actinolite schists, the stibnite mineralization to graphite (bituminous) schists. The latter extend along the whole productive zone, attaining thicknesses of 30 to 60 m, whereas that of the sedimentary members of the ore zone varies between 50 and 150 m.

Amphibolites form the immediate under-, as well as overlier of the ore bearing

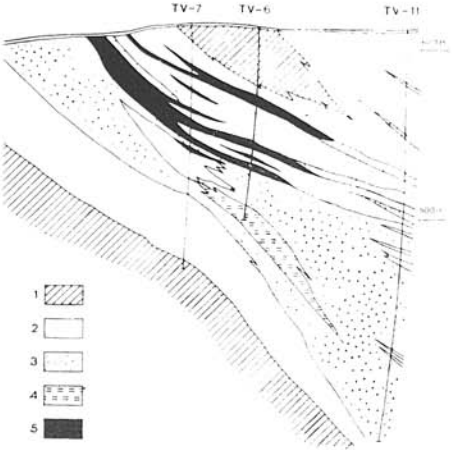


Fig. 2. Geological section of the Turecký vrch pyrite deposit. After B. Žákovský 1962. 1. Amphibolites 2. Actinolite schists 3. Graphite schists 4. Biotite phyllites 5. Pyrite ore.

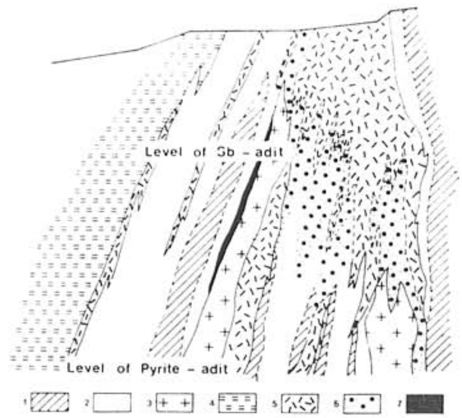


Fig. 3. Cross-section of stibnite deposit. Pezinok. B. Cambel 1959.
1. Amphibolites 2. Actinolite schists 3. Granitoids 4. Biotite micaschists to gneisses 5. Graphite schists with Sb-ores 6. Graphite schists with dispersed pyrite 7. Pyrite ore.

schists. They might represent submarine lava flows with rich pyroclastic deposition, partly also small intrusions of gabbroidic rocks metamorphosed into spotted amphibolites (B. Cambel l. c.).

Parallel to the striking of the stibnite ore occur zones enriched in quartz, locally of dark colour. True quartz-stibnite veins, formed by deposition in open space are not developed. B. Cambel (l. c.) reports also that richer stibnite ores are generally restricted to weekly and medium silicified parts, whereas the highly silicified ones of the productive zone carry only poor mineralizations.

Sections across the stibnite deposit Pezinok—Kolársky after B. Cambel and I. Chrappa are reproduced in Fig. 3.

The mineralogical association is relatively rich and has been recently studied by B. Cambel (l. c.) and St. Polák (1955). Described were: pyrite, arzenopyrite, löllingite, chalcopyrite, gudmundite, pyrrhotite, sphalerite, stibnite, berthierite, jamesonite, native antimony, kermesite, valentinite, senarmontite, quartz, carbonates . . .

Three mineralization stages are distinguished in stibnite deposits of the M. Karpaty Mts.: 1. quartz — pyrite — arzenopyrite, 2. stibnite — carbonate — quartz, 3. stibnite — kermesite. Supergene processes produced a rich association of secondary minerals, too. In spite of certain mineralogical differences from one ore deposit (Pezinok, Pernek, Kuchyňa) or indication to the other, this scheme is reported to be generally valid (B. Cambel l. c.).

Some characteristic features and relations of the minerals analyzed for sulphur isotope ratios are presented in Fig. 17—28.

B. Cambel (l. c.) gathered evidence in favour of a hydrothermal, postgranitic origin and Variscan age of the Pezinok — Kolársky vrch stibnite deposit and similar mineralizations of the M. Karpaty Mts. This view was shared by the prevailing part of geologists, who have studied the area.

I. Čillík — P. Soboliě — R. Žákovský (1959) have emphasized the hydrothermal origin and neoide formation of the Sb-mineralization at the end of Alpine folding.

Recently based on the discovery of a gently dipping, subhorizontal, sheet of high grade ore, a metasomatic origin has been postulated for the rich, and a hydrothermal one for the impregnation ores (J. Pastor 1972). See also Fig. 16.

The works of A. Maucher (1965), R. Höll (1966), A. Maucher — R. Höll (1968), R. Höll — A. Maucher (1972), L. Lahusen (1972) and others have brought new ideas regarding the genesis of stibnite deposits. A. Maucher and R. Höll (1968) were the first to indicate that antimony mineralizations of the M. Karpaty Mts. are to be regarded as belonging to the "time and strata bound" Sb-Hg-W Formation of Lower Plaleozoic age, which may continue to the stibnite deposits of the Spiš-Gemer Ore Mountains.

In 1970 the author has pointed to the presence of biogenic sulphur, enriched in S^{32}, in certain antimony minerals of the M. Karpaty stibnite deposits (J. Kantor in B. Cambel — J. Kantor 1972). Molybdenum-poor scheelite was found to be a wide spread mineral of the crystalline area, almost never lacking in heavy concentrates of stream sediments (J. Kantor 1974).

The present paper is aimed to bring further isotopic evidence in favour of the genetical interpretation of the mineralizations.

Isotopic investigation of sulphide sulphur

Samples were obtained from drill cores and mines, exceptionally from dumps. Some were kindly given at our disposal by B. Cambel. Individual sulphide minerals were used for isotopic investigations with the exception of few cases where attempts to separate monomineral concentrates have failed.

The purity of concentrates was checked under a binocular microscope or by X-ray difraction, when previous mineragraphic observations revealed the necessity of such control.

The sulphur dioxide was obtained by oxidation of the sulphides with cuprous oxide and after purification sealed into ampules.

The mass-spectrometer measurements were made on a modified MI-1305 instrument (Sumy, URSS). Sulphur isotope ratio results are expressed as permil values relative to the meteoritic standard:

$$\delta S^{34} (^0/_{00}) = \frac{S^{34}/S^{32}\text{ sample} - S^{34}/S^{32}\text{ standard}}{S^{34}/S^{32}\text{ standard}} \times 1000$$

The masspectrometric analyses were caried out under the guidance of Mr. M. Rybár by Mrs. M. Hanušová and Miss. H. Spišáková, the preparation of sulphur dioxide by Mr. M. Garaj and Mrs. V. Wiegerová. Monomineral fractions were prepared by Mrs. M. Strešňáková and Mr. D. Zaťovič and the X-ray identification by Mrs. J. Ďurkovičová. The graphic illustrations were drawn by Mrs. M. Čeklovská. Their assistance is gratefully acknowledged.

Isotope ratios in the pyrite deposit Turecký vrch

The variations in isotopic constitution of pyrite sulphur of the deposit Turecký vrch were studied on drill cores of the boring TV-6 (Fig. 2) and on one sample of TV-2. The δS^{34} and S^{32}/S^{34} values for the samples are listed in Table 1.

Additional data pertaining to the Rudolf adit pyrites may be found in the upper part of Table 2. Ore types after B. Cambel are indicated: QS = quartz-sulphide, GQS = graphite-quartz-sulphide, AS = amphibole-sulphide ore.

The log of the boring TV-6 with δS^{34} permil values is reproduced in Fig. 4 with the lithology given after the documentation by the Geological exploration geologists.

With the exception of two samples, all are enriched in the light isotope S^{32}, the δS^{34} values ranging from -3.9 to -21.2 ‰. The spread of about 17 ‰ is considerably larger than expected in sulphides formed from homogenized hydrothermal solutions, and with negative values also indicative of the fact that bacterial reduction of sulphate-sulphur has played an important role in the precipitation of the sulphides.

The four orebodies of the boring TV-6 are 3—5 m thick. Owing to the usual variations in the distribution of sulphur isotopes in stratiform deposits formed under the influence of sulphate-reducing bacteria, representative mean isotope ratio values may be obtained either from one analysis of a representative sample, or calculated from a larger number of data for individual point samples.

In spite of this an increase in light sulphur from the lowest ore-body to the upper one is apparent from our data, too.

Table 1. Turecký vrch, boring TV-6, pyrite deposit

Nr.	Depth (m)	Mineral	S^{32}/S^{34}	δS^{34} (‰)
667/S	20,00—21,30	pyrite	22,510	−12,9
668/S	33,50—35,30	pyrite	22,545	−14,4
669/S	39,90—40,80	pyrite	22,618	−17,6
670/S	40,80	pyrite	22,489	−11,9
670a/S	40,80	pyrite	22,496	−12,3
670b/S	40,80	pyrite	22,636	−18,4
671/S	42,60—44,00	pyrite	22,648	−18,9
671a/S	42,60—44,00	pyrite	22,697	−21,0
671b/S	42,60—44,00	pyrite	22,646	−18,8
671c/S	42,60—44,00	pyrite	22,700	−21,2
672/S	44,50	pyrite	22,700	−21,2
672a/S	44,50	pyrite	22,701	−21,2
672b/S	44,50	pyrite	22,630	−18,1
674/S	46,70—48,20	pyrite	22,433	−9,5
673/S	47,30	pyrite	22,306	−3,9
675/S	69,40	pyrite	22,638	−18,5
676/S	70,40—71,60	pyrite	22,568	−15,4
677/S	75,90—76,90	pyrite	22,556	−14,9
677a/S	75,90—76,90	pyrite	22,614	−17,4
678/S	77,80—78,50	pyrite	22,556	−14,9
1036/S	80,60—81,40	pyrite	22,530	−13,7
679/S	81,40—82,90	pyrite	22,537	−14,1
680/S	82,90—84,90	pyrite	22,565	−15,3
430/S	50,0 m (TV-2)	pyrite	22,553	−14,8

Table 2. Isotopic composition of pyrite-sulphur

Nr.	Locality	S^{32}/S^{34}	δS^{34} (‰)	Remarks
	TURECKÝ VRCH:			
236b/S	Rudolf adit	22,527	−13,6	GQS
74/S	Rudolf adit	21,793	+19,6	mobilized pyrite
236a/S	Rudolf adit	21,743	+21,9	veinlet in sample 236b/S
240/S	Rudolf adit	22,540	−14,2	GQS
66/S	Rudolf adit	22,643	−18,7	GQS
405/S	Rudolf adit	22,682	−20,4	GQS
	PEZINOK (CAJLA):			
239/S	Sb-adit	22,289	−3,1	py-veinlet in black SiO_2
401/S	Sb-adit	22,418	−8,8	AS
208/S	Sb-adit	22,425	−9,2	AS
402a/S	Sb-adit	22,454	−10,4	
402b/S	Sb-adit	22,457	−10,5	
207/S	Sb-adit	22,478	−11,5	
433/S	Sb-adit	22,500	−12,4	AS
424/S	Sb-adit	22,501	−12,5	
70/S	Sb-adit	22,521	−18,4	GQS
241/S	Kolárska-adit	22,321	−4,5	SiO_2-carbonate-pyvein
423/S	Pyrite-adit	22,420	−8,9	impreg. in granite
72/S	Pyrite-adit	22,493	−12,1	AS
404a/S	Pyrite-adit	22,663	−19,5	QS
404/S	Pyrite-adit	22,690	−20,7	QS; pyrrhotite
422/S	Ferdinand-adit	22,531	−13,8	
403/S	Ferdinand-adit	22,603	−16,9	GQS

The macro- and microtextural features of the ores are variegated depending on conditions of deposition, the mutual interchange of bands containing various proportions of pyroclastic, tuffaceous material, bituminous to graphitic substances, quartz of chemogenic and clastic origin, carbonates a. s. o. Synsedimentary and metamorphic deformations have added to the complexity of these features.

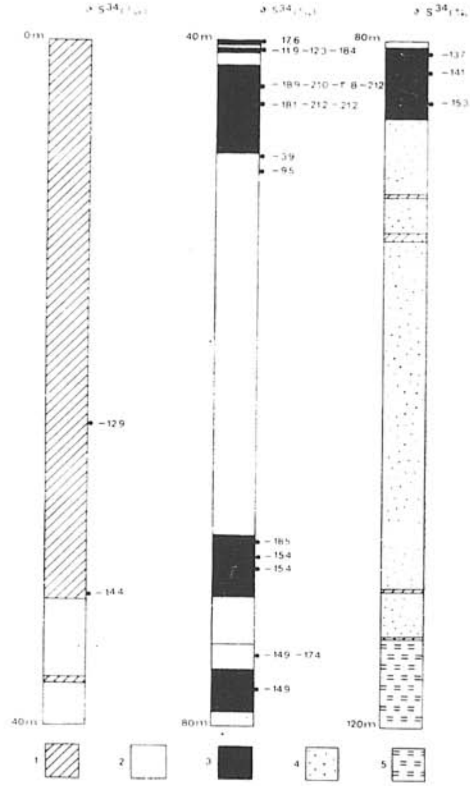
A common type of ore displaying macrobanding is illustrated in Fig. 5, the parallel bands differing in mineralogical and textural composition. The large, irregular layer at the top of the specimen consits of chemogenic quartz associated with small amounts of carbonates. Thin graphitic bands (black) are concentrated in the central parts. Tuffaceous material with variable amounts of quartz and graphite dominate in the rest of the bands. Pyrite is strictly confined to the individual bands in variable, often very different amounts. Concretionary pyrite occurs in the upper right part of the specimen, bellow the quartz-band.

For pyrite sulphur of two 2—3 mm thick bands, about 5 mm appart, δS^{34} values of −11.9 and −12.3 permil, whereas for the concretionary pyrite the δS^{34} value −18.4 were measured. An enrichment in S^{32} from bottom to top of the specimen follows from these measurements.

In the dominating number of the bands, the pyrite grains and porphyroblasts are similar to those illustrated in Fig. 12. But few bands might be found, where it is developed in the form of intergranular rims and tiny intragranular replacements (Fig. 6).

Pyrite-quartz mineralizations occurying within the deposit in bands and layers, few

Fig. 4. Log of the boring TV-6, Turecký vrch. with δS^{34} values.
1. Amphibolites 2. Actinolite schists 3. Pyrite ore 4. Graphite schists 5. Biotite phyllites.



centimeters to few decimeters thick, represent another ore type (Fig. 7). Two pyrite varieties are distinguished:

a) Thinly laminated pyrite in irregular, angular, rarely rounded aggregates reaching up to 2 cms in size. (The only form visible in Fig. 7). Thin laminae of pyrite and nonopaque minerals (quartz, organic matter a. s. o.) alternate. Particularly well shown is microfolding and various distortions providing evidence of deformation of the sulphides in a plastic, unconsolidated state (Fig. 8).

b) Crystalline pyrite, exceptionally reaching 1 mm in size. Acquires a much better polish than the older laminated type. Occurs generally in quite subordinate amounts, distributed dominantly in the quartz, along the borders or in veinlets cutting the laminated aggregates (Fig. 9).

The monomineral concentrate, consisting of both pyrite types has a δS^{34} value of -21.2 ‰. Identical ratios (-21.2) displayed the laminated variety. The crystalline pyrite was found to be enriched in the heavy isotope S^{34} ($\delta S^{34} = -18.1$) relative to the older, laminated type. The identity in isotopic constitution between the laminated and bulk sample is due to only small contents of crystalline pyrite in the latter.

The transition zones between the banded and quartz-pyrite ores may also display different textures from those already mentioned. After sequences consisting of continuous and alternating pyrite-host rock bands (as in Fig. 5), these become less regular, wedgeshaped, and this tendency may be more accentuated at the contact with the

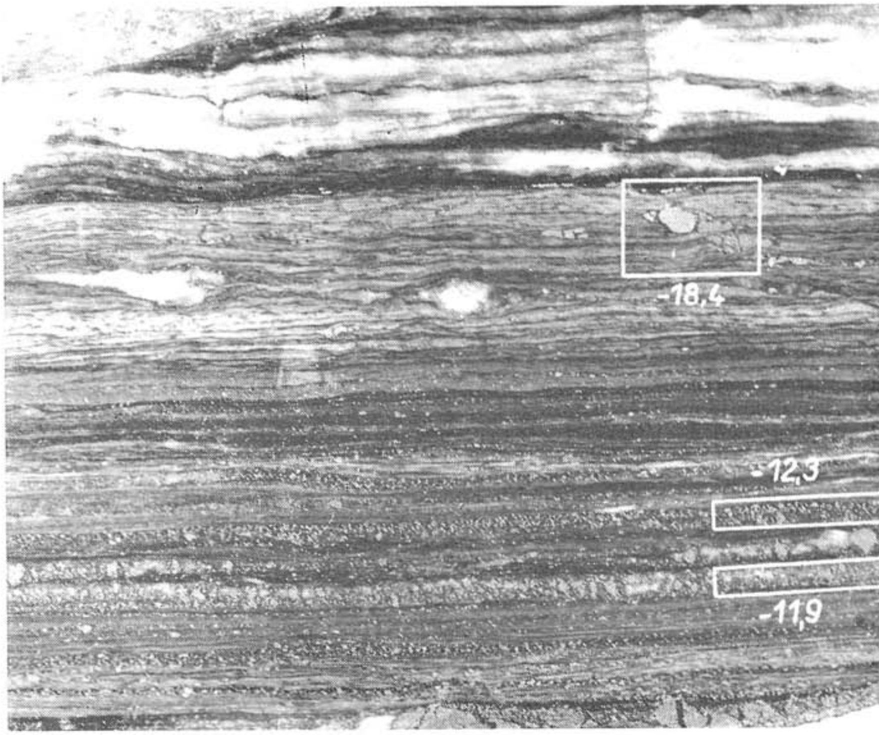


Fig. 5. Banded ore. Alternating bands of pyrite, tuffitic-fine-detrital-, dark, organodetrital material and chemogenic quartz. The latter in a thicker band and seams in the upper part of the polished sample. Natural size. δS^{34} values indicated.

quartz-pyrite layer (Fig. 10). In the latter, thinly laminated pyrite occurs in fragments of irregular shape and varying dimensions. Deformation is common, the laminae consisting of highly prolonged lense shaped pyrite sheets or at places are preserved in a straight, planparallel, continous form. Fig. 11, 13, illustrates details of the pyrite-quartz layer reproduced in the upper part of Fig. 10. Crystalline pyrite is in quartz-pyrite bands sparse, and always later than the laminated one.

The bulk pyrite (consisting of both the laminated and crytsalline form) of the quartz-pyrite layer has $\delta S^{34} = -21.0\ ^0{}_{00}$. For the laminated pyrite the δS^{34} value of $-21.2\ ^0{}_{00}$ and for the younger crystalline pyrite that of $-18.8\ ^0{}_{00}$ have been measured. The admixture of the later, heavier sulphur carrying pyrite is in the analysis of the bulk sample apparent.

In the lower part of the same specimen (Fig. 12) irregular and coarser grained porphyroblastic pyrite occurs dispersed in the wedgeshaped bands. The porphyroblasts enclose small amounts of irregular rounded inclusions of chalcopyrite, hexagonal pyrrhotite and sphalerite. The fine pyrite dispersed in the schistose band (bottom of the sample, Fig. 10, 12) showed with the δS^{34} value of -18.9 to be less enriched in light sulphur than the laminated one. It's isotope ratio is identical with that of the younger, crystalline pyrite accompaying the thinly laminated variety. The latter was observed

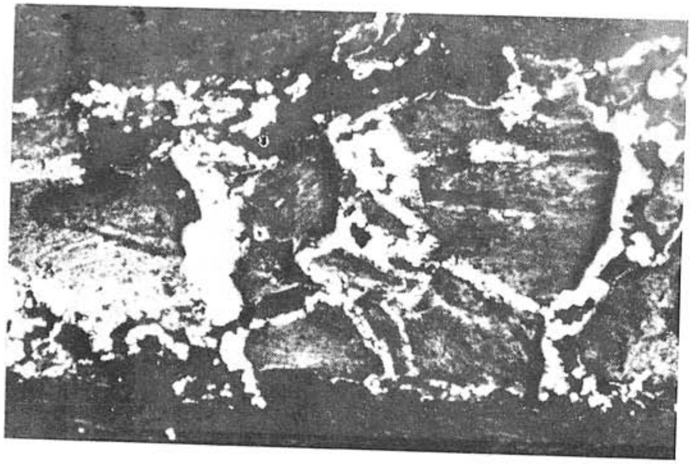


Fig. 6. Rarer type of pyrite-host rock band Pyrite as inter- and intragranular replacement of tuffitic (?) band. Same specimen as in Fig. 5., magn. 80 ×.

Fig. 7. Pyrite-quartz layer. Polished sample natural size.

Fig. 8. Laminated pyrite displaying microfolding as result of late diagenetic deformation in plastic state. Lower, right edge — coarser crystalline pyrite. Detail of the sample shown in Fig. 7. Polished section, magn. 90 ×.

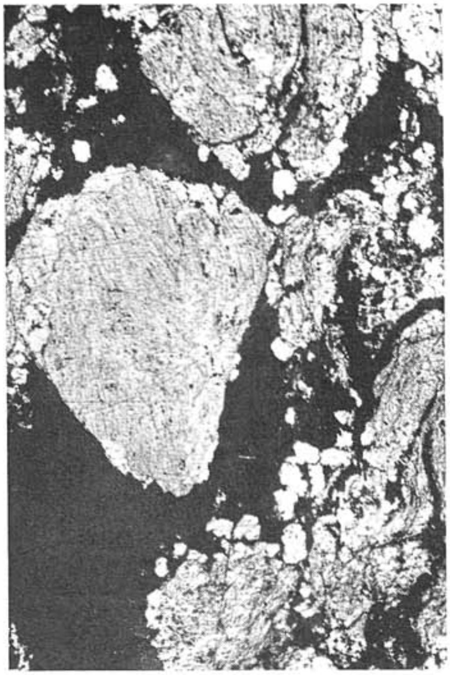


Fig. 9. Fragments of deformed, laminated pyrite (gray) embedded in quartz (black) containing crystalline pyrite (white). Same specimen as in Fig. 7. Polished section, magn. 8 ×.

in quartz layers, less frequent in highly siliceous hostrock, whereas the schistose bands carry as a rule crystalline pyrite only.

Textural and isotopic relations of this kind between both pyrite types are abundont throughout the whole Turecký vrch deposit. Their appearance after etching with $KMnO_4 + H_2SO_4$ is illustrated in Fig. 14. The younger, coarser crystalline pyrite is more resistant (white), whereas etching of the laminated aggregates readily reveals the extreme fineness of grain size, indicative of colloform deposition. Recrystallization phenomena may be observed in the laminae, too. In Fig. 15 deformation of laminated pyrite into minute folds in the vicinity of somewhat coarser pyrite is shown. As in the preceding cases light sulphur is preferentially concentrated in the laminated variety ($\delta S^{34} = -17.4$), the heavy isotope in the coarser crystalline one ($\delta S^{34} = -14.9$).

Differences in δS^{34} values between coexisting laminated and crystalline pyrite range 2.1 to 3.1 and are summarized in Table 3.

The heavier sulphur in the younger, crystalline pyrite may be the result of bacterial reduction in a system partially closed by burial under younger layers, by the shielding activity of the SiO_2-gel layer a. s. o.

Textural features indicating synsedimentary deformation and syngenetic origin of the pyrite ores in the M. Karpaty Mts. have been described by St. P o l á k (1956).

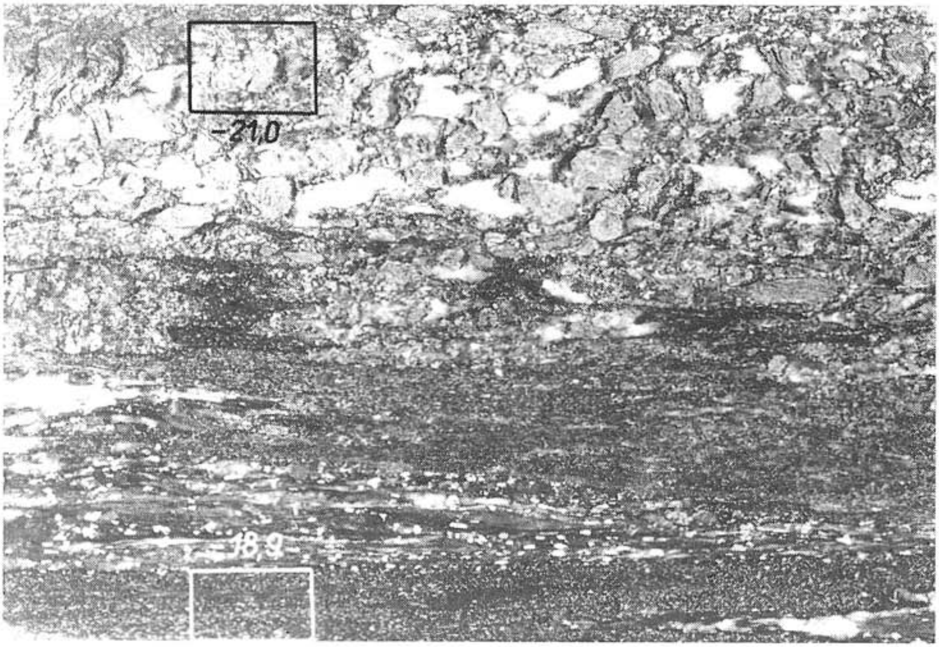


Fig. 10. Wedging out of pyrite-host rock bands in the vicinity of a pyrite-quartz layer (upper part). Polished surface, natural size.

Extreme enrichment in heavy sulphur (δS^{34} = +19,6 and +21,9) showed pyrite from an about 5 mm thick veinlet, cutting syngenetic pyrite ore, for which in the immediate neighborhoud of the veinlet the value of $-13,6\,\%_0$ has been measured. Bacterial reduction of residual sulphate in the solutions circulating through the veinlet would result in production of sulphides carrying heavy sulphur. It might have also originated from solutions which in the earlier stages of evolution have preferentially leached and carried away the more mobile light isotope whereas in the later stages

Table 3

Nr.	pyrite	δS^{34}	$\triangle\ \delta S^{34}$ ($\%_0$)	Remarks
671c	Lamin.	−21,2		pyrite-quartz band
671b	cryst.	−18,8	2,4	pyrite-quartz band
672a	Lamin.	−21,2		pyrite-quartz band
672b	cryst.	−18,1	3,1	pyrite-quartz band
671a	Lamin.	−21,0		pyrite from schists
671	cryst.	−18,9	2,1	pyrite-quartz band
677a	Lamin.	−17,4		pyrite-quartz band
677	cryst.	−14,9	2,5	pyrite-quartz band

the heavier sulphur might have been transported, modified by sulphate-reducing bacteria, and deposited.

In the boring TV-6 highest heavy sulphur contents (δS^{34} = −3.9 and −9.5) were measured in pyrite of actinolite schists, underlaying the ore body with highest enrichment in light sulphur (δS^{34} = −18.1 to −21.2).

Though no clear evidence is provided by a sufficient number of analyses, pyrites from amphibolites appear to carry heavier sulphur than pyrites of the ore bodies.

Isotope ratios in sulphides of the stibnite-deposit Pezinok — Kolársky vrch

In the stibnite-deposit samples were taken so as to represent the whole mineralization as well as the ore types distinguished by geologists working in the area. The δS^{34} values fall in the range — 1.0 to −13.5 ‰ and are listed in Table 4.

Table 4. Pezinok (Cajla), stibnite deposit

Nr.	Mineral	S^{32}/S^{34}	δS^{34} (‰)	Remarks
452 S	stibnite	22.270	−2.2	
444 S	stibnite	22.271	−2.3	
447 S	stibnite	22.274	−2.4	
1021 S	stibnite	22.289	−3.1	
448 S	stibnite	22.293	−3.3	
1023 S	stibnite	22.302	−3.7	
1022 S	stibnite	22.324	−4.7	
685 S	stibnite	22.370	−4.7	
1075 S	stibnite	22.366	−6.5	
685 S	(stibnite)	22.356	−6.1	+ berthierite
685a S	(berthierite)	22.427	−9.2	+ stibnite
449 S	berthierite	22.442	−9.9	
451 S	berthierite	22.464	−10.8	
686 S	arzenopyrite	22.242	−1.0	
684 S	arzenopyrite	22.245	−1.1	
1027 S	arzenopyrite	22.287	−3.0	
450 S	arzenopyrite	22.355	−6.0	
1027a S	pyrite	22.262	−1.9	
683 S	pyrite	22.281	−2.7	
1024 S	pyrite	22.393	−7.7	
426 S	pyrite	22.410	−8.5	
1037 S	gudmundite	22.354	−5.9	
1074 S	gudmundite	22.398	−7.9	
1038 S	gudmundite	22.525	−13.5	

All samples displayed negative δS^{34} values with respect to the meteorite standard, and a spread which is not common in hydrothermal deposits derived from a well homogenized source.

The dominating type of Sb-ores, disseminated in black phyllites, is developed in the surroundings of the open-cut workings and the Sb-adit. Samples for isotopic study were taken across the ore body 6 m above the Sb-adit (Fig. 16).

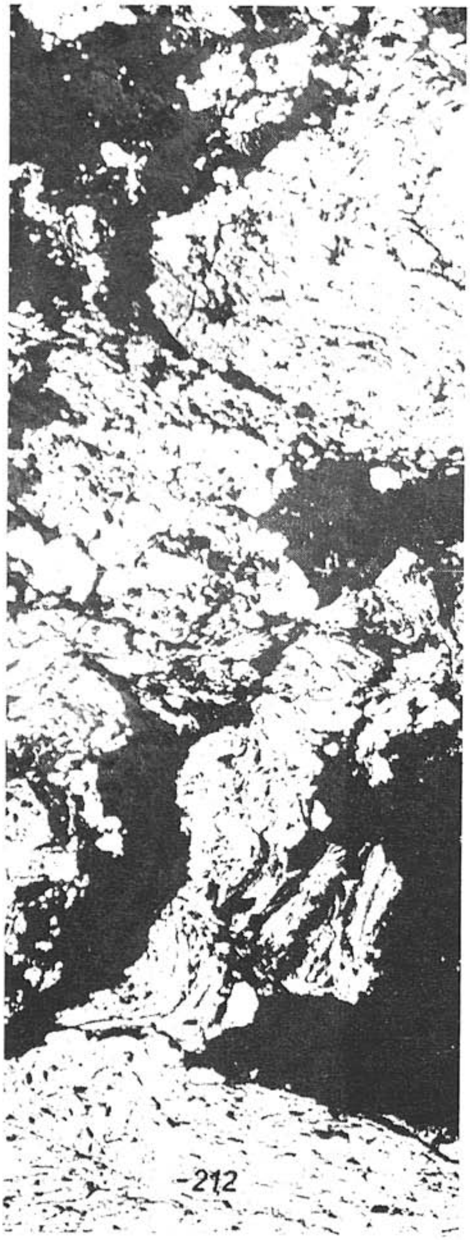


Fig. 11. Pyrite-quartz layer with irregular fragments of deformed, thinly laminated pyrite and few coarser grained pyrites. Detail from upper part of Fig. 10. Polished section, magn. 12 ×.

Fig. 12. Idioblastic pyrite in wedgeshaped pyrite-schistose bands. Detail from lower part of Fig. 10. Polished section, magn. 12 ×.

Fig. 13. Common type of thinly-laminated pyrite from pyrite-quartz band. No plastic deformation. Polished section, magn. 150 ×.

Fig. 14. Contact of laminated (gray) and crystalline (white) pyrite. Etched with $KMnO_4 + H_2SO_4$. Colloform deposited pyrite in the laminae is readily attacked by etching. Polished section, magn. 150 ×.

The following variation ranges of δS^{34} values were found:

stibnite	−2.3 to −4.7 ‰
berthierite	−9.2
arzenopyrite	−1.1 −3.1
pyrite	−1.9 to −2.7
berthierite + stibnite	−6.1
For other parts of the same ore-type:	
gudmundite	−5.9 to −13.5 ‰
stibnite	− 6.5

The common relation of stibnite ($\delta S^{34} = -2.4$) to carbonate is reproduced in Fig. 17. In samples 6 m above the Sb-adit an unusual type of gudmundite with higher grinding hardness (probably due to higher As contents) and numerous poikiloblastic inclusions of stibnite was observed, embedded in stibnite (Fig. 18, δS^{34} of stibnite = −4.7).

In recently discovered, rich Sb-ores, which are by some authors (J. Pastor 1972) regarded as formed by metasomatic replacement, δS^{34} values varied:

stibnite	−2.2 to −4.7 ‰
arzenopyrite	−1.1 −6.0
pyrite	−2.7 −8.5
berthierite	−9.9 −10.8

Fig. 15. Microfolds in laminated pyrite. Initial stage of crystallization. Etched with $KMnO_4$ + H_2SO_4. Polished section, magn. 150 ×.

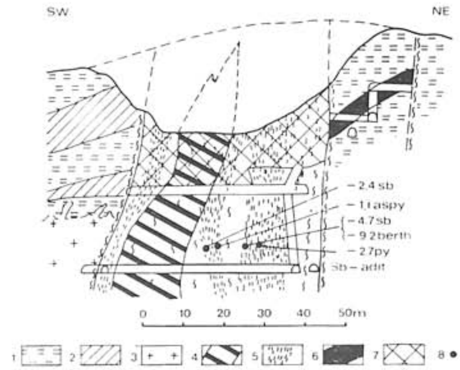


Fig. 16. Geological section of the stibnite deposit Pezinok — Kolársky vrch. After J. P a s t o r 1972.
1. Biotite gneisses ± sericitized 2. Amphibolites 3. Granitoids 4. Aplite 5. Disseminated Sb-ore 6. Rich Sb-ore 7. Parts of deposit removed by exploitation 8. Localization of analyzed samples with δS^{34} values: Sb—stibnite, aspy—arzenopyrite, berth—berthierite, py—pyrite.

From the limited number of analyses hitherte carried out a tendency towards concentration of the light sulphur (and berthierite?) in the lower parts — towards the lying wall — of the deposit seems to be indicated. (See Fig. 19 for spatial distribution.)

Berthierite is a common constituent of the ores. Two types may be distinguished in certain parts of the deposit: One in the form of irregularly shaped aggregates of acicular crystals, embedded in carbonates containing impregnations of finer crystals, the other in coarser-grained aggregates with a rim which does not contain any sulphides (Fig. 20, $\delta S^{34} = -9.9$).

The association of berthierite with carbonates is widespread, as well as it's later formation. See berthierite veinlet in Fig. 21, with the common arzenopyrite and rare chalcopyrite.

Arzenopyrite occurs disperzed in idiomorphic crystals, which may display marked zonal growth even without etching (Fig. 22, $\delta S^{34} = -6.0$). It has also been observed in irregular to rounded clusters, which is the commoner form for the rarer löllingite (Fig. 23). Owing to low contents of sulphur in the later, attempts to determine the isotope ratio were unsuccessful.

Idiomorphic gudmundite is commonly found in the Sb-ores. The generally larger crystals formed later than arzenopyrite, as manifested by overgrowth of gudmundite bands over arzenopyrite (Fig. 24), or by inclusions of arzenopyrite in gudmundite (Fig. 25, δS^{34} of arzenopyrite $= -1.0$).

Few samples contained gudmundite in close association with monoclinic pyrrhotite,

Fig. 17. Stibnite in carbonate, partly along cleavage. Polished section, magn. 150 ×.

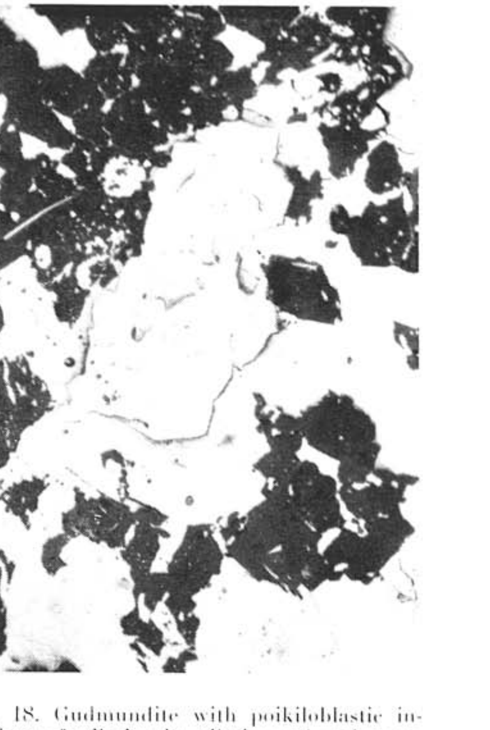


Fig. 18. Gudmundite with poikiloblastic inclusions of stibnite, in stibnite and carbonate. Polished section, magn. 150 ×.

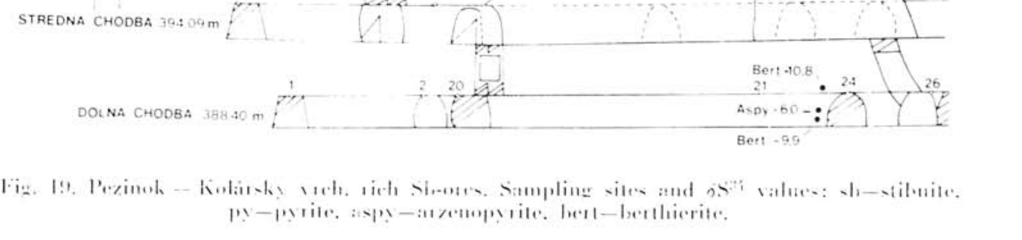


Fig. 19. Pezinok — Kolársky vrch, rich Sb-ores. Sampling sites and δS^{34} values: sb—stibnite, py—pyrite, aspy—arzenopyrite, bert—berthierite.

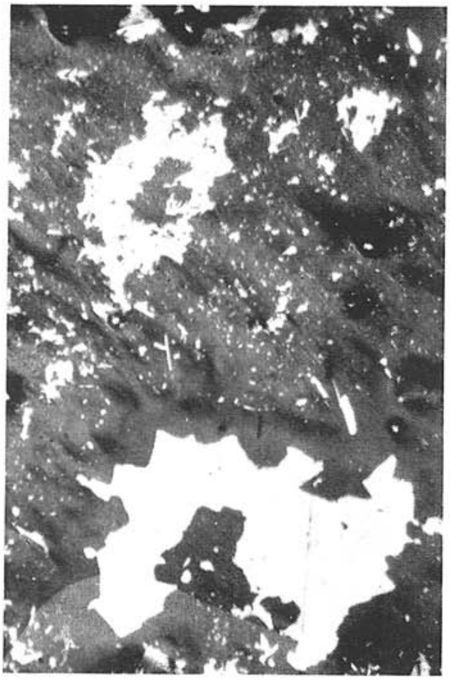


Fig. 20. Berthierite in tiny, acicular crystals and in coarser grained aggregates. Polished section, magn. 80 ×.

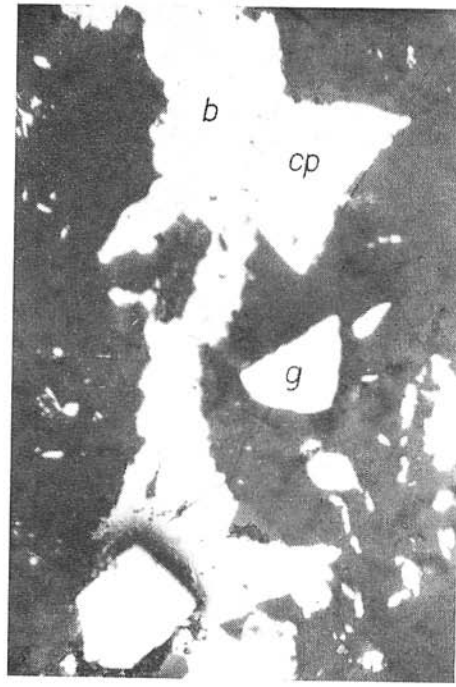


Fig. 21. Berthierite veinlet in carbonate. Chalcopyrite (cp), gudmundite (g) and arzenopyrite (white, relief). Polished section, magn. 450 ×.

both in the form of idiomorphic crystals (Fig. 26). Owing to lack of direct contact, their relation remained uncleared.

Pyrrhotite developed in the form of myrmekitic rims in gudmundite along its contacts with berthierite or stibnite (Fig. 27, 28, δS^{34} of berthierite = − 10,8). Gudmundite and pyrrhotite appear earlier than berthierite with stibnite.

Between the dispersed and the rich (metasomatic type of J. Pastor) Sb-ores no significant differences in sulphur isotope ratios were found.

Differences are reported by J. Pastor (l. c.) as to shape, thickness, position, grade and mineralogy:

The rich ore grades 5—10 % Sb, is 3—8 m thick, gently (5—20°) inclined, has sharp boundaries against the over — and underlaying rocks and low contents of pyrite and arzenopyrite.

The main deposit of dispersed ores is a large lense-shaped body 20—40 m thick of tectonized graphite phyllites, inclined 70—80° towards SW and of considerably lower grade.

δS^{34} values for sulphides of the stibnite deposit are presented in Table 4 and Fig. 29. In the histogram are included isotope ratios for pyrites showing closest relations to the Sb-minerals. The plots for those of the Sb-adit, which might be regarded by some authors as belonging to the syngenetic pyrite ores, and as having no genetic relations

Fig. 22. Zonal arzenopyrite in carbonate. Polished section, magn. 450 ×.

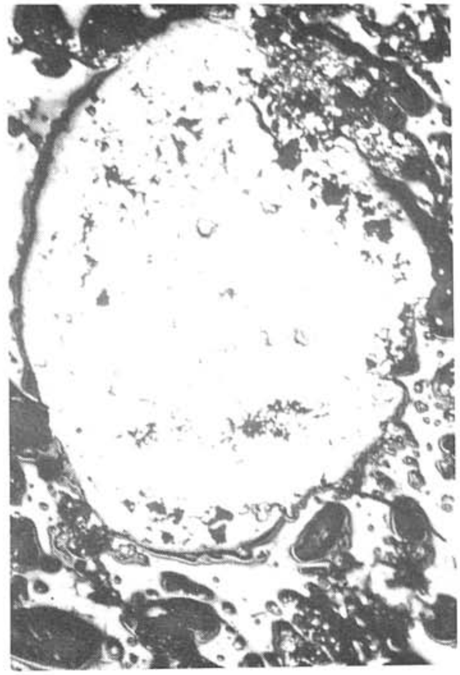


Fig. 23. Spheroidic aggregate of very fine-grained löllingite embedded in stibnite and quartz. Polished section, magn. 80 ×.

to the Sb-mineralization, are shown in the lower part of the histogram together with δS^{34} plots for pyrites of the Turecký vrch deposit.

The views expressed regarding the origin of the Sb-ores of the M. Karpaty Mts. may be summarized: hydrothermal of Variscan age (B. Cambel l. c., St. Polák l. c.), hydrothermal of Alpine age (I. Čillík et al. l. c.), hydrothermal -of metasomatic and impregnation type (J. Pastor l. c.), "time and strata bound" i. e. synsedimentary as well as epigenetic of Lower Paleozoic age (A. Maucher — R. Höll l. c.).

From the geochemistry of sulphur isotopes follows: Hydrothermal solutions of deep-seated origin, related to magmatic chambers, are homogenous. The δ^{34} values vary within narrow limits and the isotopic composition is close to the meteorite standard.

Synsedimentary deposition of sulphides might be accompanied by processess, which modific the isotope ratios, such as the activity of sulphate reducing bacteria, mixing of sulphur of different origin a. s. o. The resulting sulphides display often large variations in isotopic constitution as well as negative δS^{34} values.

The sulphide samples analysed in this study might be characterized (Table 4, Fig. 29) as follows:

The isotopic composition of sulphur is not homogenous. For the Sb-deposit Pezinok—Kolársky vrch the spread in δS^{34} values reaches at least 12.5 permil.

Consistently negative δS^{34} values appear, indicating enrichment in S^{32} with respect to the meteoritic sulphur. The sulphides contain biogenic sulphur. Highest S^{32} contents

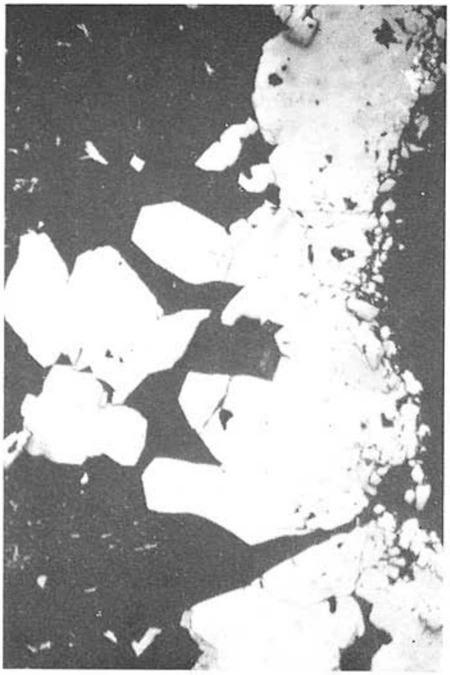


Fig. 24. Coaser gudmundite rimming earlier, fine-grained arzenopyrite (relief). Polished section, magn. 150 ×.

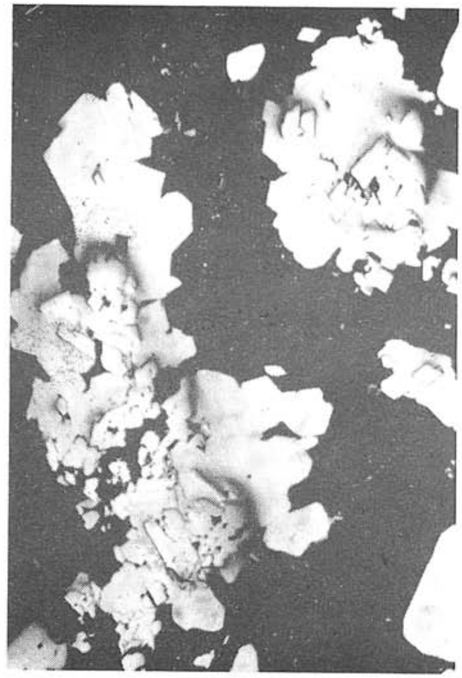


Fig. 25. Arzenopyrite (relief) enclosed in gudmundite. Carbonates — black. Polished section, magn. 150 ×.

are found in those Sb-minerals which are iron-rich, such as berthierite and gudmundite, whereas the lowest enrichment was found in stibnite and arzenopyrite. The last two minerals have isotope ratios which are more compatible than in any other one of the stibnite deposit with the idea of hydrothermal origin from a deep-seated source. But the results for the complex of all analyzed samples are not in accord with such an assumption.

The derivation of the stibnite mineralization from assimilation of the pregranitic pyrite deposits by the granitoide magma, mixing with juvenile Sb-sources and deposition of the paragenetic association from so produced hydrothermal solutions has also to be considered within the frame of proposed metalogenetic schemes. Higher homogenization, i. e. lower spread in δS^{34} values than found in sulphides of the Sb-deposit would result.

For the interpretation of the observed isotopic constitution and spread in δS^{34} values, two genetical schemes are to be considered, by which biogenic sulphur could have been incorporated in the sulphides of the stibnite deposit.

a) An epigenetic-hydrothermal origin would require: 1. Transport of Sb and a part of S from a deep-seated source. 2. Dissolution and mobilization of the synsedimentary pyrite mineralization from deeper parts of the productive zone. 3. Deposition of sulphides with variable amounts of the „juvenile“ (in composition closer to meteoritic S)

Fig. 26. Idiomorphic crystals of monoclinic pyrrhotite in carbonate. Larger gudmundite near lower edge of the photograph. Polished section, magn. 220 ×.

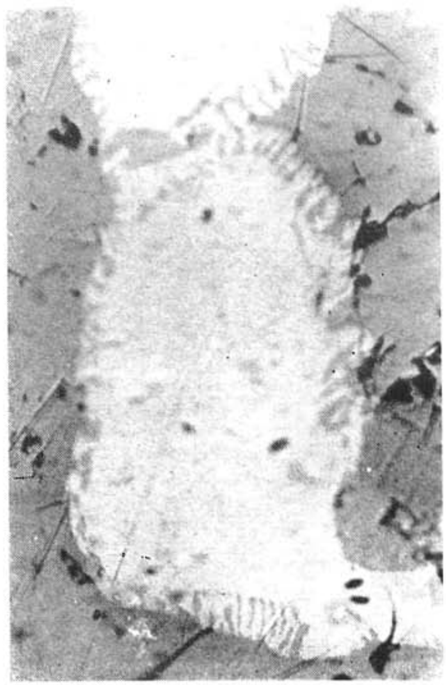


Fig. 27. Myrmekitic intergrowth of pyrrhotite along gudmundite (white)-berthierite boundary. Polished section, magn. 650 ×.

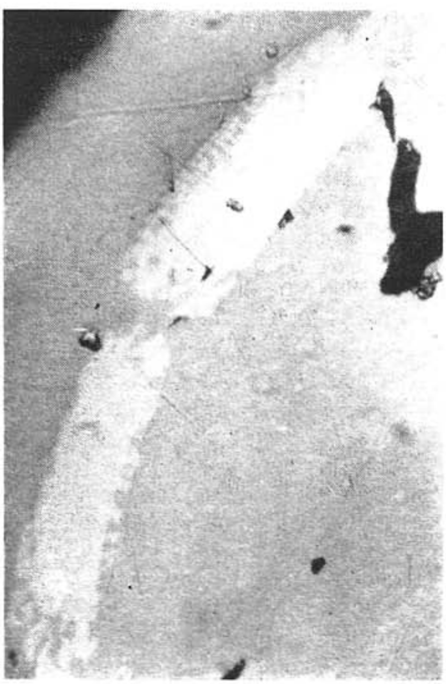


Fig. 28. Prismatic gudmundite with myrmekitic pyrrhotite along berthierite-gudmundite boundary. Polished section, magn. 650 ×.

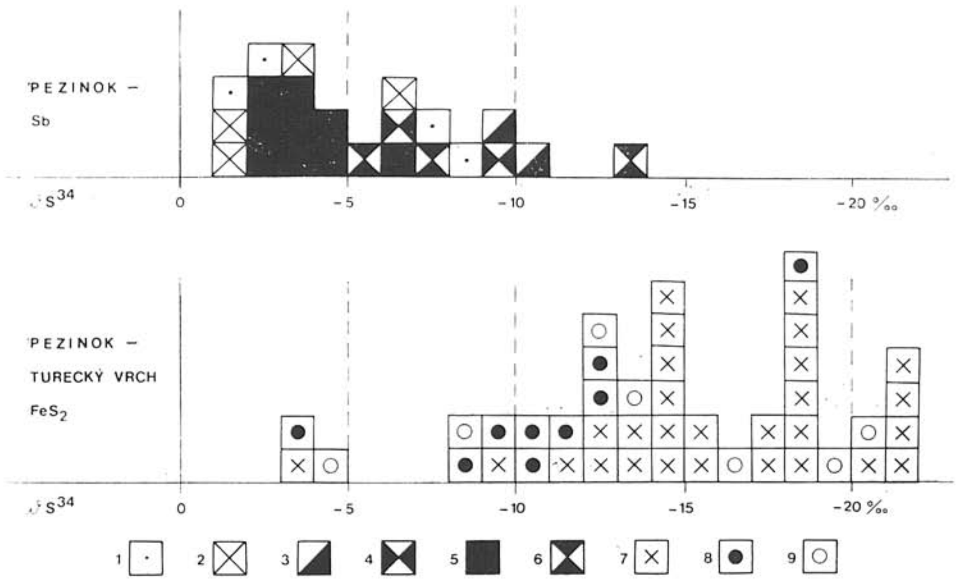


Fig. 29. Histogram of δS^{34} values. Upper part: Pezinok, stibnite deposit. Lower part: Pezinok — Turecký vrch, pyrite mineralization. 1. Pyrite 2. Arzenopyrite 3. Berthierite 4. Berthierite + stibnite 5. Stibnite 6. Gudmundite 7. Pyrite, Turecký vrch deposit 8. Pyrite, Pezinok, Sb-adit 9. Pyrite, other localities of zone I A.

and remobilized, in S^{32} enriched sulphur. 4. Geological features which are typical for epigenetic, hydrothermal deposits.

b) More or less direct formation under supergenic conditions would lead to negative δS^{34} values and their larger spread. In undoubtedly synsedimentary deposited pyrite of the Turecký vrch deposit a variation range comparable to that for the sulphides of the stibnite mineralization was found, the latter displaying less negative δS^{34} values. In the time and strata-bound mineralization, as proposed by A. Maucher and R. Höll (l. c.) also for stibnite deposits of the Malé Karpaty Mts., epigenetic and synsedimentary deposition might be closely related in time and space. If accompanied further by processes of remobilization, sulphur isotope patterns similar to those observed in our study may result.

In sulphides of both, the pyrite deposit Turecký vrch, as well as in the stibnite deposit Pezinok — Kolársky vrch, light in S^{32} enriched sulphur, which is generally concentrated by sulphate reducing bacteria, plays an important role.

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