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SULFUR ISOTOPES OF THE METAMORPHOSED PYRRHOTITE-PYRITE DEPOSIT OF HEĽPA, NÍZKE TATRY MTS., CZECHOSLOVAKIA

(Figs. 1–19)

Abstract: The metamorphosed deposit of Heľpa occurs in the Pre-Carboniferous crystalline of the Nízke Tatry Mts. Close spatial relation of the sulfides to a basic, submarine volcanism exist. δS^{34} values for sulfides of the ore bodies range $-14{,}3$ to $-24{,}5$ ‰ and indicate bacteriogenic origin of the sulfur. Remobilized and accessory sulfides in country rocks contain more S^{34} ($\delta S^{34} = -2{,}1$ to $-9{,}9$ ‰). As result of metamorphic fractionation is the sulfur in pyrite 0,6 to 1,1 ‰ heavier than in coexisting pyrrhotite. It is suggested that Fe, Cu, Zn were suplied by hydrothermal activity accompanying the basic magmatism, whereas the light sulfur was produced in the sedimentary basin by sulfate reducing bacteria.

Резюме: Метаморфизованные пирротин-пиритовые месторождения около Гельпы выходят в вепоридах кристаллического массива Низких Татр докарбонского возраста. Между сульфидными оруденениями и подморским диабазовым вулканизмом существуют относительно узкие пространственные взаимоотношения. Данные δS^{34} для серы рудных тел колеблятся в рамках $-14{,}3$ до $-24{,}5$ ‰ и свидетельствуют о ее бактериогенном происхождении. Метаморфически мобилизованные сульфиды также как и акцессорные сульфиды из вмещающих пород содержат более тяжелую серу (δS^{34} $-2{,}1$ до $-9{,}9$ ‰). Как результат фракционирования во время метаморфозы сера в пиритах на 0,6 до 1,1 ‰ тяжелее чем в совместно находящихся пиротинах. Предполагается, что Fe, Cu и Zn происходят из гидротермальных растворов, которые сопровождают диабазовый вулканизм, в то время как легкая сера является продуктом сульфатредуцирующих бактерий.

The pyrrhotite-pyrite deposits are located about 6 km to the N from the village Heľpa in the Nízke Tatry Mts. (Lower Tatras, Central Slovakia) at elevations between 1200 nad 1300 m a. s. l. The area is built by kata- to mesozonally metamorphosed crystalline schists of the veporide Kraklová-zone.

Geological investigations of the region have been made by V. Zoubek, A. Gorek (1953) and A. Klinec (1966). Geochemical problems were studied by B. Cambel, J. Jarkovský (1967, 1969). Besides the distribution of trace elements in pyrites and pyrrhotites, observations regarding the geological evolution and genesis of the ores are contained in the paper too. S. Ďurovič (1952) has published analyses of the sulfide ores from a purely chemical point of view. Certain data may be found in unpublished reports (S. Hruškovič 1955, Lukáč 1958).

Essential geological data pertaining to the area are given in the papers of V. Zoubek, A. Gorek (l. c.) and B. Cambel, J. Jarkovský (l. c.). Acording to these authors the productive complex consisted of a monotonous sequence of argillaceous, argillo-arenaceous, subordinately arenaceous sediments. Diabases, their tuffs and tuffites occur as intercalations. They are characteristic for the ore-bearing part of the sequence. By all investigations spatial as well as genetic relations between the sulfide mineraliza-

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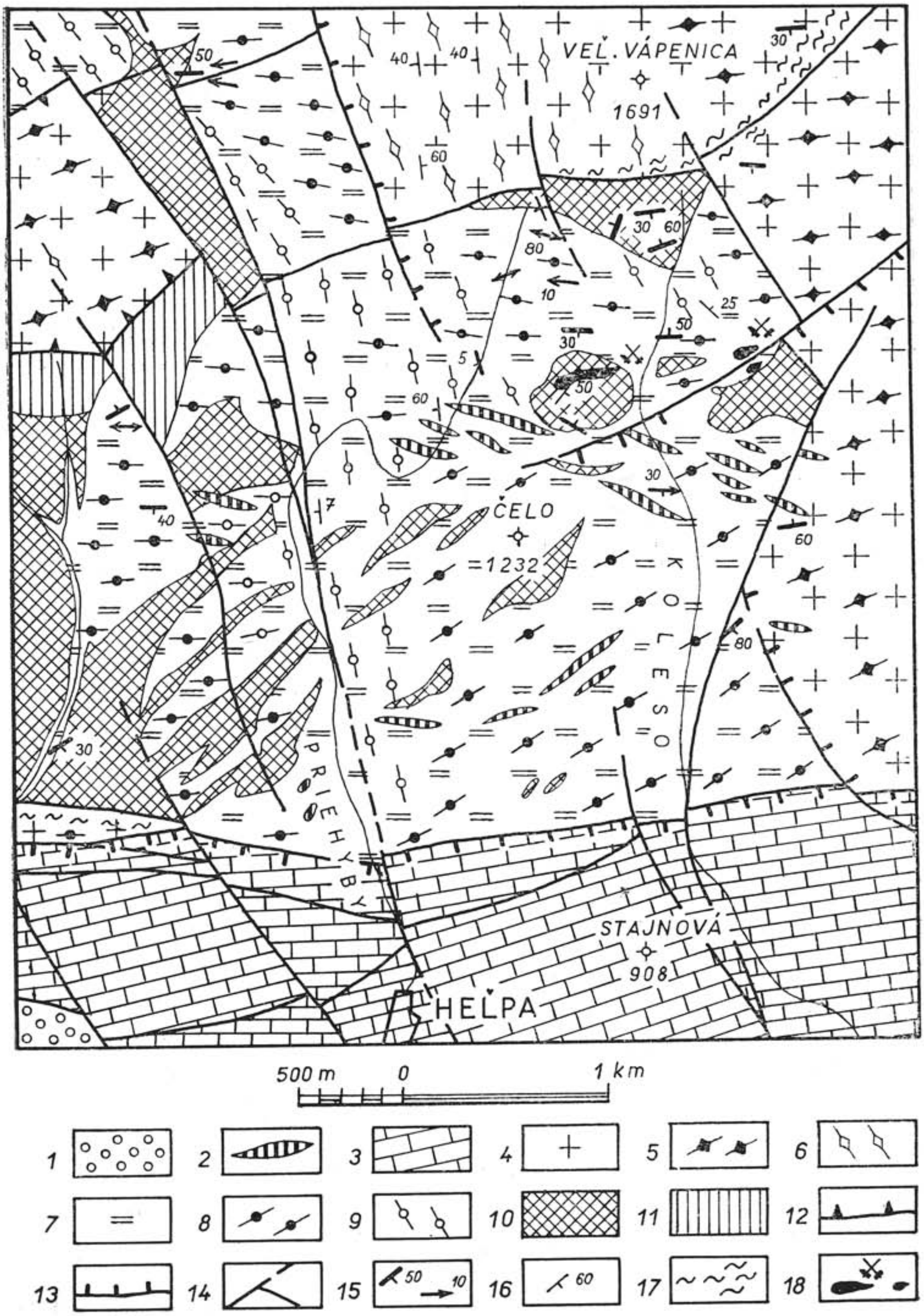
VEĽ. VÁPENICA
1691
ČELO
1232
KOLESO
PRIEHYBY
STAJNOVÁ
908
HELPA
500 m
0
1 km
1
2
3
4
5
6
7
8
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11
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13
14
15
16
17
18

Fig. 1. Tectonic map of the area North of Helpa, Nízke Tatry Mts. (A. Klinec 1971). 1 — paleogene conglomerates, breccias, 2 — pegmatites, quartz veins, 3 — mesozoic, — 4 granitoids, 5—6 — dynamometamorphic orientation (5 — older, 6 — younger), 7 — micaschists, 8—9 — dynamometamorphic orientation (8 — older, 9 — younger), 10 — amphibolites and metabasic rocks, 11 — migmatites, 12 — overthrusts, 13 — faults, 14 — dislocations, 15 — planes of crystalline schistosity and lineation of minerals, older, 16 — planes of crystalline schistosity, younger, 17 — mylonites, 18 — mines and ore-bodies.

tion and the basic magmatism are indicated. Products of the latter rarely exceed several tens to hundred meters in thickness.

The stratigraphic appurtenence of the sulfide bearing sequence with diabases is still debatable. Indiscutable is only it's Pre Carboniferous age. Data are lacking whether we have to deal with the Lower Paleozoic according to B. Cambel (1962) and an earlier view of V. Zoubek (1953), or with Pre-Cambrian as supposed by M. Máška, V. Zoubek (1960).

The productive complex has been during the later (Assyntian? M. Máška, V. Zoubek l. c.; variscan? V. Zoubek 1953, B. Cambel 1962) cycle metamorphosed (biotite-, biotite-muscovite paragneisses, amphibolites, micaschists, actinolite schits a. s. o.). Gabbros — as hypoabyssal equivalents of the diabasic volcanism — are reported from the area by V. Zoubek, A. Gorek (l. c.) and B. Cambel, J. Jarkovský (l. c.).

According to V. Zoubek and A. Gorek, the progressive metamorphism was accompanied by migmatitization, especially of paragneisses. Lense-shaped bodies of aplitic granites and granitogneisses are reported from the surrounding of the ore deposits.

In certain areas, the high metamorphic facies have been preserved, whereas in others a more or less intensive retrograde metamorphism took place. Biotite, amphibole, feldspars are replaced by chlorite, epidote, zoisite, carbonates, sericite, acide feldspars a. s. o.). End products of complete recrystallization are phyllonites.

The conclusions of V. Zoubek and A. Gorek (l. c.) and B. Cambel, J. Jarkovský (l. c.) mentioned above were recently modified by A. Klinec, who during the last decade has studied the Crystalline of the Veporides.

As basic framework of the Vepor-Crystalline A. Klinec (1966) distinguished two tectonic units. The deepest element is represented by the Hron-complex which contains predominantly crystalline schists. In tectonic position over it lies the Kráľova Hoľa-complex, consisting of granites and migmatites. This position was found to be typical for all sections of the Veporides.

The pyrrhotite-pyrite mineralization is confined to the Hron-complex (micaschists, amphibolites-facies of garnetiferous amphibolites). For the younger, alpine metamorphism, oriented pressure and the mineral facies of green schists are characteristic. The recrystallization is week to medium intense. It is complete in certain parts only, producing diaphtorites.

Another form of the alpine rejuvenation is according to A. Klinec the formation of pegmatite and aplite veins. They contain microcline, quartz, biotite and produce alteration at the contacts with the country-rocks. They strike E—W, are steeply inclined and are generally no more than few meters thick.

Rocks of the Hron-complex display marked planes of crystalization-schistosity. The E—W to NE—SW striking and 30 to 50° to SE diping amphibolites alternate with micaschists. The neighbourhood of the deposits is intersected by NW—SE striking dislocations which have lead to an almost complete reorientation of the system mentioned above. The structural elements display therefore around the sulfide deposits a chaotic orientation.

Dislocations strike NE—SW and NW—SE and locally develope into faults.

The geological and tectonic situation is reproduced in the sketch-map Fig. 1, page 262.

Sulfide Deposits

The pyrrhotite-pyrite mineralization is known along the southern slopes of the Veľká Vápenica in a total length of 2 kms. The westernmost occurrence consists of impregnations of low sulfide contents in the outcrops which were not explored.

To the NE are situated the main deposits made up of lense-shaped ore-bodies (map, Fig. 2, page 264). They strike parallely with the crystalline shists (E—W) in a 1 km long zone and are divided into 3 segments: the western, middle and eastern deposit. As already pointed out by V. Zoubek, A. Gorek (l. c.), the sulfides occur in basic rocks, at the contacts of amphibolites or at least in their proximity.

The western deposit attainig 250 m in strike and 40 to 50 m in thickness is made up of a system of lenses. The present shape is the result of primary deposition as well as of leater tectonization that has lead also to the formation of a „tectonite envelope" between the rigid sulfide masses and the more plastic crystalline schists. At shallow depth the sulfide bodies are intersected by a fault, probably an E—W striking and S diping overthrust of regional character. The continuation of the deposit below this overthrust is unknown. The western deposit was explored by 4 galleries and a series of shallow borings. Sulfides of the boring F were systematically investigated for their isotopic composition.

In the middle deposit a disseminated mineralization was explored by 2 galleries.

In the eastern deposit poorer ores prevail over the massive ones. The sulfide body attains 20 m in thickness, but pinches out rapidly both, in striking and diping. An enrichment of the marginal parts in pyrite is reported by S. Hruškovič. The

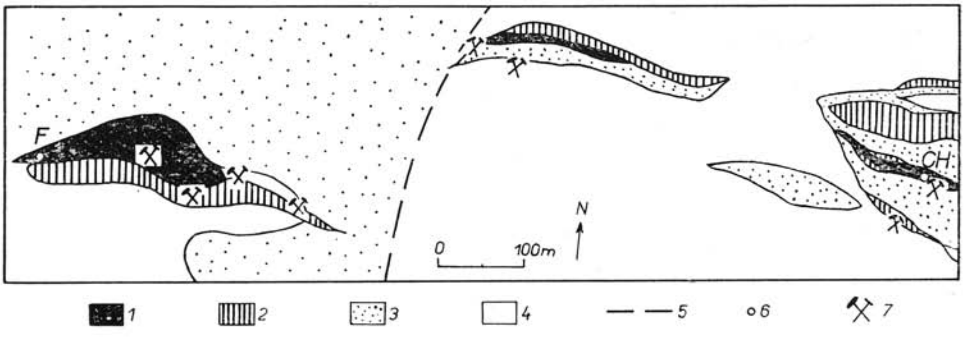

Fig. 2. Heľpa. Map of the ore-bodies (V. Zoubek, A. Gorek 1951). 1 — ore, 2 — amphibolites and basic rocks, 3 — chlorite-muscovite micaschists and phyllonites, 4 — paragneisses, 5 — faults, 6 — boring (investigated for S-isotopes), 7 — mines.

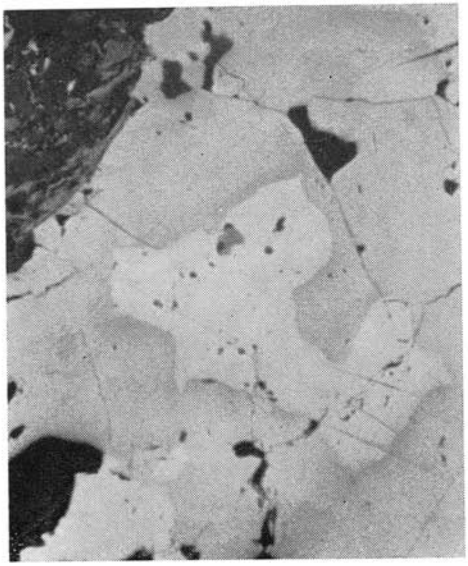

Fig. 3. Chalcopyrite (light grey) in pyrrhotite. Graphite-rich part (upper left). Polished section, 420×.

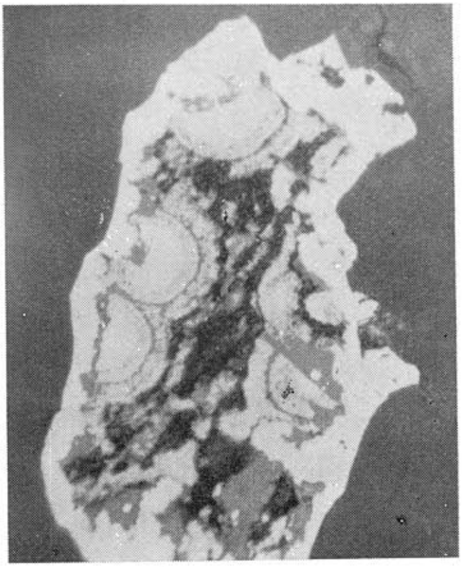

Fig. 4. Supergene transformation of pyrrhotite into a marcasite-pyrite mixture with metacolloidal texture. Polished section, 650×.

mineralization was explored by two galleries and several borings. Systematic isotopic studies were carried out on sulfides of the boring CH. In contrast to the S-diping western deposit the eastern one is inclined towards North.

The mineralogy of the Heľpa deposits is simple, monotonous, and varies in all sections within similar limits. Pyrrhotite dominates among the ore minerals. The less frequent pyrite forms porphyroblasts irregularly scattered in pyrrhotite, but may be absent in certain parts of the ore-bodies. B. Cambel, J. Jarkovský (. c.) report pyrite mineralization, not accompanied by pyrrhotite, from the graphite rich marginal parts of the deposits. They consider that it represents the primary, syngenetic pyrite which — due to the protective action of graphite — is recrystallized only and was not metamorphosed into pyrrhotite. Small amounts of chalkopyrite and sphalerite are usually present in the ores (Fig. 3). Arsenopyrite occurs sporadically. Although looked for, pentlandite was not detected in the pyrrhotite ores.

Marcasite, fine-grained marcasite-pyrite and pyrite are common products of supergene alteration (Fig. 4).

The non-opaque minerals of the ores are represented by quartz, amphiboles, garnets, feldspars, carbonates, micas, ilmenite, rutile, magnetite a. s. o.

The following ore-types and mineralizations may be distinguished at Heľpa:

1. Impregnations of sulfides in amphibolites, paragneisses and in products of their retrograde metamorphism. More or less connected with the main ore-bodies (Fig. 5).

2. Quartz — sulfide ores with variable amounts of both minerals. Pyrrhotite preponderating, subordinately pyrite. Chalcopyrite and sphalerite are generally present in small amounts. Silicates may be present of entirely lacking. By enrichment in pyrrhotite massive sulfide-quartz ores develope, whilst for the quartz-graphite-sulfide ones

Fig. 5. Amphibolite impregnated by pyrrhotite (white). Ilmenite (light grey, relief), surrounded by rutile (light grey). Polished section, 150×.

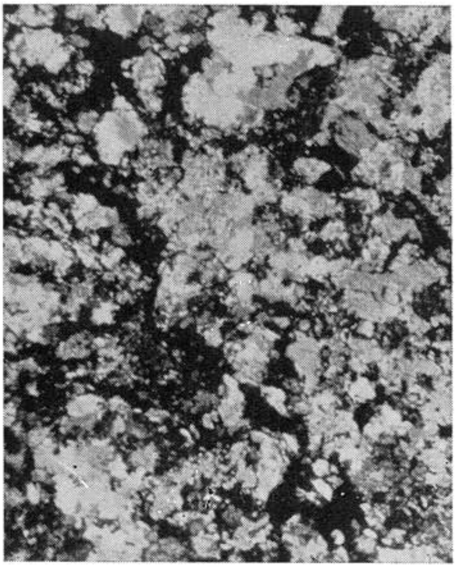

Fig. 6. Quartz-sulfide ore. Low content of pyrrhotite in undulatory quartz. Thin section, nicols semi-crossed, 11 ×

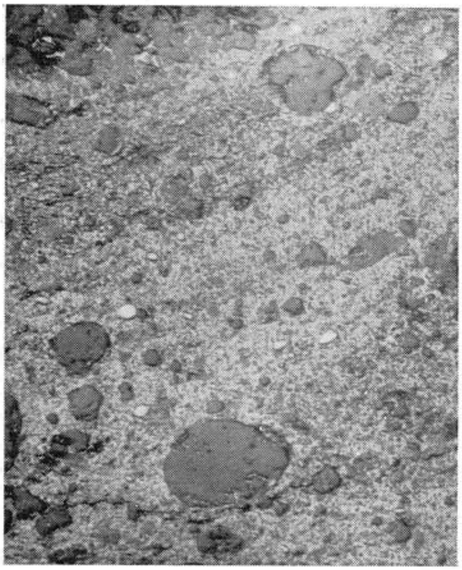

Fig. 7. Massive, very fine-grained pyrrhotite ore. Gangue mostly rounded quartz (dark grey). Pyrite in pecular rounded form (white). Preserved sedimentary textures? Polished section, 11 ×.

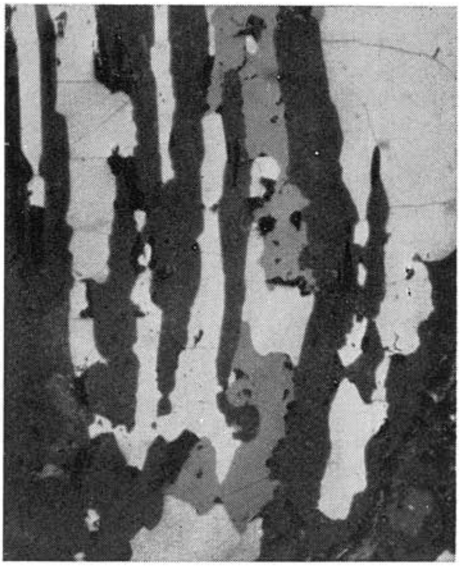

Fig. 8. Sphalerite (grey) and pyrrhotite (white) between flakes of partly corroded mica (black). Polished section, 150×.

higher contents of graphite are characteristic. Quartz-sulfide ores prevail at the Heľpa deposit (Fig. 6, 7).

3. Sulfide-silicate ores consist of the usual assemblage of ore minerals with dominating pyrrhotite. Amphiboles are the common representants of rock-forming minerals (amphibole-sulfide ores). They are accompanied by variable quantities of feldspars, quartz, micas, garnets a. s. o. (Fig. 8). Certain parts of the ore-bodies are formed by sulfide-garnet ores (Fig. 9). The garnet — often green and Cr-bearing — is at places associated with carbonates (Fig. 10).

In all ore-types ic pyrrhotite generally finer grained than the accompanying, porphyroblastic pyrite. Translation lamellae so typical for tectonized but not recrystallized pyrrhotite are in the Heľpa deposit rare.

4. Veinlets of sulfides. As youngest mineralization they cut the ore bodies as well as the country rocks. The boundaries are sharp, or formed by disseminations. The veinlets were mostly formed by metamorphic mobilization, some may be of hydrothermal origin.

The ore bodies at Heľpa display the same kata- to mesozonal metamorphism as the surrounding crystalline schists.

The average composition of the ore: 14—18 % S, 20—26 % Fe, 20—30 % SiO_2, about 0,03 % Ni. The distribution of trace elements in pyrites and pyrrhotites was studied by B. Cambel and J. Jarkovský (1967, 1969, Fig. 11, page 269). They emphasize the importance of Co/Ni ratios for genetical interpretations and reporte values for various ore-types:

	Ni %	Co %	Co/Ni
quartz-sulfide ores	0,018	0,124	1 : 0,11
graphite-quartz-sulfide-ores	0,013	0,111	1 : 0,12
mineralized amphibolites	0,025	0,720	1 : 0,35
mineralized paragneisses	0,013	0,267	1 : 0,05
mean for all pyrites	0,016	0,139	1 : 0,336
mean of all pyrrhotites	0,0724	0,0035	

The first genetical interpretation of the pyrrhotite-pyrite deposits near Heľpa, based on the observation that the mineralization occurs in metabasic rocks, at their contacts with the metasedimentary rocks or at least in the vicinity of amphibolites, was given by V. Zoubek and A. Gorek (l. c.). This distribution of the sulfide ores indicated genetical relations to the basic magma.

V. Zoubek and A. Gorek regarded pyrrhotite as oldest mineral, pyrite as younger, formed by replacement of the pyrrhotite. The sulfides in the metabasic rocks were held for later than the silicates as they fill fractures in the latters or form rims around them. These facts were supposed as positive criteria of liquation. In their interpretation the sulfide magma remained as the youngest constituent in the basic rocks or was injected into the country rocks. The liquid-magmatic process was locally followed by an overimposed pneumatolysis. As products of the pneumatolytic activity were regarded the pyritization of pyrrhotite and transformations of the silicates (sericitization of the feldspars, leucoxenization of ilmenite, occurrence of primary muscovite, of carbonates a. s. o.). They concluded that the Heľpa deposit is a typical representant of the transitional group between the liquid-magmatic and pneumatolytic deposits as outlined by Schneiderhöhn.

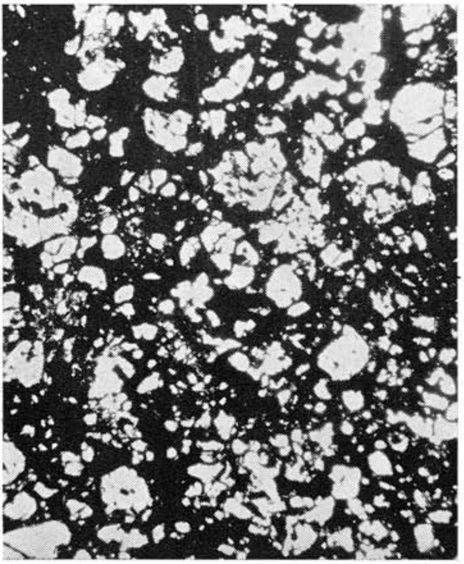

Fig. 9. Garnet-sulfide ore consisting of pyrrhotite (black) and green, chromium-bearing garnet (white). Sparse amphibole. Thin section, parallel nicols, 40×.

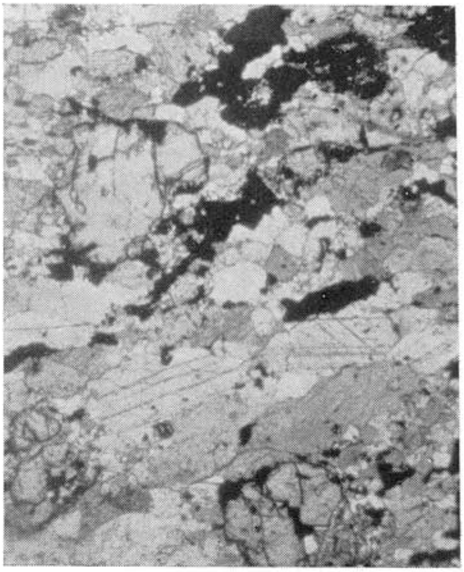

Fig. 10. Sulfides (black) disseminated in garnet-carbonate rock. Thin section, parallel nicols, 40×.

Another genetical scheme was worked out by B. Cambel (in B. Cambel, J. Jarkovský 1967). As basis served to him his own investigations of the pyrite-pyrrhotite deposits in the Malé Karpaty Mts, as well as J. Polák's (1956, 1957) observations of the same mineralization. The pyrrhotite of the Malé Karpaty deposits was found to be derived by metamorphism from the original synsedimentary deposited pyrites. By detailed investigations was revealed that the main mass of sulfides is confined to actinolite-schists i. e. to metamorphosed pyroclastics of the basic, submarine volcanism. Transitions were found between the pyroclastics and graphite phyllites as well as between mineralizations in both rock-types.

For the Heľpa deposit B. Cambel reports: occurrence of the main sulfide mineralization in metamorphosed, pyroclastic rocks; the presence of a graphitic substance in the ores;transitions between massive sulfides and dispersed ones in the metasedimentary rocks; pyrrhotite as non primary, metamorphis mineral. He distinguished similar ore-types as in the Malé Karpaty Mts, i. e. quartz-sulfide- and quartz-graphite-sulfide ores as the most important ones; mineralized amphibolites (actinolite schists) and paragneisses. The latters with sulfide disseminations of mineralogical value only.

As results of his investigations B. Cambel postulated for the Heľpa deposits a syngenetic, exhalate-sedimentary origin.

Distribution of Sulfur Isotopes

Sulfur isotopes were at the Heľpa deposits studied as part of a larger research programme covering the distribution of sulfur isotopes in mineral deposits of the West Carpathians.

Mr. B. Cambel has kindly supplied us with samples collected in the at present unaccessibles mines and from old borings. In a part of these sulfides the distribution of microelements was investigated by B. Cambel, J. Jarkovský (1967, 1969). A comparison of the distribution of the sulfur isotopes with that of the trace elements is therefore possible.

For the masspectrometric analyses monomineral fractions only were used and their purity checked under a binocular microscope. The sulfides were combusted to sulfur dioxide with the aide of CuO in a vacuum system.

The isotopic composition of the samples is given as permillage deviation δS^{34} against the meteoritic standard with the adopted ratio $S^{32}/S^{34} = 22{,}22$

$$\delta S^{34} = \frac{S^{34}/S^{32} \text{ sample} - S^{34}/S^{32} \text{ standard}}{S^{34}/S^{32} \text{ standard}} . 1000$$

The δS^{34} values and S^{32}/S^{34} ratios for the sulfides of the Heľpa deposits are given on Table 1, page 271. A graphical presentation of the distribution of sulfur isotopes is reproduced on the histogram Fig. 12, page 270.

Negative δS^{34} values are characteristic for all sulfides of the deposits. The sulfur is depleted in S^{34} with regard to the meteoritic standard. The histogram has a discrete

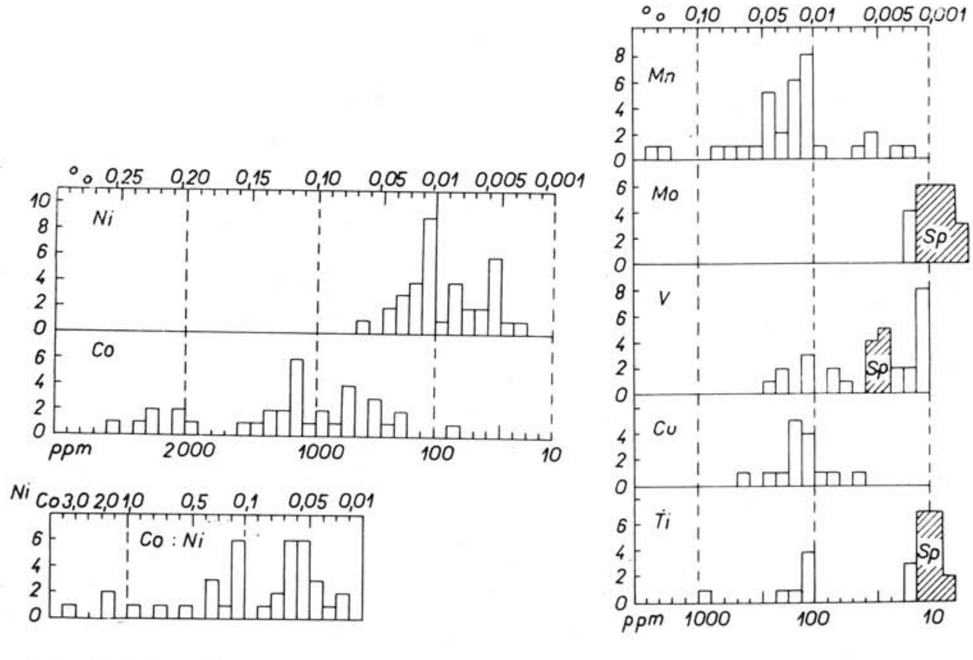

Fig. 11. Heľpa. Trace elements in pyrite. After B. Cambel, J. Jarkovský 1967.

maximum in the vicinity of $\delta S^{34} = -20$ ‰. Most of the sulfides range −14,3 to −24,5 ‰. Only few sulfides are less enriched in the lighter isotope, exhibiting permillage deviations between −2 and −10.

The isotopic constitution of sulfur is discussed along with various genetic schemes that have been proposed for the Heľpa deposit (liquid-magmatic, exhalative-sedimentary, biogenic origin).

Deposits of liquid-magmatic origin represent deep-seated processes in gabbroidic magmas. The resulting sulfides — pyrrhotite, chalcopyrite, pentlandite a. s. o. — are generally enclosed in gabbros and norites (Sudbury-type). The sulfidic magmas are regarded as of mantle origin or at least as derived from the lowest parts of the crust. A high degree of homogenisation of the sulfur isotopes has to be supposed in both cases.

Fig. 12. Heľpa. Histograms of δS^{34}-values.
A: 1 — sulfides.
B: 1 — pyrrhotite of ore-bodies, 2 — pyrite of ore-bodies, 3 — impregnations in country — rocks and mobilized sulfides.
C: Eastern deposit: 1 — pyrrhotite, 2 — pyrite. Western deposit: 3 — pyrrhotite, 4 — pyrite, 5 — as B-3.

Table 1. Heľpa. Isotopic composition of sulfides

No.	δS^{34} (‰)	S^{32}/S^{34}	No.	δS^{34} (‰)	S^{32}/S^{34}
234/S py	− 2,1	22,27	95/S py	−19,6	22,66
218/S py	− 4,1	22,31	189/S py	−19,8	22,67
235/S po	− 4,7	22,32	90/S py	−19,9	22,67
219/S py	− 9,9	22,44	222a/S py	−20,2	22,68
232/S po	− 14,3	22,54	220/S py	−20,3	22,68
225/S po	− 14,8	22,55	89/S py	−20,6	22,69
200/S po	− 15,7	22,57	88/S py	−20,7	22,69
231/S po	− 15,8	22,58	94/S py	−20,8	22,69
217/S po	− 16,1	22,58	189a/S po	−20,8	22,69
93/S py	− 16,3	22,59	219a/S po	−20,9	22,69
200a/S po	− 16,8	22,60	87/S py	−20,9	22,69
221a/S po	− 17,5	22,62	216/S po	−21,0	22,70
213/S po	− 18,4	22,64	233/S po	−21,2	22,70
90a/S m	− 19,1	22,65	87a/S po	−21,7	22,71
215/S po	− 19,5	22,66	94a/S po	−21,8	22,72
222/S py	− 19,6	22,66	214/S po	−23,1	22,74
			188/S py	−24,5	22,78

py — pyrite, po — pyrrhotite, m — marcasite.

It was inferred that the sulfur od ultrabasic to basic rocks is identical with the primordial sulfur (A. P. Vinogradov 1958). H. G. Thode, H. B. Dunford, M. Shima (1962) report slight variation in isotopic constitution of sulfur from large intrusive bodies of basic rocks (Insizwa Sill, S. Africa). The limits are narrow, the mean permillage values of + 1 approaches closely that of meteoritic sulfur. M. Shima, W. H. Gross and H. G. Thode (1963) noticed similar relations in basic intrusions of Canada (Cobalt Sill, Leitsch Sill) and USA (Palisades Sill).

W. G. Smitheringale, M. L. Jensen (1963) did not reveal by their investigations of the tholeitic rokcs of the Newark group (USA) important deviations against the meteoritic sulfur.

All available data led W. P. Ault and J. L. Kulp (1959) to infer that the mean isotopic composition of the sulfur from the crust and mantle has a δS^{34} value of

+ 3,6 ‰. For the sulfur of mantle origin slight positive δS^{34} values with a mean close to 1 ‰ results as highly probable from the studies mentioned above.

The sulfur isotopic composition of the rich ores of the Heľpa deposit ranges −14 to 24 ‰ with a maximum near −20 ‰. This marked difference against primordial and meteoritic sulfur is incompatible with a mantle origin (uncontaminated) of the sulfur. A simple model of liquid-magmatic genesis is therefore not applicable, neither from results of isotopic investigations, nor from geological and geochemical evidences (B. Cambel l. c.).

The exhalative-sedimentary origin requires close spatial as well as genetical relations of the sulfide mineralization to the ophiolitic magmatism. Sulfur, iron, copper, zinc a. s. o. are supposed to have been concentrated by magmatic differentiation of the basic magma and transported into the sedimentary basins by hydrothermal solutions and emanations. Deposits of this type should carry sulfur with slight positive values of the permillage deviation. The contrary is valid for Heľpa, where the sulfides are strongly depleted in the heavy isotope 34. A complex isotopic evolution of the sulfur either in the magmatic chamber (contamination by biogenic sulfur) or during deposition and metamorphism of the ore bodies is therefore suggestive.

Almost all ore samples microscopically investigated by us contained fine graphite flakes. Polished sections devoid of it are rather rare. It is often enclosed in pyrrhotite or in the gangue, where richer concentrations are common (Figs. 13, 14). The graphite indicates the presence of sedimentary, biogenic components in the sulfide ores as well as in a non unimportant part of the amphibolitic rocks (Fig. 15). B. Cambel's view

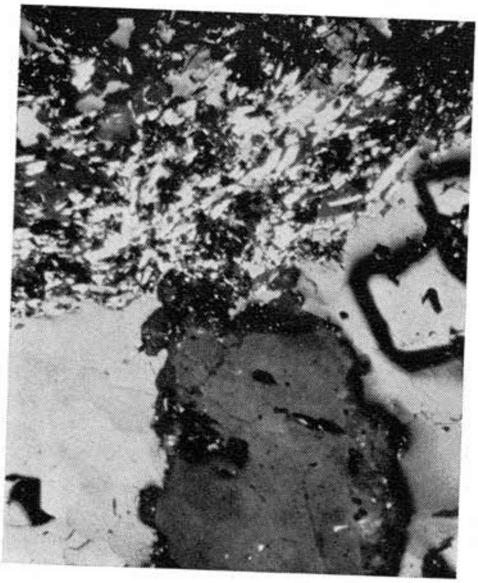

Fig. 13. Quartz-graphite-sulfide ore. Aggregate of pyrrhotite grains (left). Idioblastic pyrite (relief), and gangue rich in graphite flakes (white, upper side). Polished section, nicols semi-crossed, 80×.

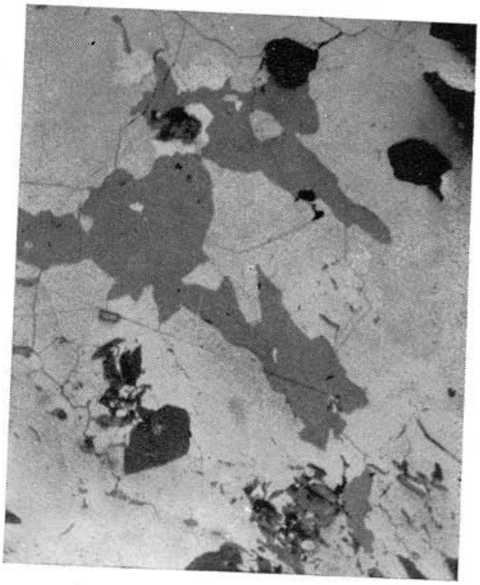

Fig. 14. Sphalerite (dark grey) in pyrrhotite (light grey). In the pyrrhotite small flakes of graphite (idiomorphic dark grey) and chalcopyrite (lighest grey, upper part). Polished section, 150×.

that at least a part of the amphibolitic rocks is of pyroclastic origin was thus confirmed by our investigations. Gradual transitions from amphibolites into the metasedimentary rocks are also reported by B. Cambel.

In spite of geological evidences the isotopic composition of sulfur is not fully in favour of an exhalative-sedimentary origin of the ores. A basic source magma from the mantle or lower parts of the crust — if uncontaminated by biogenic sulfur of sedimentary sulfides — should exhibit considerably higher contents of S^{34} than observed in the Heľpa deposits.

Origin of sulfides enriched in S^{32}. Under exogenic conditions leads the bacterial reduction of sulfates to highest partition of sulfur isotopes. End-products of this biological activity are hydrogene sulfide (sulfides) enriched in S^{32} on one and sulfates on the other hand. The latter, remaining in solution, is by withdrawal of S^{32} gradually enriched in S^{34}. Light sulfur in sulfides and heavy in sulfates are characteristic of the activity of sulfate-reducing bacteria (H. G. Thode et al. 1951, A. G. Harrison, H. G. Thode 1958, N. Nakai, M. L. Jensen 1964, Mechtieva 1967, Kaplan, Ritenberg 1962, Krouse et al. 1966 and others).

Owing to wide variability of conditions under which sulfates undergo anaerobic reduction in basins, sedimentary sulfides display broad variations in the isotopic composition of their sulfur.

Where reduction of a large reservoir of sulfates under constant rate took place, sulfur isotope ratios in sedimentary sulfides may vary within relatively narrow limits only (Rössler, Pilot, Harzer, Krüger 1968).

Isotope exchange reactions provide the anorganic way of fractionation. The temperature dependance of the fractionation factor between various compounds was studied by H. Sakai (1957). In volcanic gases sulfur dioxide is enriched in S^{34}, the light isotope S^{32} being preferably incorporated into hydrogene sulfide. A high temperatures of 500—800 °C the difference in δS^{34} between both compounds was found to be of the

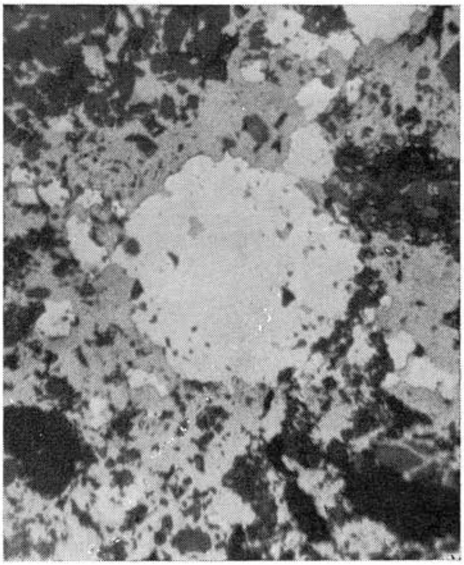

Fig. 15. Sphere-like pyrite aggregate (white) in a mixture of fine-grained pyrrhotite (grey) and gangue (dark grey to black). Relictic sedimentary texture? Same sample as on Fig. 7. Polished section, 420×.

order of several tenth of permillage and amounted to 2,7 ‰ at the temperature of 100 °C (H. Sakai, H. Nagasawa 1958).

The bacterial reduction of sulfates is thus the main natural process by which significant accumulations of light sulfur may be produced.

The considerable enrichment of the sulfides in the deposits of Heľpa in light sulfur gives evidence in favour of biogenic reduction in the history of evolution of the ores. Two possibilities have to be considered regarding the time of reduction:

a) A process more or less contemporaneous with the syngenetic deposition of the sulfides and the submarine volcanism.

b) Bacterial reduction and formation of syngenetic pyrites with light sulfur in the early history of evolution of that part of the crust. Assimilation of the sulfides in later orogenic cycles.

The ubiquitous presence of graphite indicates that the deposition of the sedimentary, sedimentary-volcanogenic rocks as well as that of the sulfides was accompanied by more or less intensive organic life. Exact data regarding the quantitative distribution of graphite at Heľpa are still lacking.

The graphite content of the sulfide ores, of the country rocks and the high negative permillage values are compatible with the biogenic origin of the sulfur and a syngenetic deposition of the sulfides. The iron has been supplied by submarine emanations and springs accompanying the basic volcanism.

The deposits of Heľpa are further characterized by close relations of the mineralization to the metabasic rocks, as well as by a relatively low spread in the isotopic constitution (variation within about 10 ‰).

Sedimentary sulfides of biogenic origin show generally broader variations. Similar limits are reported for the Nairne pyrite deposit of South Australia by M. L. Jensen and A. W. G. Whittles (1969). The pyritic horizons occur near the base of the Cambrian up to 8 kms thick Kanmantoo group, which comprises graywakes, quartzites, siltstones. Pyrite and pyrrhotite are the principal ore minerals of the sulfide beds. The mineralization has been traced for some 100 kms.

M. L. Jensen and A. W. G. Whittles (l. c.) report 19 isotopis analyses, the δS^{34} values ranging −13,5 to −20,6 ‰ for the primary mineralization and −11,7 to −13,6 ‰ for the secondary sulfides in a faulted zone. The lack of eruptive members in the sequence of the Kanmantoo group, the remarkable constancy of the ore beds, their concordant position within the sedimentary members of the series and the isotopic constitution of sulfur are all characteristics that imply a sedimentary, bacteriogenic origin of the sulfur of the Nairne deposit, as suggested by M. L. Jensen and A. W. G. Whittles (l. c.).

Another example of sedimentary sulfides that display variations in the isotopic composition within relatively narrow limits is reported from the Zechstein of the German Democratic Republik (Rössler, Pilot, Harzer, Krueger l. c.).

A graphic presentation of the δS^{34} values, for the Nairne, Heľpa and several other deposits is given in Fig. 16, page 275.

Fig. 16. Distribution of sulfur isotopes in deposit of various genetical types and Heľpa. Sudbury-type (Sudbury, Porcupine, Dovyren); basic sills (Insizwa, Palisade); exhalative-sedimentary (Sulitjelma, Skorovas); metamorphosed to rejuvenated with biogenic sulfur (Rhodesian deposits); sedimentary (Nairne). 1 — sulfides, disseminated, 2 — sulfides of ore-bodies. Compiled from Jensen 1957, MacNamara a. o. 1952, Thode a. o. 1962, Shima a. o. 1963, Vinogradov, Grinenko 1964, Anger 1966, Naldrett 1966, Dechow, Jensen 1965, Jensen, Whittles 1969, present authors.

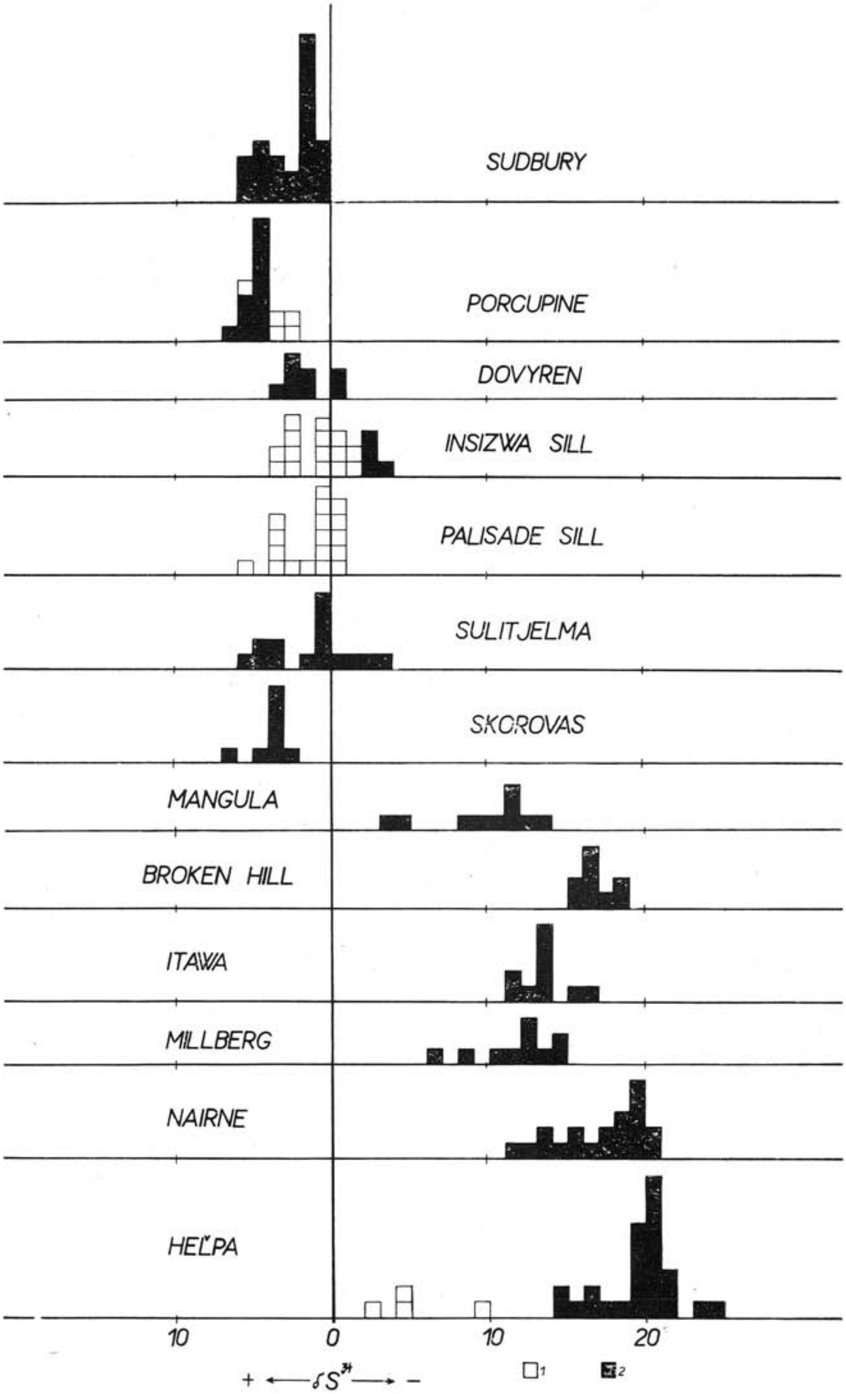
SUDBURY
PORCUPINE
DOVYREN
INSIZWA SILL
PALISADE SILL
SULITJELMA
SKOROVAS
MANGULA
BROKEN HILL
ITAWA
MILLBERG
NAIRNE
HEĽPA
10
0
10
20
+ ← δS^{34} → −
□ 1
■ 2

Table 2. Trace-elements and δS^{34} values in pyrite

	Mn	Mo	V	Cu	Ti	Ni	Co	Co/Ni	ςS^{34}
87/C — 138 Qs	0,044	< 0,002	0,002		< 0,002	0,0129	0,071	1:0,18	— 20,9
88/S — 189a GQS ch	0,026	< 0,002	< 0,002		sp.	0,0104	0,098	1:0,1	— 20,7
89/S — 130 Imp	0,04	< 0,002	0,0032		< 0,002	0,030	0,230	1:0,13	— 20,6
90/S — 126a GWs	≈ 0,30	< 0,0028	0,0467		0,093	0,0078	0,115	1:0,068	— 19,9
189/S — 133 GQS	0,0113	< 0,002	0,0047		< 0,002	0,008	0,132	1:0,06	— 19,8
188/S — 132 GQS	0,048	< 0,002	0,0087		< 0,002	0,0108	0,209	1:0,05	— 24,5
93/S — 207 Imp	0,0112			0,0089		0,0132	0,0525	1:0,3	— 16,3
95/S — 213 QS	0,026		sp.	≈ 0,037		0,090	0,126	1:0,07	— 19,6

Table 3. Heľpa. Co, Ni and δS^{34} relations

Ore-type	Locality	No	Ni (%)	Co (%)	Co : Ni	δS^{34}
1. QS	HZ	87/138	0,0129	0,071	1 : 0,18	−20,9 py
	HZ	87/138				−21,7 po
	HZ	95/213	0,090	0,126	1 : 0,07	−19,6 py
2. GQS	HZ	90/126a	0,0078	0,115	1 : 0,068	−19,9 py
	HZ	90/126a				−19,1 m
	HZ	189/133	0,008	0,132	1 : 0,06	−19,8 py
	HZ	188/132	0,0108	0,209	1 : 0,05	−24,5 py
3. GQS ch	HZ	88/189a	0,0104	0,098	1 : 0,1	−20,7 py
4. Impreg.	HZ	89/130	0,030	0,230	1 : 0,13	−20,6 py
	HV	93/207	0,0132	0,0525	1 : 0,3	−16,3 py

Explanations: QS — quartz-sulfide ore, GQS — graphite-quartzsulfide ore, GQS ch — ore and impregnations in graphite-bearing crystalline schists, Impreg. — disseminated sulfides in country-rocks, HZ — Heľpa, western deposit, HV — Heľpa, eastern deposit, py — pyrite, po — pyrrhotite, m — marcasite.

Les probable interpretation would be the palingenetic origin of the sulfur in the Heľpa deposit. It would imply assimilation by the basic magma of strata rich in sedimentary, biogenic pyrite, the homogenization of the sulfur and it's transport by hydrothermal solution and emanations. The isotopic composition of the sulfur from the submarine springs would have been in the sedimentary basin modified to a limited extent only. Further data are expected from detailed investigations of the distribution of sulfur isotopes in the metabasic, especially hypoabyssal rocks of the area.

The distribution of sulfur isotopes in the pyrrhotite-pyrite deposits of Heľpa is sumarized in table 1, page 271 and on the histogram A of Fig. 12, page 271.

For certain sulfides the contents of trace elements were studied by B. Cambel, J. Jarkovský (l. c.). On table 2, page 270 the δS^{43} values and the microchemism are reproduced. No marked relation between the contents of microelements and the isotopic composition can be recognized from this limited number of analyses.

The Co/Ni ratios in pyrites are regarded by B. Cambel and J. Jarkovský as indicators of genetical conditions, as well as of the grade of metamorphism of sulfide deposits. The Co, Ni contents, Co/Ni ratios and permillage deviations from meteoric standard are given in table 3, page 276. With the exception of pyrite impregnations from paragneisses, the isotopic composition of sulfur varies in all ore-types within similar limits. If all isotopically analyzed samples are considered, there is a tendency for the heavy sulfur to be concentrated in the amphibole-rich rocks. This would confirm that at least a part of the sulfur was bacterially reduced from the sea water sulfate of the basin.

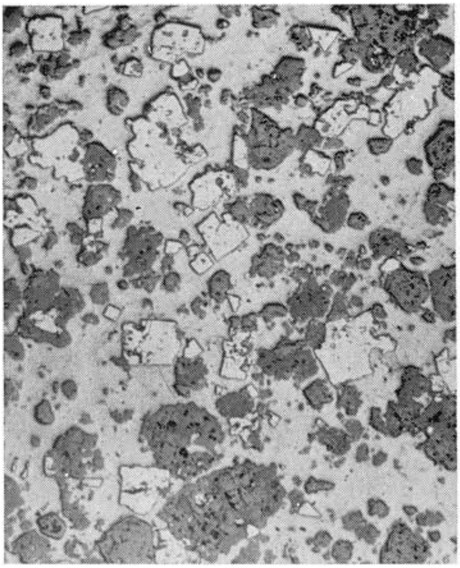

Fig. 17. Pyrrhotite-pyrite ore, common type. Idioblastic pyrite (white), corroded and embedded in pyrrhotite (light gray). Non-opaque minerals (dark grey): quartz, garnets, amphiboles. The average content of pyrite is lower than shown on the microphotograph. Polished section, 11×.

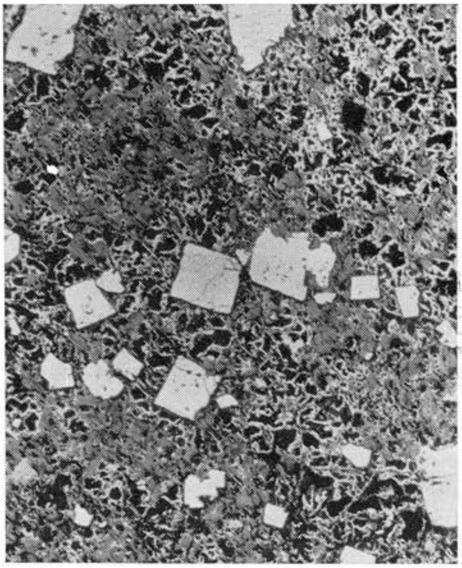

Fig. 18. Supergene alteration of compact pyrrhotite-pyrite ore. Pyrrhotite altered into a mixture of marcasite with subordinate pyrite. The original pyrite porphyroblasts are untuched by alteration. Irregular black patched. holes. Polished section, 11×.

Table 4. Coexisting pyrite-pyrrhotite

No	Mineral	S^{32}/S^{34}	δS^{34}	Mineral	S^{32}/S^{34}	δS^{34}	f	$\Delta \delta$
87/S	py	22,69	−20,9	po	22,71	−21,7	1,0009	0,8
94/S	py	22,69	−20,8	po	22,72	−21,8	1,0013	1,0
189/S	py	22,67	−19,8	po	22,69	−20,8	1,0009	1,0
200/S	py	22,57	−15,7	po	22,60	−16,8	1,0013	1,1
222/S	py	22,66	−19,6	po	22,68	−20,2	1,0009	0,6
mean value							1,00106	0,9
$90/S^{+}$	m	22,65	−19,1	py	22,67	−19,9	1,0009	0,8
$219/S^{++}$	py	22,44	−9,9	po	22,69	−20,9	1,0111	11,0

py — pyrite, po — pyrrhotite, m — marcasite, $^{+}$ — supergene marcasite replacing pyrrhotite, $^{++}$ — mobilized pyrite cutting pyrrhotite ore-body.

The lowest δS^{43} values (−2 to −5 ‰) were found in disseminated sulfides in gneisses, micaschists, amphibolites and their retrogradely metamorphosed equivalents. The obviously do not belong to the main mineralization.

Histogram B of Fig. 12 reproduces the distribution of sulfur isotopes between pyrites and pyrrhotites of the ore bodies. No definite relation between isotopic constitution and mineral species is evident. Results of detailed investigations are summarized in the upper part of table 4, page 278. They pertain, to the common pyrrhotite-pyrite ores with pophyroblastic pyrite (Fig. 17). The mineral pairs were separated from the same sample and from closest proximity of each other. They may be regarded as cogenetic with respect to the metamorphic recrystallization by which their lattices were modified. In all studied mineral-pairs heavy sulfur is

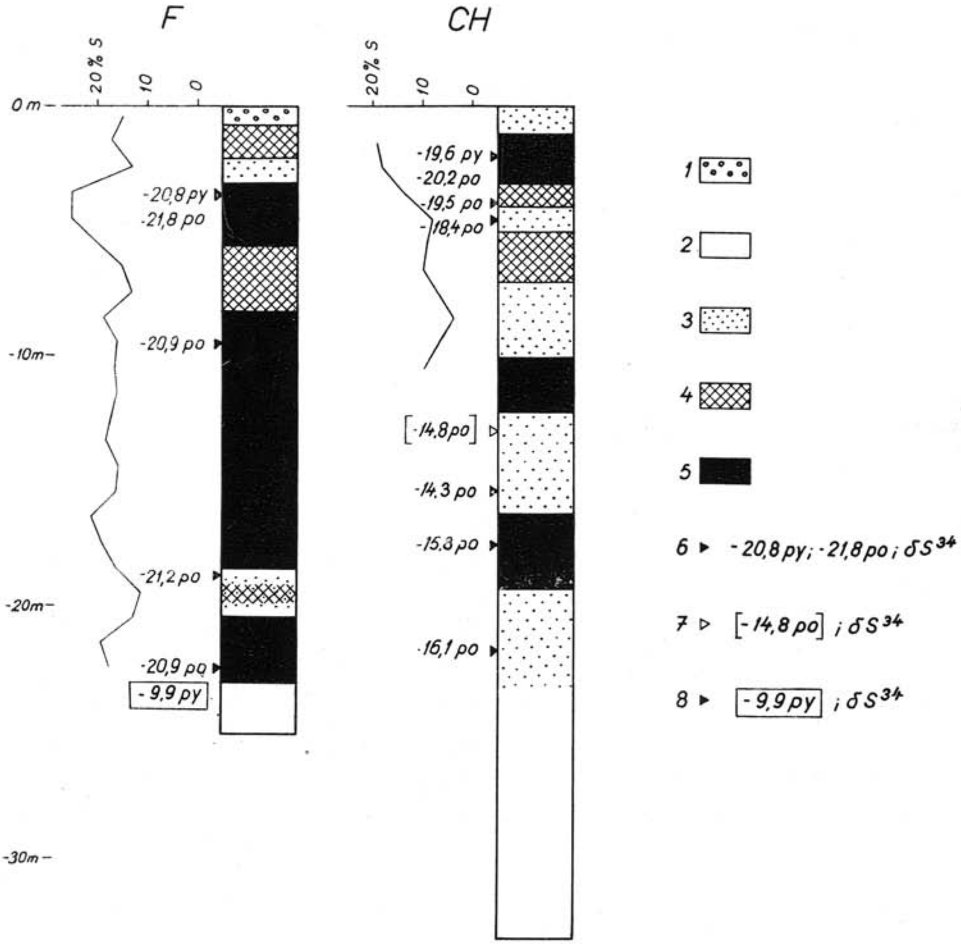

Fig. 19. δS^{34} values in the boring F (western deposit) and CH (eastern deposit). 1 — loam, 2 — amphibolite, 3 — sulfide impregnations, 4 — ore, 5 — massive ore, 6 — δS^{43} values of pyrite (py) and pyrrhotite (po) of the boring, 7 — as 6, for sulfides in the vicinity of the bore-hole, 8 — mobilized pyrite.

concentrated in pyrite, while pyrrhotite contains more S^{32}. The differences in δS^{34} vary between 0,6 and 1,1‰ with a mean of 0,9 ‰.

In one sample where the pyrite porphyroblasts were surrounded by a very fine-grained marcasite-pyrite (subordinate) mixture pseudomorphous after pyrrhotite (Fig. 18), the opposite relation was found. The porphyroblastic pyrite contained more S^{32} than the secondary marcasite (lower part of table 4, page 278).

Considerable differences in isotopic composition of sulfur were revealed between the massive pyrrhotite of the ore body and the pyrite of a thin veinlet of metamorphous mobilization origin intersecting the pyrrhotite (δS^{34}: of pyrrhotite = −20,9 ‰, of pyrite = −9,9 ‰). As in the preceeding case the secondary and younger sulfides were depleted in S^{32}.

Similar relations are reported by M. L. Jensen and A. W. G. Whittles (l. c.) from the Nairne deposit. In an intensively tectonized part are the bedded pyrite-pyrrhotite ores replaced by young melnikowite-pyrite, marcasite and collomorphous pyrite. These secondary sulfides contain the heaviest sulfur of the Nairne deposit (δS^{34} −11,7 to −13,6 ‰, Fig. 16, page 275.

The investigation of the spatial distribution revealed the presence of the lighest sulfur in sulfides of the western deposit (δS^{34} −19 to −25 ‰) whereas for the eastern one an impoverishment in S^{32} seems to be characteristic (δS^{34} −14 to −20 ‰, Fig. 12 C, page 271).

Vertical variations across the western (boring F) and eastern deposit (boring CH) are reproduced in Fig. 19, page 279. In the boring F the permillage values range −20,9 to −21,8. The heaviest sulphur (−9,9 ‰) characterizes pyrite mobilized into a thin veinlet. Variations within broader boundaries (−14,3 to −20,2 ‰) were found in the boring CH of the eastern deposit. The heavier sulfides appear to be confined to feebly mineralized parts of the amphibolitic rocks and to deeper parts of the boring.

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Review by B. Cambel.